(14) Hoffmann, M.; Kämpf, G.; Krömer, H.; Pampus, G. *Adv. Chem. Ser.* **1971**, *No. 99*, 351.
(15) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1978**, *11*, 960.
(16) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1980**, *13*, 994.
(17) Noolandi, J.; Hong, K.-M. *Ferroelectrics* **1980**, *30*, 117.
(18) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 258.
(19) Richards, R. W.; Thomason, J. L. *Macromolecules* **1983**, *16*, 982.
(20) Bates, F. S.; Berney, C. V.; Cohen, R. E. *Macromolecules* **1983**, *16*, 1101.
(21) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093.
(22) Shibayama, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1983**, *16*, 1434.
(23) Kämpf, G.; Krömer, H.; Hoffmann, M. *J. Macromol. Sci.—Phys.* **1972**, *B6* (1), 167.
(24) Dlugosz, J.; Keller, A.; Pedemonte, E. *Kolloid-Z. Polym.* **1970**, *242*, 1125.
(25) Odell, J. A.; Dlugosz, J.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 861.
(26) Folkes, M. J.; Keller, A. In "The Physics of Glassy Polymers"; Haward, R. N., Ed.; Applied Science Publishers Ltd.: London, 1973.
(27) Gallot, B. *Adv. Polym. Sci.* **1978**, *29*, 85.
(28) Odell, J. A.; Keller, A. *Polym. Eng. Sci.* **1977**, *17*, 544.
(29) Mathis, A.; Hadziioannou, G.; Skoulios, A. *Polym. Eng. Sci.* **1977**, *17*, 570.
(30) Folkes, M. J.; Keller, A. *Polymer* **1971**, *12*, 222.
(31) Mori, K.; Hasegawa, H.; Kawai, H.; Hashimoto, T., to be submitted to *Macromolecules*.
(32) Guinier, A.; Fournet, G. "Small-Angle Scattering of X-rays"; Wiley: New York, 1955.
(33) Hosemann, R.; Bagchi, S. N. "Direct Analysis of Diffraction by Matter"; North-Holland Publishing Co.: Amsterdam, 1962.
(34) Hashimoto, T.; Suehiro, S.; Shibayama, M.; Saijo, K.; Kawai, H. *Polym. J.* **1981**, *13*, 501.
(35) Fujimura, M.; Hashimoto, T.; Kawai, H. *Mem. Fac. Eng., Kyoto Univ.* **1981**, *43*, 224.
(36) Pukuła, T.; Saijo, K.; Hashimoto, T. *Macromolecules*, in press.

Dynamic Mechanical Relaxations in Polyethylene

Yash P. Khanna,* Edith A. Turi, and Thomas J. Taylor

Corporate Technology, Allied Corporation, Morristown, New Jersey 07960

Virgil V. Vickroy and Richard F. Abbott

Plastics and Functional Chemicals Division—Chemical Sector, Allied Corporation, Baton Rouge, Louisiana 70892. Received August 13, 1984

ABSTRACT: The influence of key physicochemical variables such as density, molecular weight, branching, and thermal history on the dynamic mechanical behavior of polyethylene has been studied. On the basis of our own results and the subject literature, the mechanisms for the α-, β-, and γ-relaxation processes are reviewed. The mechanism of α-relaxation appears to be well established; i.e., it is due to motions of the interfacial regions (tie molecules, folds, loops, etc.) which require chain mobility in the crystal as a precursor and its temperature depends solely on the crystallite (lamellae) thickness. Our results on β-relaxation suggest it to be a glass transition. The γ-relaxation process involves the motion of a short polymer segment (e.g., three to four CH_2) belonging to the bulk amorphous fraction and the chain ends within the crystalline or amorphous phases. The data on energy dissipation and stiffness for various polyethylenes are also presented.

Introduction

Recently we have had applied dynamic mechanical analysis (DMA) to polyethylene in order to understand or explain the product behavior in applications. Interpretation of dynamic mechanical properties of polyethylene in the literature, however, has been quite controversial. Not only the interpretation of dynamic mechanical behavior but also the published data differ because of differences in instrumentation, experimental conditions, sample history, etc. A study[1] was, therefore, undertaken to have a better understanding of the dynamic mechanical properties of polyethylene and, subsequently, to use these results for defining structure/property relationships and relate them to the product performance. Apparently, a somewhat related study by Popli et al.[2] was under way and has appeared in the literature recently. These authors have presented an update of the controversial literature on the mechanical relaxations in polyethylene and, therefore, we will not bring up all the previously reported data. Although Popli et al. discussed only the α- and β-relaxations, we have studied γ-relaxation as well in addition to the viscoelastic properties of polyethylene in the solid state. Preliminary results of our study have appeared elsewhere.[3]

In this manuscript we discuss the dynamic mechanical properties of polyethylene in the light of our results and the subject literature. Accordingly, the mechanisms responsible for the three major, α-, β-, and, γ-relaxations are proposed.

Experimental Section

Materials. The following eight samples were selected for this study:

sample no.		description	source
1	LDPE	linear, LL-1001	Exxon
2		conventional NBS 1476	NBS
3	HDPE	high molecular weight, Lot 90449	Hercules
4		6097	Union Carbide
5		Paxon 4100, Lot 273908	
6		Paxon 4100, Lot 293922	
7		Milk-Bottle Grade	Allied
8		Milk-Bottle Grade	

Sample Preparation. Except for IR and NMR, all the experimental work was carried out on molded samples. Square pieces measuring 2 in. × 2 in. and about 50-mil thickness were compression molded. Thermal history was varied as follows:

Samples 1–8 were molded and then *slow cooled* in the molding press to maximize the crystalline content. A portion of the slow-cooled samples 1, 2, 3, and 8 was subsequently *annealed* under vacuum in an oven for 25 h at 70 and 100 °C. Except for samples 4 and 6, all samples were also *quenched* in water from

0024-9297/85/2218-1302$01.50/0 © 1985 American Chemical Society

the molding press in order to reduce the crystallinity. Thus, molded samples were available for DMA which differed in thermal history, e.g., quenched, slow cooled, and annealed.

Density. Density measurements were made at 23 °C using the ASTM D-1505 density gradient method. Data reported are the average of duplicate measurements.

Molecular Weight. The intrinsic viscosity $[\eta]$ was measured at 135 °C by using a Cannon-Ubbelohde viscometer. The solutions (0.1%) were prepared by dissolving the polyethylene in Decalin at 150 °C for 2 h. The results represent an average of two measurements.

The $[\eta]$ values were converted into weight-average molecular weight ($\bar{M}_w$) by using the following relationship:[4]

$$[\eta] = 6.77 \times 10^{-4}[\bar{M}_w]^{0.67}$$

X-ray Diffraction. The X-ray diffraction (XRD) patterns were recorded on a Phillips APD 3600 automated system using Cu Kα radiation.

Crystalline index was obtained by measuring the area under the reflections 110 ($2\theta = 21.7°$) and 200 ($2\theta = 24.2°$) and the total area of the crystalline and amorphous scattering.

Infrared (IR) Spectroscopy. The pellets were molded into about 10 mil thick films for the IR study. The spectra were obtained with a Perkin-Elmer 983 double-beam ratio recording disperse infrared spectrophotometer.

Nuclear Magnetic Resonance (NMR) Spectroscopy. Polyethylene samples were analyzed by ^{13}C FT-NMR by using a Varian XL-200 spectrometer operating at 50 MHz. The samples were prepared by dissolving 400 mg of polyethylene at 150 °C for 1-3 days in 2 mL of an 80/20 mixture of 1,2,4,-trichlorobenzene and benzene-d_6. The spectra were obtained at 120 °C.

Differential Scanning Calorimetry (DSC). A Perkin-Elmer DSC-2 interfaced with a 3600 data station was used in an argon atmosphere for studying the melting behavior. Samples 2, 3, 5, and 8 (slow cooled) were studied for the heating rate dependence (1.25, 10, 80 °C/min) of their melting temperature. The instrument was calibrated for each heating rate with an indium standard to give the onset of melting at 156.6 °C. To determine the precise melting temperature at a given heating rate by DSC, one has to eliminate the thermal gradients within the sample and the thermal resistance between the sample pan and its holder. Thermal gradients were reduced by crimping a small sample, 1.0 ± 0.1 mg in an aluminum pan. Thermal resistance, R_0 at a heating rate, T_p, was determined by the slope ($=T_p/R_0$) of the initial portion of the indium melting peak at that heating rate. To correct for the thermal resistance, a straight line of slope T_p/R_0 was drawn from the polyethylene peak to the base line, and the intersection point provided the corrected peak temperature, i.e., the corrected average melting temperature of the crystals. The significance of the correction procedure is that if it is applied to indium melting, the peak temperature and the onset temperature would both be 156.6 °C at any heating rate, as should be expected.

For all the samples the corrected melting peak temperature (T_m) at 1.25 °C/min was essentially the same as that at 10 °C/min heating rate, which eliminates the possibility of any significant reorganization of the crystals during heating up to the T_m in the DSC unit. Thus, the corrected T_m obtained at 10 °C/min represented the melting of the original crystals and, therefore, could be used for estimating the lamellae thickness (l, Å) using the relationship[5] $T_m = 414.2[1 - (6.27/l)]$.

Dynamic Mechanical Analysis (DMA). A Polymer Laboratories DMTA unit attached to a Hewlett-Packard 9836 computer was used in obtaining the mechanical spectra. A sample of approximately 4-cm length, 1-cm width, and 0.125-cm thickness was analyzed in the bending mode of deformation at a heating rate of 3 °C/min from −120 °C to about +100 °C under an argon atmosphere. All the samples were analyzed at a constant frequency of 1 Hz and a constant strain level.

A selected set of samples were also studied for the effect of frequency ranging between 0.1 and 90 Hz.

Results

The physical characterization results, i.e., density, molecular weight, and crystallinity, are presented in Table I. Structural characterization was carried out with emphasis on the degree and type of branching (Table II). Thermal characterization included a study of the melting behavior (Table III) and of the mechanical relaxations (Table IV). In this manuscript we shall emphasize only the dynamic mechanical properties of polyethylene and use the rest of the characterization data to support our interpretations.

The dynamic mechanical properties of the selected polyethylenes are summarized in Table IV and Figures 1–10. Dynamic storage modulus (E'), dynamic loss modulus (E''), and damping factor tan δ (E''/E') shown in

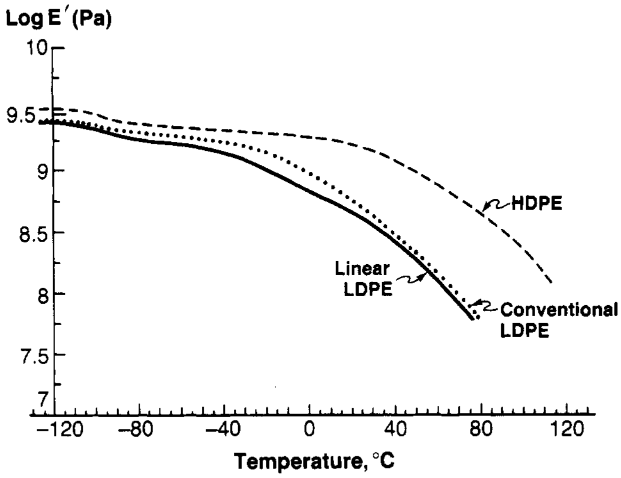

Figure 1. Dynamic storage modulus (E') vs. temperature of various polyethylenes.

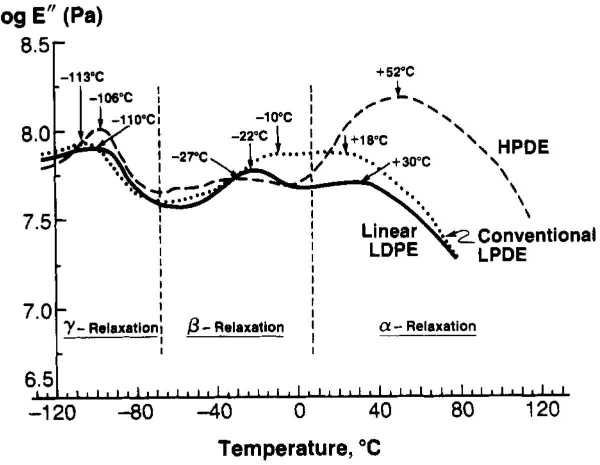

Figure 2. Dynamic loss modulus (E'') vs. temperature of various polyethylenes.

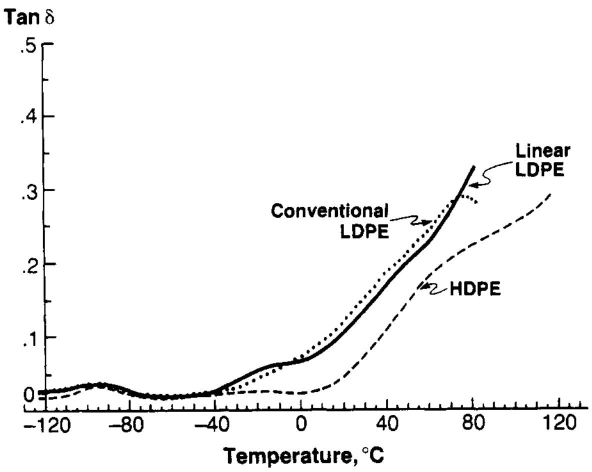

Figure 3. Damping factor (tan δ) vs. temperature of various polyethylenes.

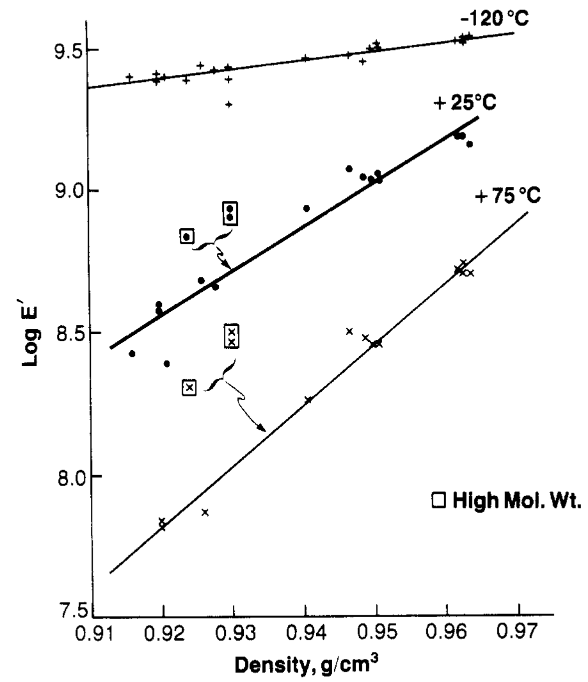

Figure 4. Relationship between E' and density for polyethylene at various temperatures.

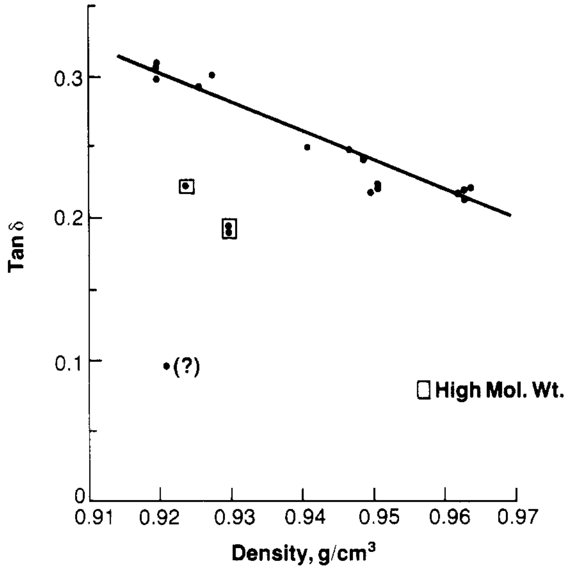

Figure 5. Relationship between tan δ (at 75 °C) and density of polyethylene.

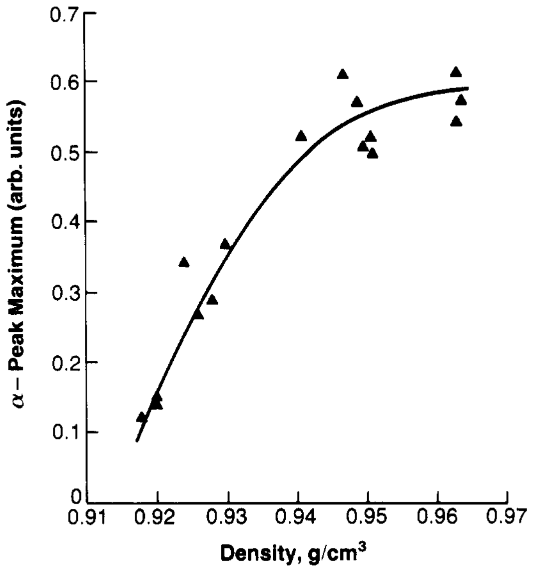

Figure 6. Relationship of α-relaxation intensity (E'' basis) to the density of polyethylene.

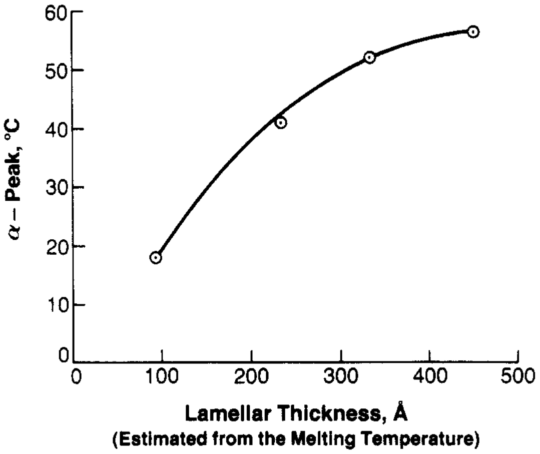

Figure 7. Relationship of α-relaxation temperature (E'' basis) to the lamellae thickness of polyethylene crystals.

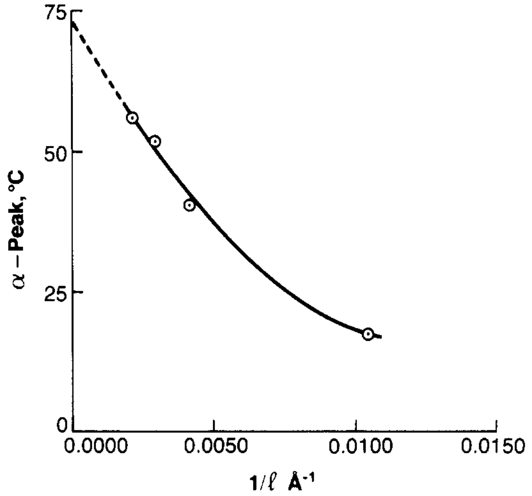

Figure 8. α-Relaxation temperature (E'' basis) vs. reciprocal lamellae thickness of polyethylene crystals.

Figures 1–3, respectively, illustrate the comparison of high-density polyethylene (HDPE), linear low-density polyethylene (LDPE), and conventional LDPE.

Dynamic Storage Modulus. The dynamic storage modulus, E', is approximately similar to the Young or elastic modulus, or stiffness. As expected, the elastic modulus or stiffness at a particular temperature increases with increase in density (i.e., crystallinity) of the polyethylene (Figure 4). Also the increase in E' per unit increase in density (D), i.e., the E'/D slope, becomes greater at higher temperatures (e.g., compare −120 and +75 °C plots, Figure 4). This can be attributed to the fact that for a given polyethylene density, say 0.920 g/cm^3, the stiffness at higher temperatures is lower, because of enhanced molecular motions and any increase in crystallinity/density reinforces the amorphous matrix and thus reduces molecular mobility, which in turn is reflected in a higher E'/D slope at higher temperatures. Another important point is that the high molecular weight HDPE exhibits higher E' than that expected from the E' vs. D plot, especially at higher temperatures (Figure 4). This suggests that the stiffness of polyethylene, although primarily influenced by density, also increases slightly with molecular weight, most likely because of increased entanglement density.

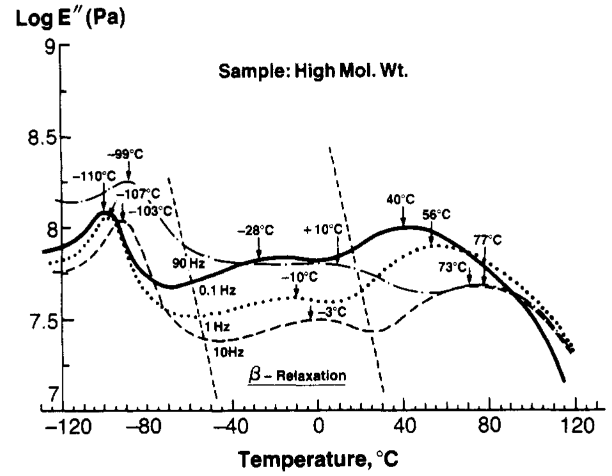

Figure 9. β-Relaxation (E'' basis) in highly linear polyethylene—effect of frequency.

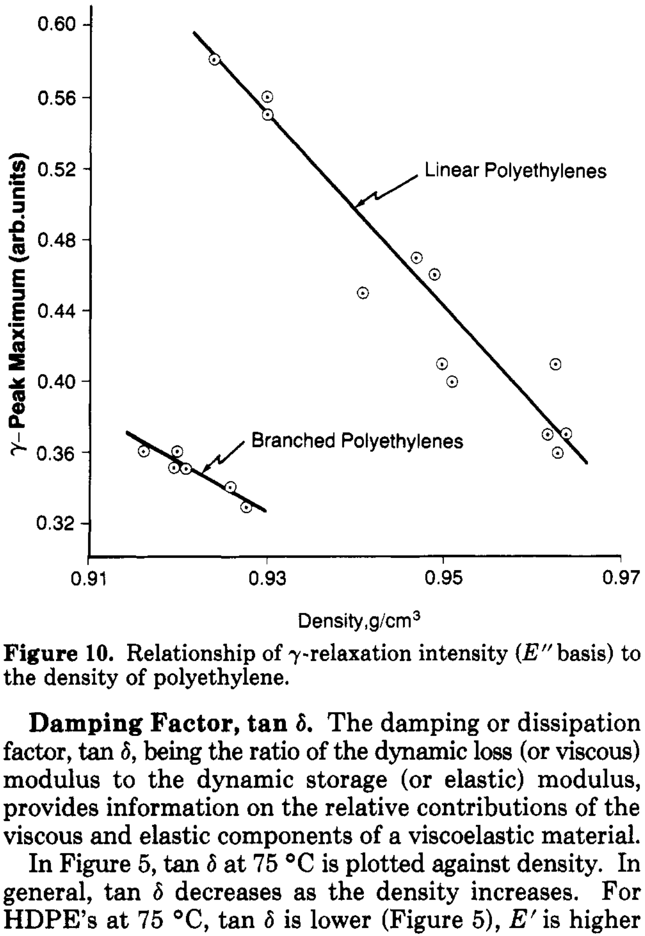

Figure 10. Relationship of γ-relaxation intensity (E'' basis) to the density of polyethylene.

Damping Factor, tan δ. The damping or dissipation factor, tan δ, being the ratio of the dynamic loss (or viscous) modulus to the dynamic storage (or elastic) modulus, provides information on the relative contributions of the viscous and elastic components of a viscoelastic material.

In Figure 5, tan δ at 75 °C is plotted against density. In general, tan δ decreases as the density increases. For HDPE's at 75 °C, tan δ is lower (Figure 5), E' is higher (Figure 4), and E'' is also higher (Figure 2) and since tan $\delta = E''/E'$ one can say that the viscous component (E'') is less dominant relative to the elastic component (E'). For LDPE's at 75 °C, tan δ is higher (Figure 5), E' is lower (Figure 4), and E'' is also lower (Figure 2) and, therefore, the viscous component must contribute more than the elastic component. Thus, the LDPE's are more dissipative (i.e., higher mechanical loss of energy) than the HDPE's. Once again, the high molecular weight polyethylene shows a deviation from the tan δ vs. density plot (Figure 5). A lower tan δ in this case is primarily due its higher stiffness (Figure 4).

Dynamic Loss Modulus. The dynamic loss modulus or viscous modulus, E'', is a measure of the energy absorbed due to a relaxation and thus is useful in clarifying the mechanisms of internal motions (Figure 2). Some of the characteristics of loss modulus or mechanical loss curves, e.g., the transitions and their intensities, are summarized in Table IV.

The significance of the mechanical loss peaks and their relationship to physical and structural parameters is discussed in detail in the subsequent section.

Discussion

According to general literature,[6] dynamic mechanical analysis of polyethylene prior to melting reveals three peaks termed the α-, β-, and γ-transitions. The α-peak at about +50 °C is very sensitive to thermal history and is ascribed to the crystalline phase. The β-peak at about −20 °C is due to branched structures and is absent in entirely linear polyethylene. The α-peak at about −125 °C, the T_g, is caused by small local short-range segmental motion of the amorphous polyethylene, involving perhaps three or four methylene groups. However, there are controversies regarding the characteristics and interpretation of α-, β-, and γ-relaxations. Following is a discussion of these relaxations based on our experimental work and the available literature.

α-Relaxation. The α-peak is observed between about 20 and 60 °C for the studied polyethylenes. The intensity of the α-relaxation increases with increasing density but then levels off at higher densities (Figure 6). The α-peak temperature shows a similar dependence on the lamellae thickness (l, Å) of the crystals estimated from their melting temperature[5] (Figure 7).

It is generally agreed that the α-peak is representative of the crystalline phase and originates from some type of motion in the crystals.[7–9] It is now well documeted[10,11] that during the α-relaxation the chains in the crystal interior are mobilized (e.g., chain rotation, translation, and twist). However, on the basis of the model compounds, e.g., $C_{94}H_{190}$, it has been clearly shown that the crystal body itself would not lead to an α-relaxation[12] and that the fold surface is necessary for the occurrence of the α-process. Working on the dynamic mechanical properties of single crystals of linear polyethylene, Sinnott[13] also convincingly demonstrated that the α-relaxation is due to the motion of the chain folds at the crystal surfaces. Recently, Boyd[14] has shown that the modulus of the amorphous polyethylene decreases much more than that of the crystalline polyethylene in going through the α-process. In complying with all the available information, Boyd[14] has proposed a model for the α-relaxation according to which the mechanical α-process occurs in the amorphous phase but requires mobility of the crystals. More specifically, α-relaxation is due to the softening of the amorphous phase (folds, loops, tie molecules) which without the crystal mobility is rigidly fixed.

Most of our findings on the α-relaxation are in compliance with Boyd's mechanism.[14] However, from the clarification point of view, we recommend that α-relaxation be attributed to the deformation of interfacial regions (chain folds, loops, tie molecules) rather than the discrete (or bulk) amorphous phase; the latter certainly will not be affected by the chain mobility in the crystals. Our present results on the α-process can be understood in view of this mechanism. For example, an increase in the α-peak intensity and then leveling off with increase in density (Figure 6) suggests that the crystal phase plays an important role but the participation of noncrystalline phase may not be ignored. Also, an increase in α-peak temperature with an increase in lamellae thickness (Figure 7) can be expected since at longer chain fold length (i.e., thicker crystals) more energy would be required for chain rotation and twisting. Similar characteristics of α-relaxation are

Table I
Physical Characterization of Polyethylenes

SAMPLE IDENTIFICATION			SAMPLE CHARACTERISTICS					
No.	Type	Source	Thermal History			Density	Mol. Wt., $\bar{M}_w$ $^{(1)}$	Crystallinity
			Slow Cooled	Annealed 25 Hrs. @°C	Quenched	g/cm³	x10^{-3}	Index %
1	LDPE	Linear LL-1001, EXXON	✓			0.920	142	49
				70		0.920		49
					✓	0.916		36
2		CONVENTIONAL NBS 1476, NBS	✓			0.926	(2)	50
				70		0.928		51
					✓	0.921		43
3	HDPE	HIGH MOL. WT. LOT #90449 HERCULES	✓			0.930	5400	64
				70		0.930		63
				100		0.930		66
					✓	0.924		55
4		6097 UNION CARBIDE	✓			0.950	248	63
5		PAXON 4100 LOT #293908 ALLIED	✓			0.951	195	69
					✓	0.941		60
6		PAXON 4100, LOT #293922 ALLIED	✓			0.951	246	67
7		MILK BOTTLE GRADE, ALLIED	✓			0.963	157	74
					✓	0.947		66
8		MILK BOTTLE GRADE ALLIED	✓			0.962	160	75
				70		0.963		75
				100		0.964		75
					✓	0.949		66

(1) Obtained from the relationship: $[\eta] = K[M]^a$

(2) Due to excessive branching, no attempt was made to determine the $\bar{M}_w$.

cited in the recent work of Popli et al.,[2] who in fact directly measured crystallite (lamellae) thickness from the Raman longitudinal acoustic mode (LAM) experiments. Now regarding the temperature of α-relaxation (T_α) our results suggest that at low frequencies, e.g., 1 Hz, T_α can vary the most between 10 and 75 °C for various polyethylenes. Data by Popli et al. based on E'' are basically in agreement with us but their T_α values as high as >120 °C on the tan δ basis appear to be questionable (note: for sharp transitions E'' and tan δ give similar data, whereas for broad transitions tan δ normally indicates the transition at a few degrees higher. However, a difference of more than 50 °C between the tan δ and E'' curves, as reported by Popli et al.,[2] is not understandable. Their tan δ peaks at >120 °C are probably associated with premelting).[6]

Finally we would like to point out the effect of thermal history on the α-relaxation. As the results indicate (Table IV, Figures 6 and 7) slow cooling or quenching of the samples significantly affects the α-peak but it is primarily due to differences in crystallinity/density. Further annealing of the slow-cooled samples (25 h at 70 or 100 °C) does not change density/crystallinity and hence the α-peak is not influenced. For branched polyethylene, Mandelkern et al.[15] had initially suggested that morphology changes (highly ordered vs. disordered spherulites) caused by slow cooling or quenching affect the α-relaxation independently.

Table II
Structural Characterization of Polyethylenes (Analysis of Branching)[1]

SAMPLE IDENTIFICATION			IR		NMR			
No.	Type	Source	Ethyl Branches	Terminal & Long Chain Branches	Ethyl Branches	Butyl Branches	Terminal Methyl Branches	Terminal Vinyl Branches
1	LDPE	LINEAR LL-1001, EXXON	19.8	0	21.0	(2) –	1.3	(2) –
2		CONVENTIONAL NBS 1476, NBS	3.3	16.9	?	3.6(±0.5)	1.5(±0.4)	(2) –
3	HDPE	HIGH MOL. WT. LOT 90449, HERCULES	(2) –	0.6				
4		6097 UNION CARBIDE	1.8	2.6	2.3(±0.1)	(2) –	2.3	1.6
5		PAXON 4100, LOT #273908, ALLIED	0.9	5.2	0.9(±0.1)	1.6(±0.3)	4.2(±0.3)	0.5
6		PAXON 4100, LOT #293922, ALLIED	0.5	6.2	0.6(±0.1)	1.9(±0.2)	4.3(±0.0)	0.5
8		MILK BOTTLE GRADE, ALLIED	(2) –	1.3	(2) –	(2) –	1.3	1.2

(1) The values are in units per 1000 CH_2.

(2) Not detected

Table III
Melting[a] of Polyethylene Crystals—Heating Rate Study

HEATING RATE, °C/minute	CONVENTIONAL LDPE	HIGH MOLECULAR WEIGHT HDPE		PAXON 4100; LOT #273908 HDPE		MILK BOTTLE GRADE; 4-2899 HDPE	
	SLOW COOLED	SLOW COOLED	QUENCHED	SLOW COOLED	QUENCHED	SLOW COOLED	QUENCHED
1.25	114.6	134.5	134.2	129.8	128.0	133.5	132.0
10	113.6	135.3	132.9	130.0	127.7	133.3	131.4
.80	116.7	139.6	138.0	133.6	129.0	140.0	139.2

[a] The melting temperature corrected for thermal resistance, sample size 1.0 mg.

Their recent work,[2] however, is in full agreement with ours that the α-peak temperature is controlled only by the crystallite (lamellae) thickness.

Using our crystallite thickness (l, Å) data, we have obtained the α-relaxation temperature for an infinitely thick crystal of polyethylene, i.e., by plotting α-peak temperature against reciprocal crsytallite thickness and extrapolating it to $1/l = 0$ (Figure 8). A value of 70–75 °C is determined for the α-relaxation temperature of the most perfect or equilibrium crystals of polyethylene.

To conclude our view on the α-relaxation of polyethylene, we believe that it is the result of motions or deformations within the interfacial regions (tie molecules, folds, loops, etc.) which are activated as a consequence of chain mobility in the crystals. The T_α varying between 10 and 75 °C depends upon the crystallite thickness, thicker crystals (lamellae) leading to higher temperature relaxation.

β-Relaxation. The β-relaxation occurs between −5 and −35 °C depending upon the type of polyethylene (Table IV). Its intensity is high for the LDPE's and very small for the HDPE's (Figure 2). The true origin of the β-relaxation is still unresolved but it is commonly attributed to the amorphous phase.[11] For example, single crystals (i.e., no discrete amorphous phase) of linear polyethylene do not exhibit a β-relaxation whereas a very small β-peak has been reported in bulk linear polyethylene containing an amorphous phase.[11,13] It is generally described that the β-transition is due to the motion of branches[8,16,17] in the amorphous matrix. On the basis of our study of polyethylenes we would like to propose that β-relaxation is simply the glass transition and that the influence of physicochemical parameters on the β-relaxation can be explained in terms of T_g. We realize that the subject of polyethylene T_g is highly controversial.[18] A subsequent publication[19] will present an analysis of the relevant lit-

Table IV
Thermal Characterization of Polyethylenes—Dynamic Mechanical Analysis

Sample Identification			Sample Characteristics						DMA												
			Thermal History			Density	Mol. Wt.	Crystallinity	Log E' Values (Pa)			Log E'' Transitions (°C)			Log E'' Values[2]			Tan δ Values			
No.	Type	Source	Slow Cooled	Annealed 25 Hrs. @ °C	Quenched	g/cm³	$\bar{M}_w \times 10^{-3}$	Index %	-120°C	25°C	75°C	γ	β	α	γ_{max}	β_{max}	α_{max}	-120°C	25°C	75°C
1	LDPE	Linear LL-1001, Exxon	✓			0.920	142	49	9.41	8.60	7.83	-111	-22	29	.35	.20	.14	.024	.119	.299
				70		0.920			9.39	8.58	7.84	-110	-22	28	.36	.19	.15	.023	.125	.308
					✓	0.916		36	9.40	8.43		-111	-18	26	.36	.27	.12	.022	.168	
2		Conventional NBS, 1476, NBS	✓			0.926	(1)	50	9.44	8.68	7.87	-114	-10	18	.34	.26	.27	.022	.138	.292
				70		0.928			9.42	8.66		-114	-14	19	.33	.35	.29	.023	.128	.301
					✓	0.921		43	9.40	8.39	7.56	-114	- 7		.35	.37		.024	.202	.096
3	HDPE	HIGH MOL. WT. LOT #90449 HERCULES	✓			0.930	5400	64	9.43	8.93	8.50	-107	-10	56	.55	.10	.37	.018	.050	.189
				70		0.930			9.39	8.90	8.47	-108	- 8	58	.55	.11	.37	.016	.049	.194
				100		0.930			9.43			-108	- 8		.56	.12		.018		
					✓	0.924		55	9.39	8.84	8.31	-108	-19	45	.58	.09	.34	.019	.066	.222
4		6097 UNION CARBIDE	✓			0.950	248	63	9.49	9.03	8.45	-108		41	.41		.51	.017	.084	.217
5		LOT #273908 PAXON 4100, ALLIED	✓			0.951	195	69	9.50	9.03	8.46	-108	-24	41	.40	.15	.52	.016	.089	.220
					✓	0.941		60	9.46	8.93	8.26	-109		35	.45		.52	.018	.112	.249
6		LOT #293922 PAXON 4100, ALLIED	✓			0.951	246	67	9.51	9.05	8.46	-108	-25	41	.40	.13	.50	.016	.088	.222
7		MILK BOTTLE GRADE ALLIED	✓			0.963	157	74	9.51	9.18	8.70	-106	-27	51	.36	.07	.54	.015	.059	.213
					✓	0.947		66	9.47	9.07	8.50	-107		43	.47		.61	.016	.082	.248
8		MILK BOTTLE GRADE ALLIED	✓			0.962	160	75	9.52	9.18	8.71	-107	-29	52	.37	.06	.54	.015	.059	.215
				70		0.963			9.53	9.18	8.73	-107	-33	53	41	.05	.61	.013	.061	.219
				100		0.964			9.53	9.15	8.70	-106	-28	53	.37	.10	.57	.013	.061	.220
					✓	0.949		66	9.45	9.04	8.48	-107	-40	42	.46	.06	.57	.017	.085	.240

1. Due to excessive branching, no attempt was made to determine the $\bar{M}_w$.
2. Measured as the peak height above the lowest point between the γ and β peaks.

erature and propose our own view on the T_g of polyethylene. In this manuscript, however, we only suggest the similarities of the β-peak to the T_g based solely on the dynamic mechanical analysis. The arguments in favor of β-peak being the T_g are listed as follows:

(1) The intensity of the β-relaxation, although not smoothly varying with density, tends to be much higher for the LDPE's (0.30 ± 0.10 vs. 0.10 ± 0.05). Thus, the higher the amorphous fraction, the more intense is the β-relaxation. Further support comes from the fact that quenched samples of LDPE's, i.e., more amorphous, exhibit a more intense β-peak (0.27 vs. 0.20 for linear LDPE and 0.37 vs. 0.26 for conventional LDPE). In such a case, β-relaxation would represent motions in the amorphous phase and, therefore, may be classified as the T_g.

(2) The high molecular weight polyethylene, HMW-HDPE, which is also highly linear (only 0.6 branch/1000 CH_2 by IR), exhibits a definite β-peak which is clearly demonstrated by the frequency dependence (Figure 9). Other HDPE's studied do not reveal a β-transition of any greater intensity in spite of the increased branching (e.g., Paxon 4100 has 5–6 branches/1000 CH_2 by IR). An explanation is that the overall crystallinity of the HMW-HDPE sample (high $\bar{M}_w$ but low branching) and that of other HDPE's (relatively low $\bar{M}_w$ but high branching) is not far apart. Therefore, the β-relaxation governed by the amorphous matrix is equally intense in all HDPE's in spite of the variation in branching. Enhanced intensity of the β-peak in LDPE's is probably a consequence of an increase in amorphous volume due to branching rather than the branches themselves.

(3) For HDPE's of $\bar{M}_w$ = (150–250) × 10^3 the β-transition can be specified as being at −30 ± 5 °C. A large breadth of this peak (e.g., Figure 9), which we attribute as the T_g, can be explained if we consider that the β-relaxation represents a distribution of T_g's resulting from the influence of high crystallinity of polyethylene.[20]

(4) The HMW-HDPE sample shows a higher β-relaxation, i.e., −14 ± 6 °C which may be the consequence of high molecular weight ($\bar{M}_w$ = 5400 × 10^3). More recently, we have analyzed a sample of low molecular weight species extracted from a HDPE batch. The most dominant transition was the β-relaxation at about −45 °C which could be attributed to the low molecular weight of the sample.

(5) A slightly higher β-relaxation of the linear LDPE at −20 ± 2 °C could be explained by the presence of branches which are side groups. For example, the linear LDPE contains about 21 ethyl branches/1000 CH_2 which would make it a random copolymer containing $[-CH_2CH_2-]_n$ and $[-CH_2CH(C_2H_5)-]_n$ units. It is well documented that the introduction of side groups increases the T_g.[21] Interestingly, the β-relaxation of conventional LDPE occurs at a much higher temperature, i.e., −10 ± 4 °C. Since this material has about 21 branches (C_2, $\geq C_4$)/1000 CH_2 (see IR and NMR), it can be regarded as a copolymer of $[-CH_2CH_2-]_n$ and $[-CH_2CH(C_2, \geq C_4)-]_n$, thus containing more bulky side groups. Because of the bulky side chains, the β-relaxation or T_g shifts to higher temperature.[21] Thus, the β-peak or the T_g of LDPE's is not that of the polyethylene homopolymer but of an ethylene copolymer. From our study we conclude that the T_g of polyethylene is the same as the β-relaxation which occurs at about −30 °C for normal HDPE.

(6) On the basis of the quantitative evaluation of the difference in heat capacity between crsytalline and amorphous polyethylene, Wunderlich[22] proposes a T_g of −36 °C (237 K), which agrees very well with our β-relaxation (T_g) at −30 ± 5 °C.

Popli et al.[2] attribute the β-peak to the motion of interfacial regions. Now recalling the α-relaxation, we believe that its breadth is partly due to a distribution of crystallite thicknesses and partly due to the motions of various interfacial species such as chain folds, loops, tie molecules, and cilia. Thus, the motions of interfacial regions may be represented within the spectrum of α-relaxation rather than giving rise to a much lower temperature β-relaxation. Also, it is not straightforward to explain our change in β-peak (T_β) from −5 to −35 °C on the basis that β-relaxation is due to interfacial regions.

To summarize our view on β-relaxation, we observed that (a) its intensity tends to increase mostly with increase in amorphous volume (e.g., by quenching and/or branching), and (b) T_β increases with increasing molecular weight and is influenced by the type and amount of branching. Most of our results on β-relaxation can be explained if we consider it to be analogous to a T_g. A subsequent publication[19] will further deal with our view that $T_\beta = T_g$ and present a critical review of the literature on this subject. In a recent article,[23] Boyd supports our view that the β-relaxation is the glass transition in polyethylene.

γ-Relaxation. The γ-relaxation for HDPE's is shown at −107 °C (±1 °C) regardless of the density or thermal history and it occurs at −111 and −114 °C for the linear and branched LDPE, respectively (Table IV). The intensity of the γ-peak tends to decrease with increasing density (Figure 10), indicating the involvement of mostly amorphous phase; the LDPE's behave differently from the HDPE's.

Several controversies still exist about the origin of the γ-relaxation. For example, Illers[24] has proved that the γ-peak is due to the amorphous fraction while Sinnott[13] and Hoffman et al.[11] propose that it is strictly due to defects in the crystalline phase. The mechanism of Sinnott and Hoffman et al. is based on the similar occurrence of a γ-relaxation in single crystals (i.e., no discrete amorphous phase) of linear HDPE and is assigned to the reorientation of loose chain ends (defects) in the polymer crystal. Sinnott[13] demonstrated that the irradiation cross-linking of interlamellar phase of PE single crystals could not eliminate the γ-relaxation; the latter also intensified upon annealing the "as is" crystals, which introduces more defects into the lamellae. Thus, the role of crystal phase defects on the γ-relaxation cannot be ignored. In order to account also for our own data such as the increased intensity of the γ-peak for quenched and HMW-HDPE samples (i.e., more amorphous fraction), we propose that γ-relaxation involves the motion of a short segment (e.g., three to four CH_2) of amorphous polyethylene in addition to the reorientation of loose chain ends within the crystalline and amorphous fractions.

Sinnott[13] has indicated that the γ-relaxation temperature increases with the number of carbon atoms between the surfaces of the crystal, i.e., the fold length. Thus, thicker crystals of HDPE's tend to raise the relaxation temperature relative to the thinner crystals of branched LDPE, i.e., −107 vs. −114 °C.

To conclude our view on the γ-relaxation, we believe that it is a predominantly but not strictly amorphous phenomenon and rather involves the motion of a short chain segment (e.g., three to four CH_2); the latter belongs mostly to the bulk amorphous phase but also includes the loose chain ends in the crystals as well as in the amorphous fraction.

Acknowledgment. We gratefully acknowledge the contributions of D. Richardson and G. Chomyn for thermal analysis, W. Hammond for NMR, K. O'Brien for IR, F. Cilurso for molecular weight data, D. Vernick for X-ray diffraction, and N. Buik for density measurements.

Registry No. Polyethylene (homopolymer), 9002-88-4; Paxon 4100, 25213-02-9.

References and Notes

(1) Y. P. Khanna, E. A. Turi, T. J. Taylor, v. V. Vickroy, and R. F. Abbott, data obtained between Sept 1983 and Dec 1984.
(2) R. Popli, M. Glotin, L. Mandelkern, and R. S. Benson, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 407 (March 1984).
(3) Y. P. Khanna, E. A. Turi, T. J. Taylor, V. V. Vickroy, and R. F. Abbott, "Proceedings of the 13th North American Thermal Analysis Society Meeting", A. McGhei, Ed., Philadelphia, Sept 23–26, 1984, p 480.
(4) P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, *J. Polym. Sci.*, **31**, 453 (1958).
(5) V. K. H. Illers and H. Hendus, *Makromol. Chem.*, **113**, 1 (1968).
(6) R. A. V. Raff in "Encyclopedia of Polymer Science and Technology" Vol. 6, H. F. Mark et al., Eds., Wiley, New York, 1967, pp 275–332.
(7) N. G. McCrum in "Molecular Basis of Transitions and Relaxations", D. J. Meier, Ed., Gordon and Breach, New York, 1978.
(8) F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).
(9) R. F. Boyer, *Rubber Rev.*, **36**, 1303 (1963).
(10) M. Mansfield and R. H. Boyd, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1227 (1978).
(11) J. D. Hoffman, G. Williams, and E. Passaglia, *J. Polym. Sci., Part C*, **14**, 173 (1966).
(12) J. M. Crissman, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1407 (1975).
(13) K. M. Sinnott, *J. Appl. Phys.*, **37**, 3385 (1966).
(14) R. H. Boyd, *Polym. Eng. Sci.*, **19**, 1010 (1979).
(15) L. Mandelkern, M. Glotin, and R. Popli, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 435 (1981).
(16) D. E. Kline, J. A. Saver, and A. E. Woodward, *J. Polym. Sci.*, **22**, 455 (1956).
(17) L. E. Nielsen, "Mechanical Properties of Polymers" Reinhold, New York, pp 180–2, 209–10, 1962.
(18) G. T. Davies and R. K. Eby, *J. Appl. Phys.*, **44**, 4274 (1973).
(19) Y. P. Khanna, unpublished Data, March 1984.
(20) R. F. Boyer, *Polym. Eng. Sci.*, **8**, 161 (1968).
(21) S. W. Shalaby, in "Thermal Characterization of Polymeric Materials", E. A. Turi, Ed., Academic Press, New York, 1981, Chapter 3, p 246.
(22) B. Wunderlich in "Thermal Characterization of Polymeric Materials", E. A. Turi, Ed., Academic Press, New York, 1981, Chapter 2, p 135.
(23) R. H. Boyd, *Macromolecules*, **17**, 903 (1984).
(24) V. K. H. Illers, *Rheol. Acta* **3**, 202 (1964).