Dynamic Mechanical Properties of a Polypentenamer and Its Hydrogenated Derivatives

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ABSTRACT: A dynamic mechanical study has been carried out on a polypentenamer and its hydrogenated derivatives. The temperature range was from −160 to 130° and frequencies of 3.5, 11, and 110 Hz were employed. The starting polypentenamer was amorphous and the completely hydrogenated derivative resembled linear polyethylene with a melting point of 130° and a degree of crystallinity of 85%. Three relaxation regions were found in the temperature and frequency range investigated and these are labeled α, β, and γ in order of decreasing temperature. The α relaxation (5–115°, 3.5 Hz) is absent in the amorphous polymers and those of low crystallinity. It is composite in nature, consisting of three partially merged peaks. Two of these peaks may correspond to the interlamellar slip motion and the intracrystalline motion concluded to be responsible for the γ relaxation in polyethylene. The β relaxation (−75 to 0°, 3.5 Hz) arises from microbrownian segmental motion in the amorphous phase accompanying the glass transition. The γ relaxation (*ca.* −115°, 3.5 Hz) is a secondary relaxation consisting of at least two components associated with the amorphous phase and the crystalline phase. The amorphous component appears to involve local reorientation of three or more backbone CH_2 units and the crystalline component may involve the motion of chain ends present as defects within the crystal.

The effect of crystallinity on the various relaxation processes occurring in synthetic polymers is a subject of continuing interest. Considerable controversy exists concerning the mechanism of many of these relaxation processes in semicrystalline polymers. Much of this arises from the lack of well-characterized materials of differing degrees of crystallinity but the same crystal structure and morphology. For example, the question of the identification of the relaxation region associated with the main glass to rubber transition in linear polyethylene has not been resolved.[1] There appear to be two main schools of thought. Stehling and Mandelkern,[2] for example, conclude that the so-called γ relaxation, occurring in the neighborhood of −120° at 1 Hz is the glass relaxation of linear polyethylene, while Illers[3] identifies the β relaxation, occurring in the neighborhood of −20° at 1 Hz as the glass relaxation.

We have previously reported characterization data and thermal analyses on a polypentenamer and its hydrogenated derivatives prepared using *p*-toluenesulfonyl hydrazide as the hydrogenation reagent.[4] It was established that the hydrogenation conditions used did not produce any backbone degradation and that it was possible to prepare a range of polymers from the amorphous polypentenamer to a product at 100% hydrogenation which was 85% crystalline with a melting point of 131°. Such a series of polymers, all of which possess the same backbone but differ in their degrees of unsaturation and thus their contents of crystalline material, offer an interesting possibility for the study of crystallinity effects on mechanical relaxation processes.

Experimental Section

Materials. The polypentenamer (PP) was kindly provided by the Goodyear Tire and Rubber Co. and is identical with the polymer used in the previous study.[4] It contained 82% trans double bonds, 17% cis bonds, and less than 1% vinyl side groups. The molecular weight averages were M_n = 94,400; M_w = 172,300. It is presumed that the PP is linear and does not consist of large rings.[5] Hydrogenation was carried out in *p*-xylene using *p*-toluenesulfonyl hydrazide by the procedure previously described.[4] The concentration of PP in *p*-xylene was tripled in the present study.

Films suitable for dynamic mechanical testing were prepared by compression molding at 250 psi at temperatures ranging from 120 to 150°. Films were quenched by removing from the press and immediately immersing in a mixture of Dry Ice and isopropyl alcohol. Annealing was carried out at 35, 65, or 75° depending on the melting temperatures of the samples involved.

Films of the amorphous PP were cross-linked with 0.5 wt % dicumyl peroxide at temperatures of 120–140° at a pressure of 250 psi for 1 hr.

Characterization of all samples was carried out as previously described.[4] In addition the residual unsaturation was checked by using the iodine titration method. Good agreement was obtained between this method and infrared analysis. Data for the samples employed are collected in Table I.[4,6]

Dynamic Mechanical Measurements. Measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.). The temperature range was from −160 to 130° and frequencies of 3.5, 11, and 110 Hz were employed. Samples were heated at 1–2°/min under dry nitrogen.

Results and Discussion

Figure 1 presents the temperature dependence of the loss tangent (tan δ) at 110 Hz for the starting PP, and two hydrogenated polypenteneamers, HPP, including sample HPP4 which was 68% crystalline, and sample HPP8, which was 85% crystalline. This figure illustrates the progression of properties from the rubber-like PP sample with its glass relaxation peak (labeled β) occurring at *ca.* −70° to the highly crystalline material HPP8 which exhibits the three relaxation regions characteristic of polyethylene. These are the α relaxation (*ca.* 80°, 110 Hz), the β relaxation (*ca.* 0°, 110 Hz), and the γ relaxation (*ca.* −115°, 110 Hz). It should be noted that the PP sample also exhibits a reasonably well-defined γ relaxation at −120° (110 Hz). Figures 2 and 3 illustrate the temperature dependences of the storage and loss moduli, E' and E'' for the same three samples under the same conditions as in Figure 1. The general features are again apparent going from the two relaxation regions in sample PP to the three in sample HPP8 (a third relaxation in the PP occurring in the neighborhood of 0° is related to the onset of rubbery flow in this polymer). In what follows, we shall discuss each relaxation region separately.

γ Relaxation. The γ relaxation in polyethylene has

(1) R. F. Boyer, *Macromolecules*, **6**, 288 (1973).
(2) F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).
(3) K. H. Illers, *Kolloid-Z. Z. Polym.*, **250**, 426 (1972).
(4) K. Sanui, W. J. MacKnight, and R. W. Lenz, *J. Polym. Sci., Part B*, **11**, 427 (1973).
(5) K. W. Scott, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **13**, 874 (1972).
(6) S. G. Gallo, H. K. Wiese, and J. F. Nelson, *Ind. Eng. Chem.*, **40**, 1277 (1948).

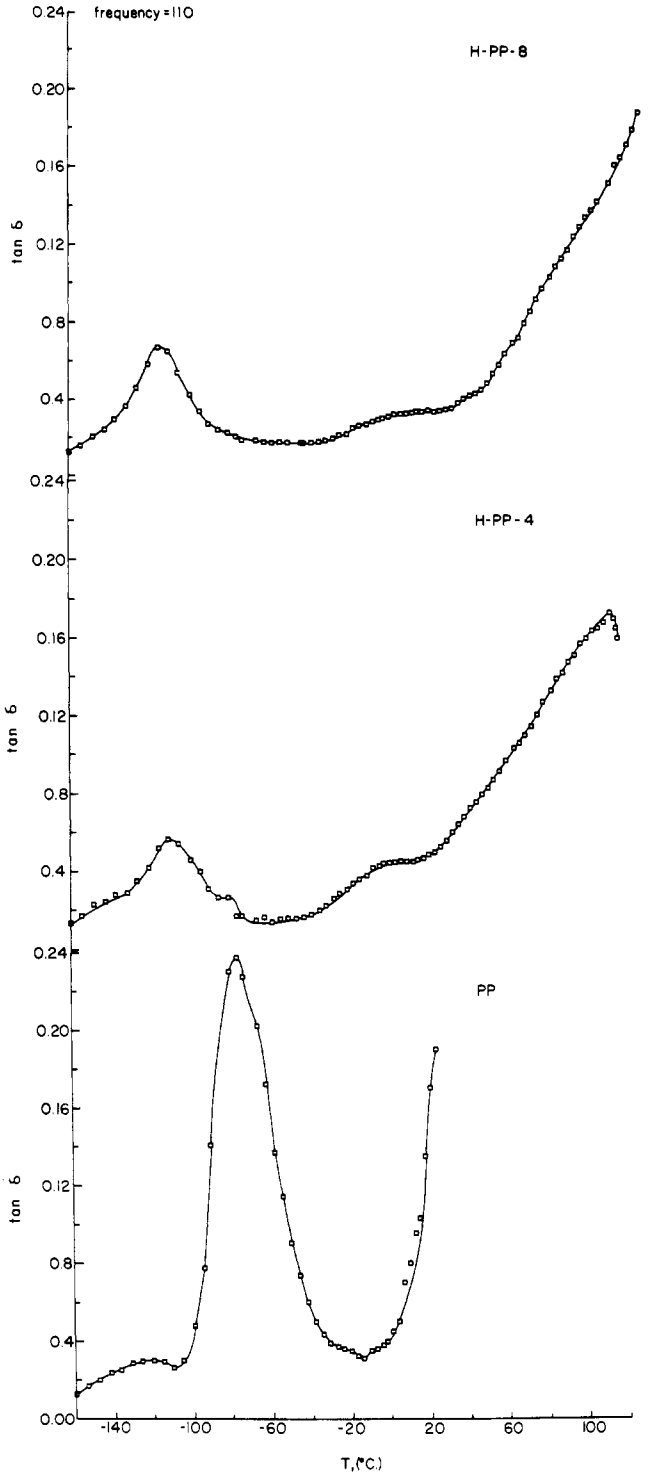

Figure 1. Temperature dependence of tan δ at 110 Hz for PP, HPP4, and HPP8.

been assigned to local motions in the amorphous phase by a number of workers,[7,8] and, more recently, has been postulated to be a composite mechanism arising from both the crystalline and amorphous phases.[9,10] In linear polyethylene, the γ relaxation has also been assigned to amorphous phase microbrownian motions accompanying the

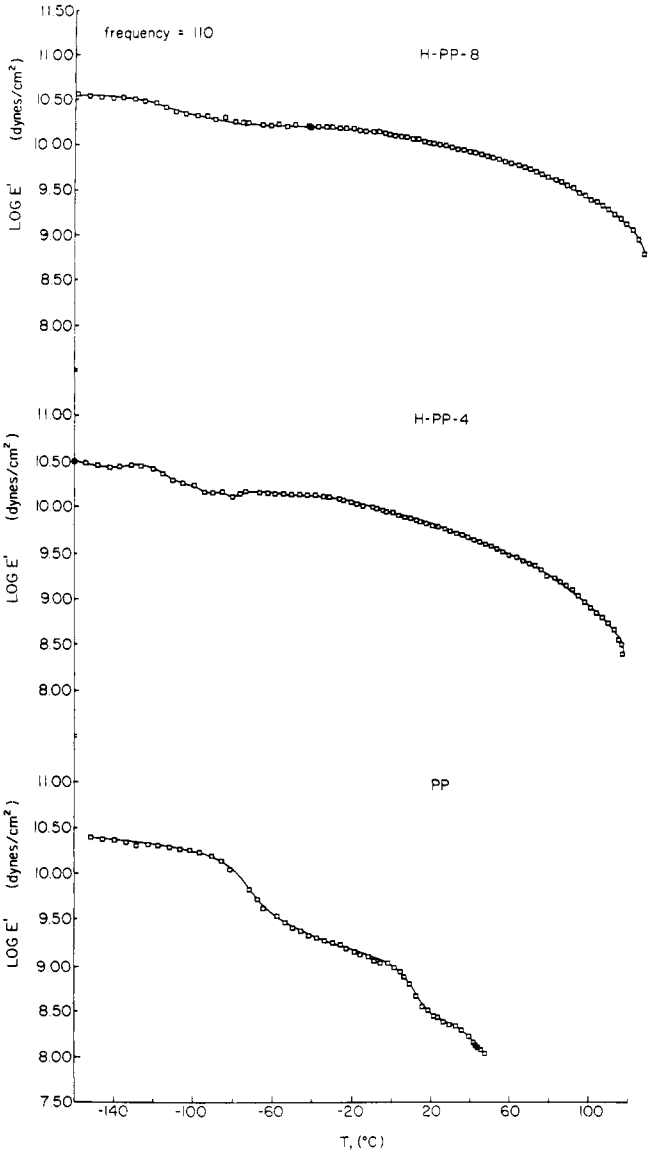

Figure 2. Temperature dependence of E' at 110 Hz for PP, HPP4, and HPP8.

glass transition as already noted in the Introduction.[2] In the case of a poly(ethylene-*co*-methacrylic acid) and its salts containing 4.1 mol % acid groups, it was possible to decompose the γ relaxation into two separate peaks. The low-temperature peak was shown to correlate in magnitude with the degree of crystallinity and was thus assigned to crystal phase motions,[11] while the higher temperature peak was assigned to amorphous phase local motions. It has been shown,[12] that for a relaxation process in which the apparent activation energy, ΔH_a^*, is the same for each relaxation time, the relaxation magnitude, $E_u - E_R$, is given by

$$E_u - E_R = (2\Delta H_a/\pi R)\int_0^\infty E''\mathrm{d}(1/T) \qquad (1)$$

Plots of E'' *vs.* $1/T$ are given in Figure 4 for annealed samples HPP1, HPP3, HPP5, and HPP8, encompassing a range of crystallinity from 0 to 85%. It is apparent from Figure 4, that the γ relaxation[13] in the hydrogenated polypentenamers exhibits a complex dependence on the de-

(7) K. Schmieder and K. Wolf, *Kolloid-Z. Z. Polym.*, **134**, 149 (1953).
(8) W. G. Oakes and D. W. Robinson, *J. Polym. Sci.*, **14**, 505 (1954).
(9) J. D. Hoffmann, G. Williams, and E. Passaglia, *J. Polym. Sci., Part C*, **15**, 10 (1966).
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(12) B. E. Read and G. Williams, *Trans. Faraday Soc.*, **59**, 1979 (1961).

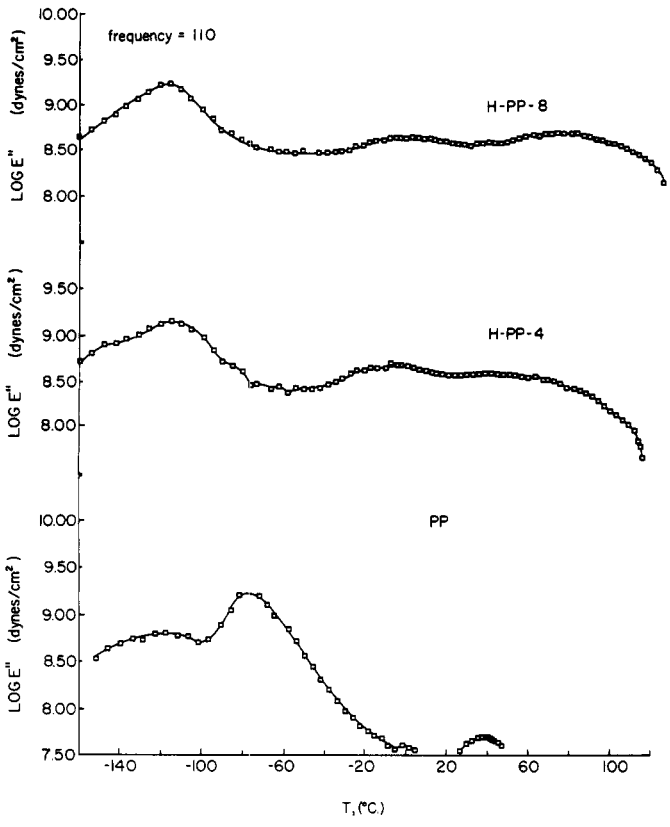

Figure 3. Temperature dependence of E'' at 110 Hz for PP, HPP4, and HPP8.

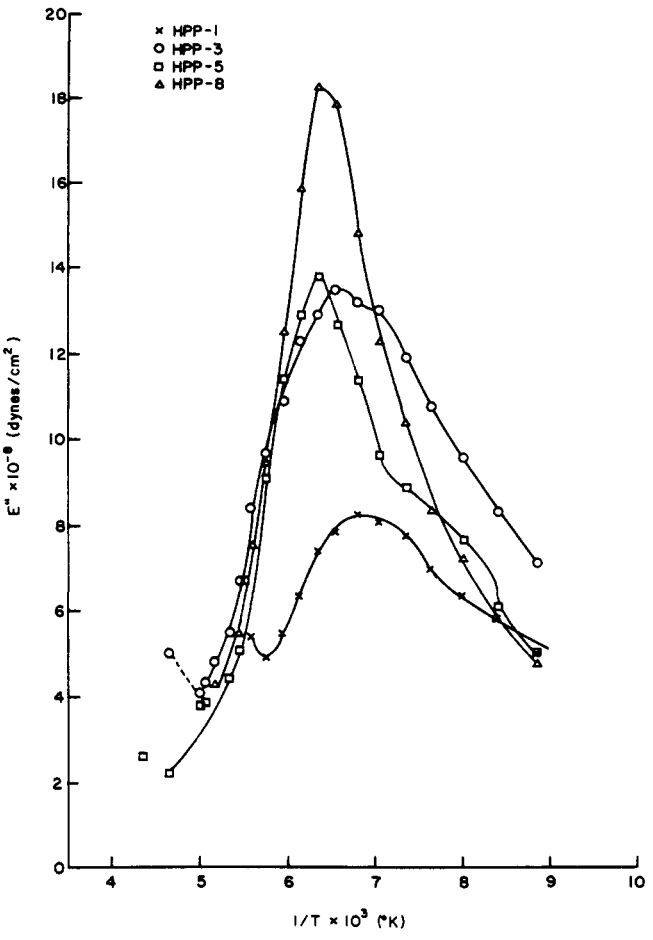

Figure 4. E'' *vs.* $1/T$ for HPP1, HPP3, HPP5, and HPP8 in the γ-relaxation region at 110 Hz.

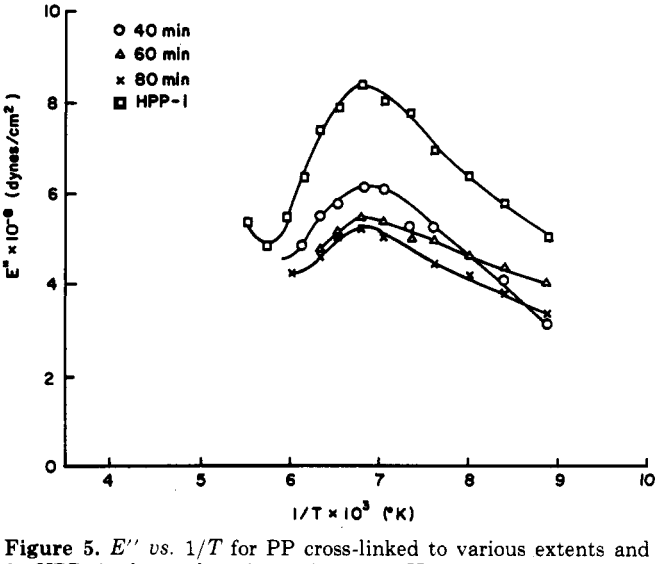

Figure 5. E'' *vs.* $1/T$ for PP cross-linked to various extents and for HPP1 in the γ-relaxation region at 110 Hz.

gree of crystallinity. Any attempts to decompose the γ relaxation in these polymers into two or more separate peaks would be completely arbitrary. It is nevertheless also clear from Figure 4 that the γ relaxation is composite in nature and appears to consist of several overlapping peaks. It seems that there may be a considerable crystalline contribution to the γ relaxation in view of its increasing magnitude with increasing crystallinity. Certainly this behavior is inconsistent with the assignment of the γ relaxation to microbrownian segmental motions in the amorphous phase. Hoffmann, Williams, and Passaglia,[9] suggest that the crystalline γ relaxation arises from motions of chain ends present as defects within the crystal. Such a mechanism may be responsible for the γ relaxation in the hydrogenated polypentenamers. It had been shown in our earlier publication[4] that considerable double-bond concentrations are present in the crystal phase, undoubtedly as defects. However, it is difficult to visualize motion about these double bonds being responsible for the γ relaxation. This is especially true since there is a very sizeable γ relaxation in HPP8 which is completely hydrogenated. The behavior of the γ relaxation in the hydrogenated polypentenamers is in qualitative accord with the findings of Illers.[14] An extensive consideration of mechanical data on linear polyethylene, cross-linked, chlorinated, and high-pressure crystallized, as well as single crystal mats led Illers to conclude that the γ process consists of three peaks. These are: γ_I at $-110°$ (1 Hz) assigned to motion in the interlamellar regions; γ_{II} at $-135°$ (1 Hz) assigned to the reorientation of short CH_2 sequences in the amorphous phase; and γ_{III} at -160 to $-170°$ (1 Hz), assigned to intracrystalline motions. The nature of the intracrystalline motions responsible for the crystal component of the γ process was not defined. In a dynamic mechanical study of large paraffin single crystals, Crissman and Passaglia[15] found no loss peaks below the melting point for pure specimens, but loss peaks did exist for impure specimens. This tends to reinforce the assignment of the crystalline γ peak to motions occurring at defects. In summary, it can be concluded that the γ re-

(13) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, N. Y., 1967, Chapter 10.
(14) K. H. Illers, *Kolloid-Z. Z. Polym.*, **231**, 632 (1969).
(15) J. M. Crissman and E. Passaglia, *J. Appl. Phys.*, **42**, 4636 (1971).

Table I
Characterization Data for Hydrogenated Polypentenamers

Sample	Residue Unsat (%)		MP (°C)[b]		Annealing Temp (°C)	% Crystallinity[c]	
	Titration[a]	Ir	Quenched	Annealed		Quenched	Annealed
PP	100	100					
HPP-1	84	82					
HPP-2	64	64	42	47	35	36	39
HPP-3	46	48	78	81	65	56	58
HPP-4	35	31	96	99	75	66	68
HPP-5	16	13	110	113	75	74	76
HPP-6	6	6	119	122	75	79	81
HPP-7	1	1	123	127	75	81	83
HPP-8	0	0	126	130	75	83	85

[a] See ref 6. [b] Determined by DSC (ref 4). [c] Average of ir, density, and DSC values (ref 4).

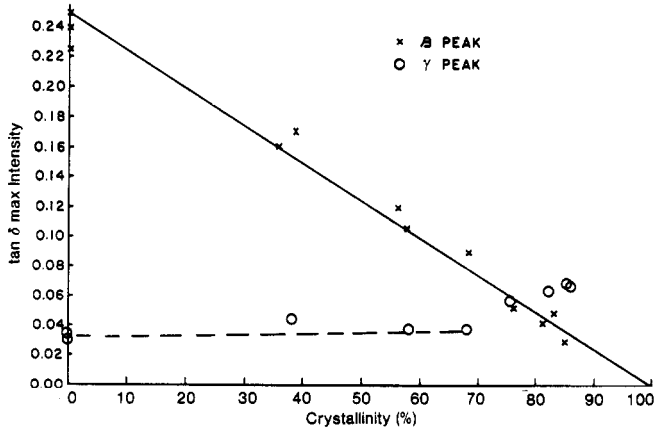

Figure 6. Tan δ_{max} for the β relaxation *vs.* % crystallinity.

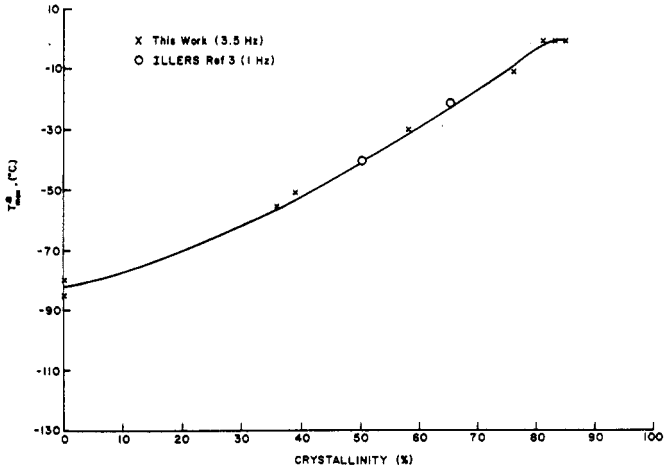

Figure 7. β-relaxation temperature, T_{max}^{β} *vs.* % crystallinity.

laxation in the hydrogenated polypentenamers occurs at least partially in the crystal phase. The mechanism is in doubt but could involve motions at defects within the crystal caused by chain ends.

A well-defined γ relaxation is present in the completely amorphous PP as shown in Figure 5. Its magnitude decreases somewhat with increasing degree of cross-linking. The peak appears to be asymmetric, exhibiting a low-temperature "tail." The peak in HPP1 shows essentially the same features but is larger in magnitude. The mechanism must remain speculative. Presumably, reorientation cannot occur about double bonds so that the increase in magnitude observed in going from PP to HPP1 may be due to the removal of some 16% of the unsaturation in the case of HPP1. It has been known for a long time that three or more CH_2 units in sequence are necessary for the appearance of a γ relaxation.[13] It was shown[16] that a considerable increase in the γ-peak magnitude occurs in polyurethanes when the number of CH_2 units present is increased from 3 to 10. This lends support to the above explanation for the increase in magnitude observed going from PP to HPP1.

β Relaxation. The β relaxations in the PP and its hydrogenated derivatives exhibit two very striking characteristics. Figure 6 shows the dependence of the tan δ peak maximum on per cent crystallinity. It can be seen that a reasonably good straight line can be drawn through the data extrapolating to 0 intensity at 100% crystallinity. For the sake of comparison, tan δ peak maxima values for the γ relaxation are also included and it is apparent that, if anything, there is a tendency for an increase with increasing crystallinity. It is realized that a long-standing argument exists concerning the proper viscoelastic function to use in the determination of whether a specific relaxation is associated with the crystal or amorphous phase. In the absence of detailed morphological information the question cannot be decided since it is not known how the stress and strain are distributed through the crystalline and amorphous portions of the sample. McCrum[17,18] has advocated assignment by hypothesis, that is, assuming a particular parameter to be proportional to the volume of lossy material present and then confirming or rejecting the assignment on the basis of other evidence. This approach seems sensible in the present case. There is no doubt that the relaxation labeled β corresponds to the glass to rubber relaxation in PP, and since the tan δ peak magnitude of the β relaxation is inversely proportional to the degree of crystallinity in the hydrogenated polypentenamer series, it appears that tan δ is the appropriate quantity to use.

Figure 7 summarizes the dependence of the temperature of the β relaxation on crystallinity. It can be seen that relatively small amounts of crystallinity produce large temperature effects. Such behavior is unusual but by no means unknown. Thus, Illers[14] summarizes the effects of crystallinity on T_g in poly(propylene oxide), polypropylene, poly(ethylene terephthalate), and isotactic polystyrene. Of these polymers, only poly(propylene oxide) exhibits a T_g which is independent of crystallinity. For the sake of comparison, Figure 7 includes data of Illers on the β maximum temperature in linear polyethylene at 1 Hz.[3] The agreement is good despite the frequency difference of the measurements. In fact, an examination of Figure 4 of ref 3 which gives the temperature dependence of the β maxi-

(16) T. Kajiyama and W. J. MacKnight, *Macromolecules*, 2, 254 (1969).

(17) L. Gray and N. G. McCrum, *J. Polym. Sci., Part C*, 4, 639 (1966).

(18) N. G. McCrum and E. L. Morris, *J. Appl. Phys.*, 4, 542 (1965).

Table II
Temperatures and Magnitudes of tan δ α Peaks at 3.5 Hz

Sample	α-Peak Temp (°C) 1	2	3	T_m (°C)[a]	α_3 Peak Magnitude
HPP3	5	20	45	81	0.16
HPP4	10	45	70	99	0.20
HPP5	40	65	90	113	0.21
HPP6	50	70	105	122	0.22
HPP7	55	75	110	127	0.24
HPP8	60	80	115	130	0.25

[a] Determined by DSC (ref 4).

mum at 1 Hz on crystallinity for linear polyethylene reveals almost exact correspondence with our Figure 7. It is true that in our case composition changes as well as crystallinity but the correspondence of the results with those for polyethylene indicates that crystallinity is the major factor in determining the temperature of the β relaxation. It thus appears that the β relaxation in PP occurs at about the same temperature as the T_g of the hypothetical amorphous polyethylene (*ca.* −75°) and is shifted to the neighborhood of 0° at high crystallinities (80–85%). Boyer[1] postulates the presence of two T_g's in polyethylene, T_g (l) which occurs at −78° and is independent of crystallinity and T_g (u) which shows a dependence on crystallinity similar to that observed for the β relaxation in the hydrogenated polypentenamers. The mechanical data presented here support the presence of a single glass transition temperature and indicate that the β-relaxation peak originates in the microbrownian segmental motion accompanying the glass transition.

α Relaxation. The α relaxation in polyethylene has been shown to be composite in nature. Two processes have been fairly conclusively shown to be involved.[13] These are interlamellar slip and intracrystalline motion. This latter has been stated by Hoffman *et al.*[9] to involve simultaneous rotation and translation of chains within the crystal. A comprehensive review is presented in ref 13 and 14. In the case of the polymers studied here, no α relaxation is present in PP, HPP1, and HPP2. From HPP3 to HPP8 a composite α relaxation is present apparently consisting of three partially merged peaks. Table II summarizes the tan δ α-peak temperatures and magnitudes at 3.5 Hz. Reference to Figures 1 and 2 show that the highest temperature peak, designated α_3, is the only one clearly defined. The α_2 and α_1 relaxations exist as shoulders on the α_3 peak and their temperature locations are thus only approximate. There is a general increase in both temperature and magnitude for all three peaks with increasing crystallinity. Although the α_3 peak shows a considerable frequency dependence, it occurs fairly close to the melting point and may be connected with the melting process in some way. If complete melting occurred at the α_3 location, it would be expected that tan δ would merely increase indefinitely rather than exhibiting a peak. Thus the α_3 peak, if it involves melting at all, must only involve partial melting or premelting phenomena. By analogy with studies on polyethylene it would be tempting to identify the α_2 relaxation with intracrystalline motions and the α_1 mechanism with interlamellar slip. There is at present, however, no direct evidence for the correctness of these mechanisms in the case of the hydrogenated polypentenamers.

Conclusions

Analysis of the relaxation behavior in the polypentenamer and its hydrogenated derivatives leads to the following conclusions about the various relaxation regions observed. It is realized that the observed behavior is complex and that other measurements such as nmr, specific heat and specific volume should be made to further elucidate these relaxations. (1) The γ relaxation (*ca.* −115°, 3.5 Hz) is a secondary relaxation of composite nature. It consists of an amorphous component which probably involves reorientation of three or more backbone CH_2 units and a crystalline component which may involve the defects within the crystal caused by chain ends. (2) The β relaxation (−75 to 0° depending on crystallinity) arises from microbrownian segmental motion in the amorphous phase accompanying the glass transition. The strong dependence of the temperature of the β relaxation on crystallinity is unusual but by no means unknown in other semicrystalline polymers. Available data indicate that the β relaxation behaves in a similar manner to the β relaxation of polyethylene. This lends support for the assignment of the β relaxation in polyethylene to amorphous phase motions associated with the glass transition. (3) The α relaxation, absent in amorphous samples and those of low crystallinity, is associated with the crystalline phase. It is composite in nature, exhibiting three partially merged peaks. Two of these peaks may correspond to the interlamellar slip motion and the intracrystalline motion postulated to be responsible for the α relaxation in polyethylene.

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