Transitions and Relaxations in Cis Polypentenamer and Its Hydrogenated Derivatives

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ABSTRACT: A study has been made of the dynamic mechanical relaxation behavior of a 97% cis polypentenamer and its hydrogenated derivatives. The starting polypentenamer is wholly amorphous and derivatives were synthesized having melting points from −11 to 131 °C and degrees of crystallinity from 2 to 80%. Three relaxations are discernible in the temperature range from −160 °C to the melting point and these are labeled α, β, and γ in order of decreasing temperature. The α relaxation occurs only in the crystalline derivatives. In the derivatives of low crystallinity, it originates from motions accompanying melting; in derivatives of high crystallinity, it originates from a combination of intracrystalline motions and interlamellar slip. The β relaxation arises from microbrownian motion accompanying the glass transition. It decreases in temperature initially as double bonds are converted to single bonds but shows an abrupt rise in temperature at the first trace of crystallinity and continues to rise thereafter. The γ relaxation is absent in the starting polypentenamer but is present in all the derivatives. It increases in magnitude with increasing CH_2 sequence length and with crystallinity. It arises from a crankshaft motion in the amorphous phase involving a few CH_2 units and motion in the crystal phase probably at chain end defects. It is suggested that the two-phase model is only applicable to polymers with amorphous phases of sufficiently different structure from the crystalline phases as to preclude the crystallization of the amorphous phase under any circumstances.

We have previously reported the dynamic mechanical relaxation behavior of a polypentenamer and some of its hydrogenated derivatives.[1] The polypentenamer used in these studies contained 82% trans double bonds and was semicrystalline with a melting point in the vicinity of 15 °C. Upon hydrogenation, the trans polypentenamer is converted into a material resembling linear polyethylene with a melting point of 130 °C and a degree of crystallinity of 85%. During the course of the hydrogenation, the relaxation accompanying the glass transition (β relaxation) shows a marked dependence on polyethylene crystallinity. Thus the temperature of the β relaxation at 110 Hz increases from ca. −90 °C for the starting polypentenamer to ca. 0 °C for the fully hydrogenated derivative. The effect of crystallinity on the glass transition (T_g) remains a matter of some controversy. Illers[2] reports data for poly(propylene oxide), polypropylene, poly(ethylene terephthalate), and isotactic polystyrene. Of these polymers, only isotactic polystyrene and polypropylene exhibit a T_g which is independent of crystallinity. Crystallinity has a negligibly small effect on the T_g of polypentenamers. Wilkes[3] has shown that T_g measured by calorimetric methods varies from −105 °C for a 100% cis polypentenamer (amorphous) to −92 °C for a 38% crystalline polypentenamer containing 88% trans double bonds. This could be due to the composition change as much as to crystallinity. Available evidence indicates that the double bonds of the trans configuration incorporate into the polyethylene crystal lattice to some extent.[1] This effect, together with the inherent crystallinity of the 82% trans polypentenamer studied previously, obscures the effect of polyethylene crystallinity on T_g. In order to further clarify this effect, a study was made of a 97% cis polypentenamer (labeled HCPP) and its hydrogenated derivatives. The HCPP is completely amorphous. In fact, it can only be crystallized after annealing for several weeks at −75 °C,[4] resulting in a melting point of −41 °C. In addition, the cis double bond cannot be accommodated in the polyethylene crystal lattice. The results of the study on the HCPP and its hydrogenated derivatives serve to amplify and confirm those obtained previously.

Experimental Section

Materials. The HCPP used in this study was kindly provided by the Goodyear Tire and Rubber Co. Infrared analysis yielded a cis content of 97% and a trans content of 3% with no detectable vinyl content. Gel Permeation Chromatography in toluene using a polystyrene calibration gave $M_n = 48.6 \times 10^3$ and $M_w = 173 \times 10^3$. Hydrogenation was carried out in *p*-xylene using *p*-toluenesulfonyl hydrazide. The details of this procedure have been discribed previously.[5]

Films suitable for mechanical testing, differential scanning calorimetry (DSC), and infrared analysis (IR) were prepared by compression molding at 80–160 °C. The films were allowed to cool to room temperature over a period of 5–15 min. Films of the three most highly hydrogenated derivatives were annealed at 75 °C for 24 h.

Measurements. IR analysis was carried out on a Perkin-Elmer Model 180 infrared spectrometer. Some of the films for IR analysis were prepared by solution casting, and some by compression molding. In addition, it was necessary to prepare KBr pellets using powdered samples in some cases due to the inability to produce thin molded films without cross-linking. The determination of the cis and trans double bond concentrations was carried out using the 968-cm^{-1} band for the trans configuration and the 1401-cm^{-1} band for the cis configuration with the methylene band at 1460 cm^{-1} as an internal reference.[6] The degree of crystallinity was determined using the 1894- and 2016-cm^{-1} absorbances according to the method of Read and Stein.[7]

DSC measurements were carried out on a Perkin-Elmer Model DSC2. The scanning rate was 10 °C/min in all cases. Cyclohexane and indium were used as thermal standards. The temperature of maximum excursion from the baseline of the melting endotherm was taken to be the melting point (T_m). Glass transition temperatures (T_g's) were taken to be the midpoint of the step in heat capacity.

Dynamic mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.). The temperature range was from −160 to 140 °C and the frequencies employed were 3.5, 11, and 110 Hz. Samples were heated at 1–2 °C/min under dry nitrogen.

Film densities were obtained at 23 °C using an ethanol–water density gradient column.

Results

Table I collects the characterization data for HCPP and the eight hydrogenated derivatives employed in this study. Based on the infrared analysis, it appears that some isomerization from the cis configuration to the trans configuration takes place during hydrogenation. For samples HYC2 to HYC7, 10% of the original unsaturation remains as trans double bonds. This means that in the case of HYC7 all of the residual unsaturation is of the trans configuration. In the crystallinity determinations, it was arbitrarily assumed that the enthalpy of fusion (ΔH_f) of the 100% crystalline derivative was 60 cal g^{-1} in each case. In view of the isomerization to the trans configuration and the known dependence of ΔH_f on trans double bond content,[5] it is clear that such an assumption must

Table I
Characterization Data for HCPP and Its Hydrogenated Derivatives

Sample	Residual unsaturation, %[a]	T_g, °C[b]	T_m, °C[b]	% crystallinity			
				DSC	θ_{1894}[c]	θ_{2016}[d]	Density[e]
HCPP	100	−100		0	0	0	0
HYC1	63	−111		0			
HYC2	51	−100		0			
HYC3	49	−87	−11	2			
HYC4	44	−80	17	8			
HYC5	39	−72	52	12			
HYC6	15		104	32	24	50	63
HYC7	10		125	43	45	77	64
HYC8	0		131	59	87	78	69

[a] From IR analysis. [b] By DSC. [c] From the 1894-cm^{-1} band by the method of ref 7. [d] From the 2016-cm^{-1} band by the method of ref 7. [e] C. A. Sperati, W. A. Frarta, and W. H. Starkweather, Jr., *J. Am. Chem. Soc.*, **75**, 6127 (1953).

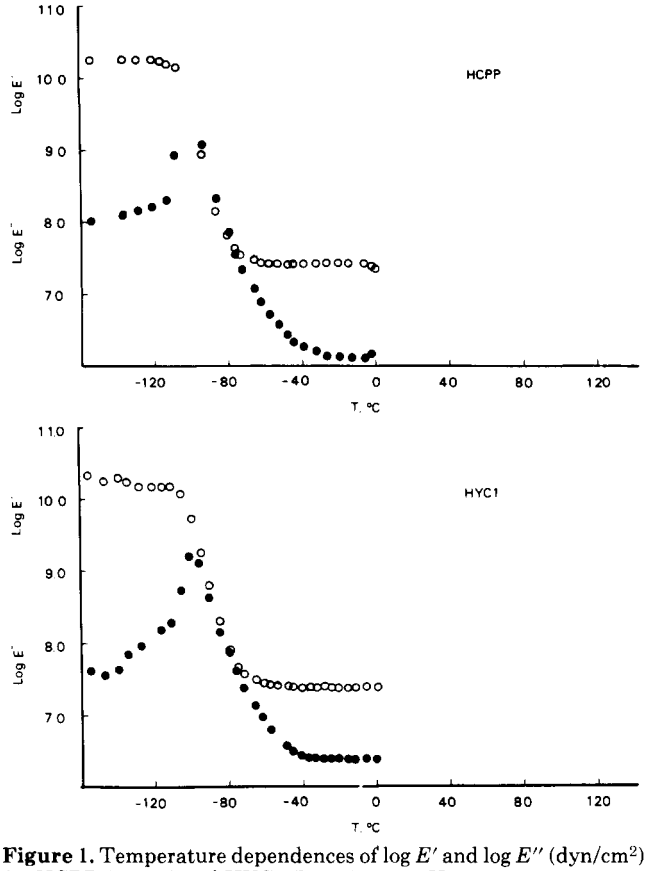

Figure 1. Temperature dependences of log E' and log E'' (dyn/cm^2) for HCPP (upper) and HYC1 (lower) at 110 Hz.

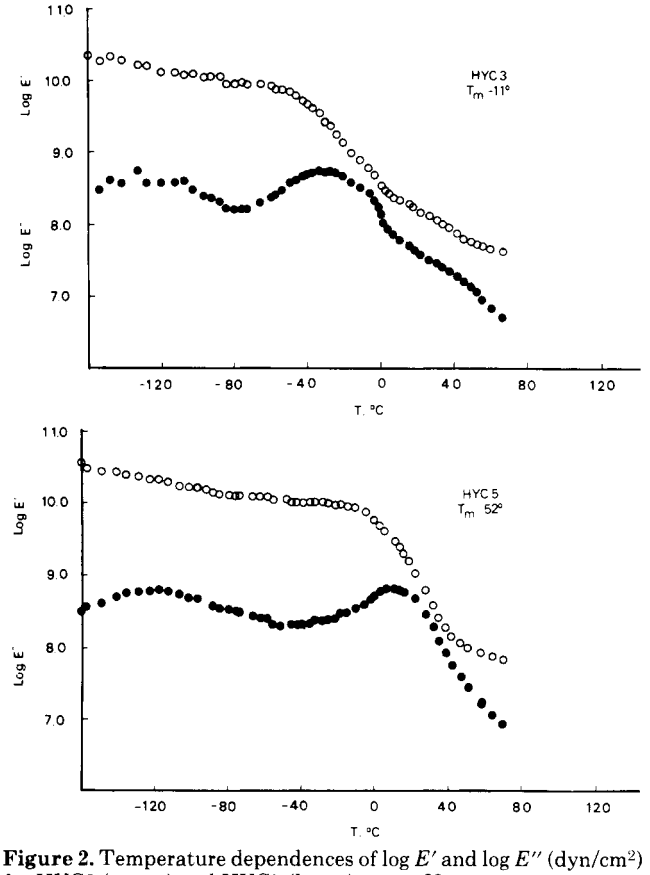

Figure 2. Temperature dependences of log E' and log E'' (dyn/cm^2) for HYC3 (upper) and HYC5 (lower) at 110 Hz.

involve error. However, the values marked DSC in Table I give the relative trend of increasing crystallinity of the derivatives. In a similar manner, the percent crystallinity determined by density measurements is based on the amorphous density of polyethylene which is not correct for the derivatives containing residual unsaturation. It was not possible to determine the crystallinities for samples HYC1 through HYC5 by the IR method since suitable films of these samples were not obtained and the IR analysis was carried out on powders in the form of KBr pellets. Overall the DSC values give the best relative crystallinity scale.

Figures 1 through 3 represent the temperature dependence of the tensile storage and loss moduli (E' and E'') at 110 Hz for the HCPP and five of its hydrogenated derivatives. These plots illustrate the progression of properties from the amorphous HCPP with its single relaxation region, labeled β, at −100 °C, to the highly crystalline HYC8 which exhibits the three relaxation regions characteristic of polyethylene.[8] These three relaxations are labeled α, β, and γ in order of decreasing temperature. In HYC8, the α relaxation occurs at 70 °C, the β at −4 °C, and the γ at −113 °C. Table II collects the relaxation data for all the samples studied together with the DSC T_g's, T_m's, and melting ranges. It may be noted that HCPP does not exhibit a γ relaxation, while all of the derivatives do possess such a relaxation at about the same temperature. The β relaxation and the α relaxation both increase in temperature with increasing crystallinity and no α relaxation occurs in the amorphous samples. There is a considerable degree of overlap among the β and α relaxations and the onset of melting in samples HYC3, HYC4, and HYC5 so that it is difficult to make meaningful temperature assignments of the relaxations in these cases. The correspondence between the DSC T_g's and the temperatures of the β relaxations is quite good for the amorphous samples but shows increasing deviations for the

Table II
Mechanical Relaxation Temperatures for HCPP and Its Hydrogenated Derivatives

Sample	T_g[a]	T_m[a]	Melting range[b]	T_α[c]	T_β[c]	T_γ[e]
HCPP	−100				−98	
HYC1	−111				−100	−120
HYC2	−100				−85	−126
HYC3	−87	−11	−37 to 9	−20[d]	−30[d]	−114
HYC4	−80	17	−38 to 59	−12[d]	−20[d]	−106
HYC5	−72	52	6 to 66	8[d]	−15[d]	−109
HYC6		104	73 to 108	20	−10	−108
HYC7		125	75 to 130	63	−4	−109
HYC8		131	75 to 133	70	−4	−113

[a] By DSC. [b] Taken as the temperatures at which the DSC trace first departed from the baseline and the temperature at which the melting endotherm returned to the baseline. [c] The temperature of the E'' relaxation peak at 110 Hz. [d] The β and α relaxations are partially merged in samples HYC3 to HYC5. [e] tan δ at 110 Hz.

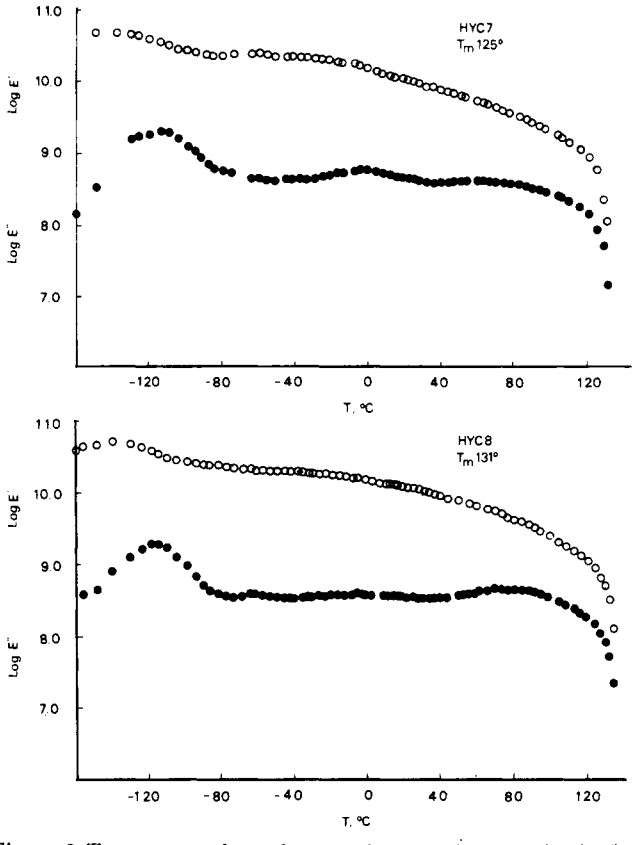

Figure 3. Temperature dependences of log E' and log E'' (dyn/cm^2) for HYC7 (upper) and HYC8 (lower) at 110 Hz.

semicrystalline materials. The overlap of the α and β relaxations makes such comparisons difficult for HYC3, HYC4, and HYC5, and no DSC T_g is observable for samples HYC6, HYC7, and HYC8.

In contrast to this behavior is that exhibited by polypentenamer isomers of differing crystallinities. Relaxation data for three such polymers of differing trans content are collected in Table III. Although the degree of crystallinity in this series varies from 0 to 25%, there is relatively little change in the DSC T_g. The magnitude of the β relaxation decreases by almost an order of magnitude, however.

Discussion

The most important results of this study are the demonstration of the remarkable change which occurs in the relaxational behavior of the derivatives upon the appearance of the first trace of crystallinity and the large influence of crystallinity on T_g and its accompanying relaxation (β relaxation).

Table III
Relaxation Data for PP Isomers

Sample	% trans configuration[a]	T_γ, °C[b]	T_m, °C[b]	T_β, °C[c]	β magnitude[d]	% crystallinity
HCPP	3	−100		−98	1.52	0
PP	82	−96	15	−88	0.24	18
HTPP	93	−95	25	−78	0.18	25

[a] By IR analysis. [b] By DSC. [c] E″ at 110 Hz. [d] tan δ at 110 Hz.

The behavior of the T_g as a function of conversion and percent crystallinity has already been summarized in Table I. It is seen that there is an initial decrease in T_g followed by a sharp increase as soon as the samples are able to crystallize. Intuitively the initial decrease is reasonable since relatively "stiff" double bonds are being replaced with "more flexible" single bonds. This is also in agreement with the conclusion of many authors[9] that the T_g of the hypothetical amorphous polymethylene is very low, in the neighborhood of −120 °C or lower. Figure 4 presents the dependences of both the DSC T_g and the β relaxation temperature on percent conversion. It is seen that there is a reasonable correspondence between the two methods and that the observed T_g behavior cannot be attributed in any reasonable way to compositional changes. Thus, if we accept the value of −120 °C for the T_g of amorphous polymethylene and use the measured value of −100 °C for the T_g of the fully unsaturated HCPP, removal of unsaturation would be expected to produce materials with T_g's intermediate between these values instead of producing the sigmoidal behavior manifest in Figure 4. It is therefore clear that the observed effects arise from the presence or absence of crystallinity in the derivatives. Furthermore, the effects cannot be ascribed to the isomerization of cis double bonds to trans double bonds during the course of the hydrogenation. Table III shows that the difference in T_g between the 97% cis configuration polymer and the 93% trans configuration polymer is only about 5 °C.

Turning to the relaxation properties, we have already presented the general outline of the behavior of the derivatives in the results section. Here we shall discuss each relaxation region separately.

The γ Relaxation. The previous publication on hydrogenated polypentenamer derivatives concluded that the γ relaxation was a secondary relaxation of composite nature, involving both an amorphous and crystalline component.[1] Figure 5 gives the dependence of E'' on $(1/T)$ in the γ dispersion region for several of the HCPP derivatives. Much the same trends are discernible as in the previous study. In the

Table IV
Characteristics of the γ Relaxation in the HCPP and Its Derivatives

Sample	T_γ, °C[a]	E_{act}, kcal	Magnitude tan δ
HCPP			
HYC1	−120	4	0.010
HYC2	−126	13	0.010
HYC3	−114	18	0.029
HYC4	−106	15	0.031
HYC5	−109	16	0.032
HYC6	−108	30	0.046
HYC7	−109	25	0.062
HYC8	−113	24	0.059

[a] tan δ at 110 Hz.

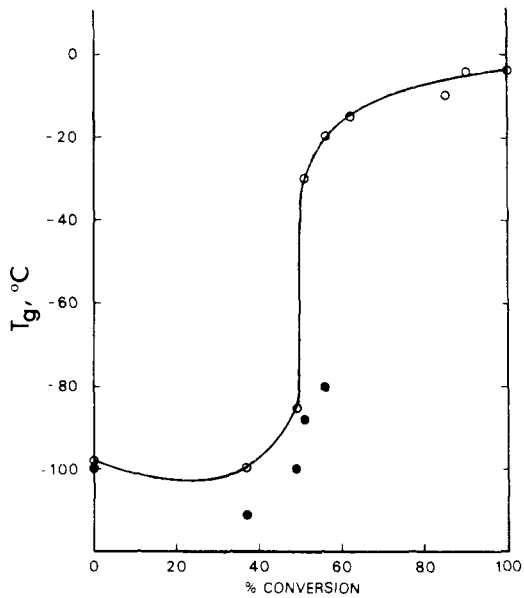

Figure 4. Dependence of T_g (●) and β relaxation temperature (○) (E'', 110 Hz) on percent conversion.

HYC1 derivative, the γ relaxation is quite small and ill defined and there is a steady increase in its magnitude with increasing hydrogenation. In the HYC8 derivative, the γ relaxation exists as two overlapping peaks. A dielectric study of cyano-substituted polypentenamer derivatives concluded that the γ relaxation consisted of an amorphous and crystalline component and that the behavior of the amorphous component was consistent with the crankshaft mechanism of Boyd and Breitling.[10] This mechanism envisions a "crankshaft" motion with three bonds between the stem bonds of the crankshaft. The present results also support the Boyd–Breitling mechanism for the amorphous γ relaxation. The supporting evidence consists of the facts that the magnitude of the relaxation increases with increasing CH_2 sequence lengths and the activation energies obtained from plots of log f_{max} vs. $1/T$ are generally in the neighborhood of 15 kcal which is within the range derived by Boyd and Breitling.

In the case of the crystalline γ relaxation, the weight of the available evidence points to motions occurring around defects within the crystals as responsible for the phenomenon.[8,11] The characteristics of the γ relaxation in the various derivatives are summarized in Table IV.

The β Relaxation. Figure 6 is a plot of the magnitude of the β relaxation vs. percent conversion. It is seen that there is an initial increase in the magnitude as double bonds are replaced by methylene sequences and this is accompanied by a decrease in the temperature of the β relaxation as previously

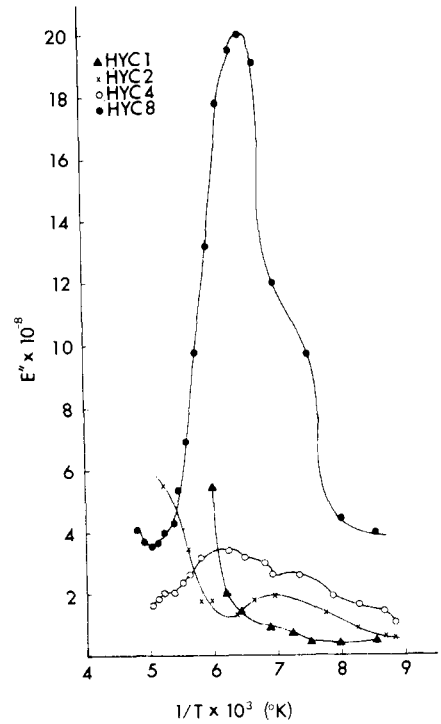

Figure 5. Dependence of E'' (dyn/cm²) on ($1/T$) for (▲) HYC1, (X) HYC2, (○) HYC4, and (●) HYC8 in the γ relaxation region.

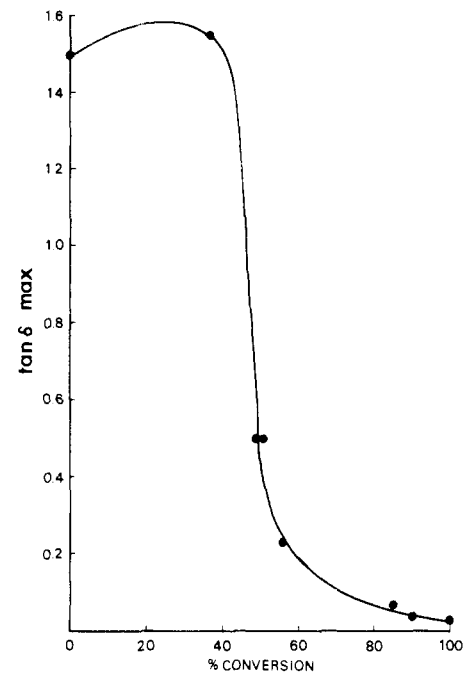

Figure 6. Dependence of the magnitude of the β relaxation (tan δ_{max}) on percent conversion.

noted. When crystallinity first occurs, which is in the 50% conversion range, there is a precipitous drop in the β relaxation magnitude accompanied by an equally abrupt temperature increase. Considerable overlap exists between the β and α relaxations in this region, but at higher conversions (above 70%), the β relaxation magnitude generally exhibits the same trends observed in the study with the trans polypentenamer derivatives.[1] It may also be extrapolated smoothly to zero at a hypothetical 100% crystallinity (not conversion). The results of this study confirm the identification of the β relaxation with motions accompanying the glass transition and demonstrate

Table V
Characteristics of the α Relaxation

Sample	$T_\alpha(E'')^a$	$T_\alpha(\tan\delta)^a$	tan δ magnitude[a]
HYC3[b]	−20	−8	0.45
HYC4[b]	−12	0	0.46
HYC5[b]	8	30	0.50
HYC6	20	76	0.13
HYC7	63	118	0.16
HYC8	70	127	0.18

[a] At 110 Hz. [b] α relaxation and β relaxation overlap.

the great influence of the crystal phase in polyethylene-like materials on this motion.

The α Relaxation. The characteristics of the α relaxation are collected in Table V. The overlap of the α and β relaxations in samples HYC3, HYC4, and HYC5 makes a quantitative discussion difficult. However, there seems little doubt that in these derivatives of very low crystallinity, the α relaxation originates in motions accompanying the melting of small imperfect crystals and not from the conventional polyethylene α mechanism involving intracrystalline chain motions prior to melting. Table V indicates that the melting range in these derivatives encompasses the temperature of the α relaxation. On the other hand, the α relaxation in samples HYC6, HYC7, and HYC8 very probably does originate in intracrystalline motions and perhaps partially in interlamellar slip mechanisms as well.

Conclusions

The series of studies on the polypentenamer derivatives together with those of other workers on a number of other polymers begin to point toward the general conclusion that the two-phase model is an adequate representation of polymer behavior only in the case where the "amorphous phase" is of a sufficiently different structure from the "crystalline phase" that it cannot crystallize under any circumstances. Thus in isotactic polystyrene, crystallinity has no effect on the glass transition temperature or relaxations accompanying it and the same is true of polypropylene (and the cis–trans isomers of polypentenamer). On the other hand, polyethylene terephthalate and the polypentenamer derivatives have glass transition behavior which is greatly affected by crystallinity. The mechanism of the interaction of the "crystalline" and "amorphous" phases is by no means clear. The elucidation of the nature of this interaction will require extensive additional investigation.

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Dynamics of Stretched Polymer Chains

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ABSTRACT: We consider the internal modes of a strongly stretched chain ($\bar{Z}/R_0 \gg 1$, $\bar{Z}$ is the average end-to-end length, and R_0 is the radius of the free coil) including both excluded volume effects and hydrodynamic interactions. It is shown that the tensile screening length $\xi_t = (\beta f)^{-1}$ for excluded volume effects[1] also plays a similar role for the hydrodynamic interactions.[2] Scaling arguments are then employed to derive expressions for the width of the quasi-elastic incoherent neutron scattering peak. All our results are restricted to dimensional power laws and lack precise numerical coefficients.

I. Introduction

The purpose of this investigation is to study the internal dynamics of deformed, isolated, flexible polymers. The deformation is achieved by an external tensile force **f** applied to the ends of the chain. Such a situation might obtain, for example, (a) with polar molecules in electric fields (assuming that the monomer moment has a component along the backbone axis), (b) in the presence of strong velocity gradients[3] (although the nature of the force is slightly more complex in this case), (c) for a chain portion between cross-links in a stretched network.

In a previous paper,[1] we demonstrated that a long, stretched, flexible polymer in the presence of excluded volume interaction could be considered as an ideal coil of "tensile blobs" of radius $\xi_t = (\beta f)^{-1}$ [$\beta = (k_B T)^{-1}$]; i.e., for distances

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