Table I
Intercepts and Slopes of Plots of K_1/K^2 for Mixtures of Polystyrene Latex Spheres

Diameters, nm	Relative composition (w/w)	Intercept $\times 10^8$ Exptl	Intercept $\times 10^8$ Theory (eq 10)	Slope $\times 10^{19}$ Exptl	Slope $\times 10^{19}$ Theory (eq 12)
91		5.49 ± 0.04^a	5.39	-0.091 ± 0.12^a	0
176		2.72 ± 0.05	2.79	0.017 ± 0.12	0
234		2.06 ± 0.06	2.09	-0.076 ± 0.16	0
91/234	95/5	3.86 ± 0.03	3.84	1.55 ± 0.10	1.89
91/234	75/25	2.96 ± 0.03	3.04	1.11 ± 0.09	1.00
91/176	83/17	4.08 ± 0.06	4.03	0.76 ± 0.15	0.73

[a] Uncertainty is taken equal to one standard deviation.

In principle, similar determination of the slope and intercept of a plot of K_2/K^4 vs. K^2 yields four simultaneous equations (eq 10–13) to be solved for the four z average moments of the size distribution, $\langle R^{-1}\rangle$, $\langle R^{-2}\rangle$, $\langle R\rangle$, and $\langle R^2\rangle$. In practice, the second cumulant may not be determinable with sufficient precision to make such analysis feasible. If only the first cumulant can be measured with precision, then there are only two equations (eq 10 and 12) available to determine the three moments $\langle R^{-1}\rangle$, $\langle R\rangle$, and $\langle R^2\rangle$. However, if there is reason to believe that the distribution of polymer sizes is adequately characterized by a two-parameter equation,[7] such as the Gaussian, log-normal, or Schulz-Zimm, then these parameters may be computed from the angular dependence of K_1 alone.

Our experimental study has been concerned with solid spherical polymers of constant density. However, the formalism developed here will apply as well to other spherical or quasi-spherical particles, such as random coiled polymers or spherical vesicles.

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References and Notes

(1) D. E. Koppel, *J. Chem. Phys.*, **57**, 4814 (1972).
(2) S. P. Lee and B. Chu, *Appl. Phys. Lett.*, **24**, 575 (1974).
(3) C. B. Bargeron, *J. Chem. Phys.*, **60**, 2516 (1974).
(4) C. B. Bargeron, *J. Chem. Phys.*, **61**, 2134 (1974).
(5) J. C. Brown, P. N. Pusey, and R. Dietz, *J. Chem. Phys.*, **62**, 1136 (1975).
(6) A. Guinier, *Ann. Phys. (Leipzig)*, **12**, 161 (1939).
(7) L. H. Peebles, Jr., "Molecular Weight Distributions in Polymers", Interscience, New York, N.Y., 1971.

Relaxations in Cyano-Substituted Polypentenamers and Their Hydrogenated Derivatives

R. Neumann, K. Sanui, and W. J. MacKnight*

Chemistry Department, Polymer Science and Engineering Program and
Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01002.
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ABSTRACT: Two series of cyano-substituted polypentenamers and their hydrogenated derivatives have been studied by dynamic mechanical and dielectric relaxation in the temperature range from −160 to 110°C and at frequencies from 3.5 Hz to 10 kHz. Series I contains 7.4 mol % cyano groups and series II contains 20 mol % cyano groups. The amorphous cyanopolypentenamers display one major mechanical and dielectric relaxation region associated with motions accompanying the glass transition and labeled β. A small secondary relaxation, labeled γ, is also discernible in the mechanical E'' results. The semicrystalline hydrogenated derivatives exhibit three relaxation regions labeled α, β, and γ in order of decreasing temperature. The α relaxation which occurs in both series I and II mechanically is resolvable by the dielectric technique only in annealed series I samples. The β and γ relaxations, on the other hand, are present both mechanically and dielectrically in all the derivatives. Enthalpies of fusion for the semicrystalline derivatives were determined using the diluent technique. It was found that the enthalpy of fusion depends on the concentration of the cyano substituents. Available evidence indicates some degree of incorporation of the cyano groups into the crystal lattice but this incorporation is considerably less than that occurring in chlorinated polyethylenes. The results indicate that the α relaxation arises from motions within the crystal phase, the β relaxation from motions accompanying the glass transition, and the γ relaxation from local motions in both the crystal and amorphous phases.

Previously we have reported on the mechanical relaxation behavior of polypentenamer and its hydrogenated derivatives.[1] It was found that the semicrystalline derivatives exhibit three relaxation regions between −150°C and the melting points at the frequencies employed (3.5, 11, and 110 Hz). These were labeled α, β, and γ in order of decreasing temperature. The α relaxation is associated with the crystalline phase being absent in the amorphous polypentenamer and the derivatives of low crystallinity. The β relaxation is associated with motions accompanying the glass transition. The γ relaxation is composite in nature, arising from local motions occurring in both the crystal and amor-

Table I
Properties of the Cyanopolypentenamers

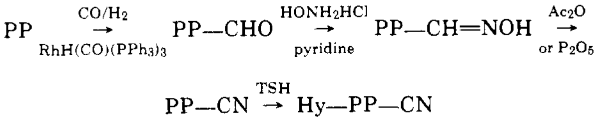
Sample	Polymer type[a]	Thermal history	T_g[b], °C	T_m, °C[b]	Wt % crystallinity[b]
A	PP-Cn (7.4)		−94		0
B	Hy-PP-CN (7.4)	Annealed		113	39
C	Hy-PP-CN (7.4)	Quenched		112	33
D	PP-CN (20)		−77		0
E	Hy-PP-CN (20)	Annealed		96	23
F	Hy-PP-CN (20)	Quenched		91	22

[a] PP-CN (*x*) indicates $[(CH_2)_3CH{=}CH]_{100-x}[(CH_2)_3CH(CN)CH_2]_x$. Hy-PP-CN (*x*) indicates $[(CH_2)_5]_{100-x}[(CH_2)_3CH(CN)CH_2]_x$.
[b] Determined by DSC (see text).

phous phases. The dielectric relaxation technique has frequently been found useful in elucidating the nature of the various relaxation processes occurring in synthetic polymers.[2] Thus oxidized polyethylenes,[3] ethylene-carbon monoxide copolymers,[4] and chlorinated polyethylene[5] have been investigated dielectrically. We have recently developed a technique for preparation of derivatives of polypentenamers with polar substituents based on hydroformylation.[6] Using this method it is possible to prepare cyano-substituted polypentenamers having up to 20 mol % CN groups. Further, this is accomplished without backbone degradation, cross-linking, or significant side reactions. The derivatives so prepared may be hydrogenated according to the method previously described for unsubstituted polypentenamers.[7] In the present study, we report on a dielectric and mechanical relaxation investigation of polypentenamer derivatives prepared in this manner. In addition, differential scanning calorimetry studies (DSC) have been carried out to determine glass transition temperatures (T_g's) in the case of the amorphous derivatives and melting points (T_m's) and enthalpies of fusion (ΔH_u) in the case of the semicrystalline, hydrogenated derivatives. The results support and amplify the conclusions concerning the relaxation mechanisms in the series of hydrogenated polypentenamers alluded to above.

Experimental Section

Materials. The starting polypentenamer (PP) was kindly provided by the Goodyear Tire and Rubber Co. and is identical with the polymer studied previously.[1] It contains 82% trans double bonds, 17% cis bonds, and less than 1% vinyl side groups. The molecular weight averages are $\bar{M}_n$ = 94,400 and $\bar{M}_w$ = 172,300. Hydroformylation of the PP was carried out using the rhodium complex catalyst.[7] The reaction sequence may be schematically represented as follows:



$$\mathrm{PP} \xrightarrow[\mathrm{RhH(CO)(PPh_3)_3}]{\mathrm{CO/H_2}} \mathrm{PP{-}CHO} \xrightarrow[\mathrm{pyridine}]{\mathrm{HONH_2HCl}} \mathrm{PP{-}CH{=}NOH} \xrightarrow[\mathrm{or\ P_2O_5}]{\mathrm{Ac_2O}}$$

$$\mathrm{PP{-}CN} \xrightarrow{\mathrm{TSH}} \mathrm{Hy{-}PP{-}CN}$$

where PP—CHO = polypentenamer derivative with formyl side groups, PP—CH=NOH = polypentenamer derivative with aldoxie side groups, PP—CN = polypentenamer derivative with cyano side groups, TSH = toluenesulfonyl hydrazide, Hy—PP—CN = hydrogenated polypentenamer derivative with cyano side groups. Details of the reaction conditions and characterization of the derivatives are described in ref 7. The properties of the derivatives employed in this study are collected in Table I. The samples were compression molded into films suitable for dielectric and mechanical testing at 140-150°C and 20,000 psi for 10 min under nitrogen. With the exception of samples C and F, they were cooled to room temperature over a period of 5 min. In addition, B and E were annealed in a vacuum oven at 80°C for 3 days. C and F were quenched in a Dry Ice-methanol mixture directly from the molding press while at 140-150°C; they were subsequently dried in a vacuum oven at room temperature.

Measurements. DSC measurements were carried out on a Perkin-Elmer DSC-2. T_g's were determined at a scanning speed of 20°C/min and T_m's were determined at 10°C/min. Pure benzoic acid was used as a standard. The temperature of maximum excursion of the melting endotherm from the base line was taken to be T_m. Enthalpies of fusion were determined from the areas under the melting endotherms. Polymer-*p*-xylene and polymer-trichlorobenzene mixtures were prepared by first adding a known volume of diluent with a calibrated microsyringe into a sample pan and weighing; 4 mg of polymer were then added and the pan was sealed by crimping, care being taken to assure a good seal. T_m's of the mixture were determined as described above.

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 110° and the frequencies employed were 3.5, 11, and 110 Hz. Samples were heated at 1-2°C/min under dry nitrogen.

Dielectric measurements were carried out using a General Radio Capacitance Measuring Assembly of the transformer ratio arm bridge type (Model 1620A) in conjunction with a three-terminal cell (Balsbaugh Type LD-3) having 53 mm diameter electrodes. Capacitance and tan δ_ϵ measurements were carried out at 0.2, 0.5, and 1, 5, and 10 kHz over the temperature range −160 to 90°C. Temperature variation was achieved by regulating the flow of dry nitrogen, chilled or heated as appropriate, through the cell. All measured tan δ_ϵ values were corrected for dc conductivity, when present, in the usual manner.[2] ϵ' values in the semicrystalline samples (B, C, E, F) may be low by as much as 10% due to irregularities in thickness.

Results

The weight percent crystallinities reported in Table I represent the ratios $\Delta H_f/\Delta H_u$. ΔH_f is the experimental enthalpy of fusion and ΔH_u is the enthalpy of fusion for the hypothetical 100% crystalline polymer. ΔH_u was obtained from a least-squares fit of $1/T_m$ vs. v_1 in polymer-diluent mixtures according to the relationship of Flory.[8]

$$(1/T_m) - (1/T_m^0) = (R/\Delta H_u)(V_u/V_1)(v_1 - X_1 v_1^2) \quad \text{(I)}$$

where T_m^0 is the melting point of the pure polymer, T_m is the melting point of the polymer-diluent mixture, v_1 is the volume fraction of diluent, V_1 is the molar volume of the solvent, V_u is the molar volume of the polymer repeat unit, and X_1 is the polymer-solvent interaction parameter. The diluents employed were *p*-xylene and trichlorobenzene and no solvent effects, that is, no v_1^2 dependencies, were observed in either case. The results are collected in Table II. It should be noted that the percent crystallinity determinations and the dynamic mechanical relaxation studies utilized samples originating from the same films, while separate films were prepared for the dielectric studies.

Table III presents a summary of the essential features of the mechanical tan δ relaxations for the various derivatives. In general, three relaxation regions occur in the Hy—PP—CN derivatives, labeled α, β, and γ in order of decreasing temperature, while two relaxation regions, labeled β and γ in order of decreasing temperature, occur in the

Table II
Enthalpies of Fusion (ΔH_u) for the Hy-PP-CN Samples Determined by the Diluent Technique

Polymer	Sample	Solvent	ΔH_u, cal/g	Error, cal/g[a]
Hy-PP-CN (7.4)	B or C	*p*-Xylene	63	±4
Hy-PP-CN (7.4)	B or C	1, 2, 4-Trichlorobenzene	57	±7
Hy-PP-CN (20)	E or F	*p*-Xylene	49	±6
Hy-PP-CN (20)	E or F	1, 2, 4-Trichlorobenzene	45	±3
Linear polyethylene			65–68[b]	

[a] Determined by least-squares fitting. [b] J. R. Knox, "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N.Y., 1968, p 9.

Table III
Characteristics of the α, β, and γ tan δ Relaxations for the PP-CN and Hy-PP-CN Derivatives at 110 Hz

	γ		β		α	
Sample	T_{max}, °C	E_a, kcal/mol	T_{max}, °C	E_a, kcal/mol	T_{max}, °C	E_a, kcal/mol
A	−110[a]		−58	21		
B	−110	31	0		97	54
C	−109	20	10		92	29
D	−110[a]		−53	31		
E	−110		12	130	70	35
F	−115		13	66		

Taken as the temperature of the peak maximum in E'' at 110 Hz.

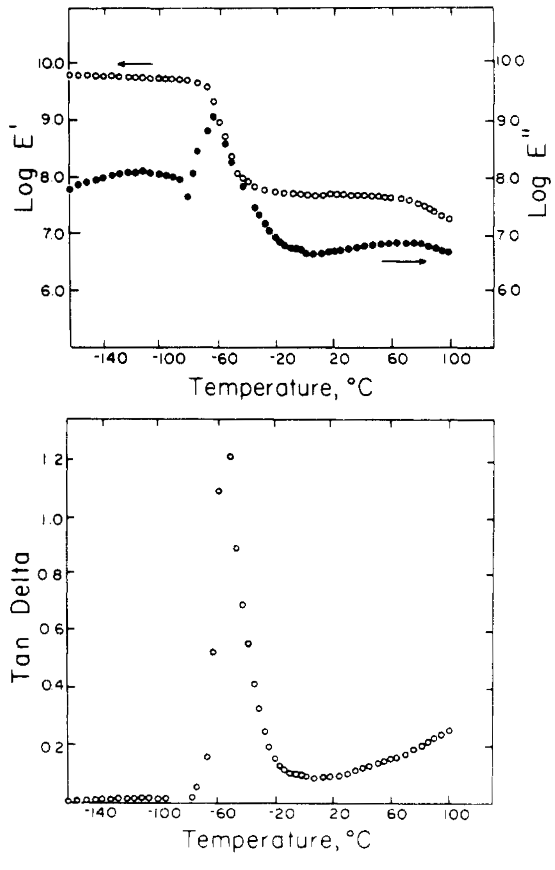


Figure 1. Temperature dependence of E' and E'' (upper) and tan δ (lower) at 110 Hz for sample D.

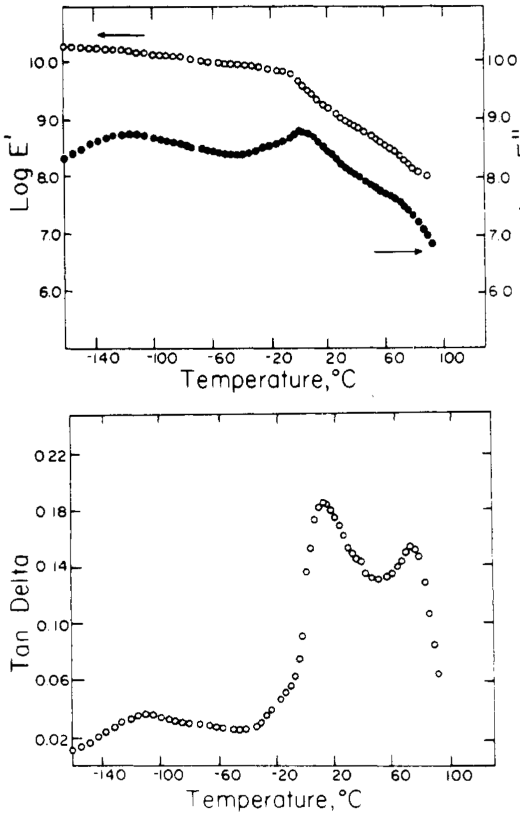


Figure 2. Temperature dependence of E' and E'' (upper) and tan δ (lower) at 110 Hz for sample E.

PP—CN derivatives. Activation energies were obtained from plots of the logarithms of the frequencies vs. $1/T_{max}$, T_{max} being the temperature at which the tan δ's assume their greatest values. The tan δ's were used for the calculations rather than E'' or D'' because of the far greater resolution in the T_{max} separation in tan δ compared to either E'' or D''. However, the γ relaxation in the PP—CN derivatives is much more prominent in the E'' plots than in the tan δ plots. Figure 1 exhibits the temperature dependencies of tan δ, E', and E'' at 110 Hz for sample *D*, while Figure 2 shows corresponding plots for sample *E*. Figure 3 gives the temperature dependence of E' and E'' at 110 Hz for sample A. Noteworthy in Figure 3 is the marked decrease in E' in the vicinity of 0°C. It is believed that this phenomenon results from the presence of a small amount of crystallinity in sample A which has a T_m in the vicinity of 0°. It is known[9] that the starting PP on which all the derivatives are based has a small crystalline content of about 10% or less with a T_m around 15°. The crystal structure is assumed to be similar to that found in high trans polypentenamers.[10] In contrast to this is the behavior of sample D which is completely amorphous. Above the β relaxation in sample D, E' takes on the typical value for a high molecular weight linear amorphous polymer of ca. 10^7 dyn/cm^2. The β relaxation in sample D is clearly associated with microbrownian segmental motions accompanying the glass transition of this polymer. This is evident from the large decrease in E' which oc-

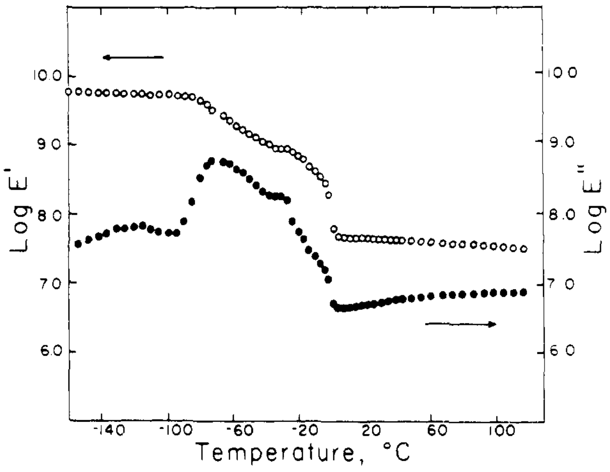


Figure 3. Temperature dependence of E' and E'' at 110 Hz for sample A.

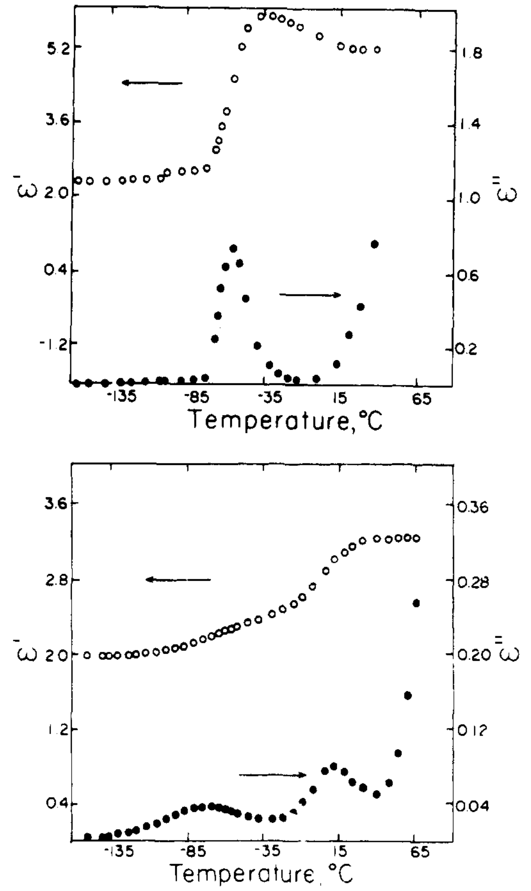


Figure 4. Temperature dependencies at 200 Hz of ϵ' and ϵ'' for sample D (upper) and sample E (lower).

curs at the β transition temperature (Figure 1). The β relaxation in sample A, on the other hand, consists of two partially merged processes. The lower temperature dispersion is most probably associated with motions accompanying T_g, while the higher temperature dispersion appears to be associated with the onset of melting. These overlapping relaxation mechanisms in sample A make comparisons between the temperature of the β process in this sample and that of sample D impossible. The overall behavior of these materials is very similar to that of PP itself, described previously.[1] The behavior of samples B, C, E, and F on the other hand is analogous to that of the hydrogenated PP's and to polyethylene.[1]

Table IV
Characteristics of the α, β, and γ Dielectric ϵ'' Relaxations for the PP-CN and Hy-PP-CN Derivatives at 200 Hz

	γ		β		α	
Sample	T_{max}, °C	E_a, kcal/mol	T_{max}, °C	E_a, kcal/mol	T_{max}, °C	E_a, kcal/mol
A			-69	18		
B	-88	13	15[a]		65[b]	33
C	-87	13	15[a]		40[c]	
D			-55	24		
E	-75	11	12			
F	-71	14	11			

[a] Shoulder (partially merged with α relaxation). [b] 10 kHz. [c] 500 Hz.

Table IV contains a summary of the dielectric relaxation results. Analogies exist to the mechanical results and the labeling scheme of α, β, and γ is employed for the dielectric loss peaks in a similar fashion to the mechanical loss peaks. Figure 4 presents the temperature dependence of ϵ' and ϵ'' at 200 Hz for samples D and E. The β relaxation in samples A and D arises from reorientation of the CN groups occurring as a consequence of motions accompanying the glass transition in these polymers. It may be noted that, since the CN groups are largely confined to the amorphous phase (see Discussion below), the dielectric β relaxation in sample A is not overlapped by the melting process to any significant extent. In fact, it may be seen from Tables I and IV that the difference between the temperatures of the dielectric β relaxations for samples A and D is the same as the differences between the T_g's of samples A and D measured by DSC. No γ relaxations are discernible in samples A and D and the γ relaxations of samples B, C, E, and F occur at considerably higher temperatures than the mechanical γ relaxations observed in these polymers. Sample B is the only polymer exhibiting a reasonably well resolved α peak. The β relaxation in B and C exists as a shoulder and its precise temperature location is difficult to specify. The α relaxation is completely absent in samples E and F and the β relaxations in these samples are of considerably greater magnitude than those in samples B and C. It is to be noted that the observed dielectric dispersion magnitudes generally increase with increasing CN concentration and it is thus postulated that they all arise from reorientations of CN dipoles which are rigidly attached to the chain backbone. The consequences of this assertion will be explored in the Discussion section.

Discussion

A reduction in ΔH_u is noted with increasing substituent content for many ethylene copolymers.[11] The theory of Sanchez and Eby[12] distinguishes two limiting cases. In the case where the comonomer units are completely excluded from the crystal lattice, it follows that

$$\Delta H_u = \Delta H \tag{1}$$

where ΔH refers to the linear, unsubstituted homopolymer. In the case where the comonomer units incorporate into the lattice as defects

$$\Delta H_u = \Delta H - X_B \Delta H_d \tag{2}$$

where X_B is the mole fraction of comonomer units and ΔH_d is the excess enthalpy associated with the formation of

Table V
Comparison of ΔH_u's for Hy-PP-CN with Those of Other Substituted Polyethylenes

Sample	Substituent (X_B)	Substituent Concentration (X_B/100 CH_2)	ΔH_u, cal/g	van der Waals "*b*" for the molecule CH_3–X_B[c]
Hy-PP-CN (7.4)	CN	1.5	60	0.12
Hy-PP-CN (20)	CN	4.0	47	0.12
Branched polyethylene[a]	CH_3	1.5	55	0.064
Branched polyethylene	CH_3	4.0	40	0.064
Chlorinated polyethylene[b]	Cl	1.4	52	0.065
Chlorinated polyethylene	Cl	4.0	36	0.065

[a] J. R. Knox, "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N.Y., 1968, p 9. [b] R. J. Roe, H. F. Cole, and E. P. Otacha, *Polym. Prepr., Am. Chem., Soc., Div. Polym. Chem.*, 12, 311 (1971). [c] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1972–1973, p D-146.

a defect in the crystal lattice caused by the presence of the substituent. It is reasonable to assume that the size of the substituent is the major determining factor concerning its presence or absence in the crystal lattice. Table V compares the ΔH_u for the two Hy—PP—CN samples studied to those of chlorinated linear polyethylenes and branched polyethylenes of the same degrees of substitution. The most direct comparison may be made between the Cl-substituted polymers and the CN-substituted polymers. It is apparent that neither follows the exclusion model prediction of eq 1 but that the CN substituent more nearly approaches it than the Cl substituent. The values of the van der Waals "*b*" constant quoted indicate that CN is considerably bulkier than Cl and thus is excluded from the lattice to a greater extent. The behavior of the branched polyethylenes indicates a somewhat greater exclusion than the Cl but less than the CN. It is to be noted that the methyl groups in branched polyethylene occur at the ends of alkyl chain branches which are mainly ethyl and butyl. Thus, although the van der Waals "*b*" constant for CH_3–CH_3 is the same as for CH_3–Cl, it is to be expected that the side groups in branched polyethylene are bulkier than the Cl substituents in chlorinated polyethylene. In a study of chlorinated polyethylenes ranging from 0.2 to 3.2 Cl groups per 100 CH_2 groups, it was found that the weight percent crystallinity measured by DSC remained at about 85% for all cases while the "*a*" unit cell dimension increased with increasing Cl content.[5] The much greater reduction in crystallinity observed in the case of the Hy—PP—CN's is also consistent with the conclusion that the CN groups are excluded from the crystal lattice to a greater extent than the Cl groups.

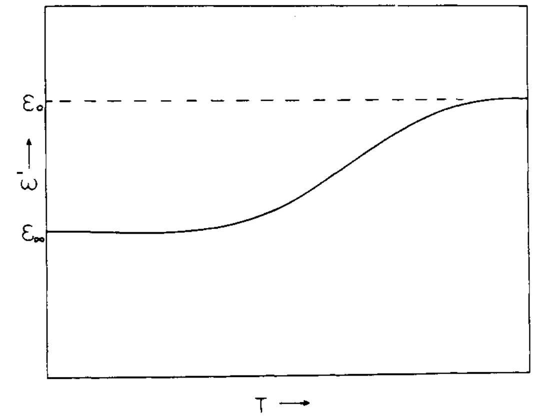


Figure 5. Schematic illustration of the dependence of ϵ' on temperature, showing the evaluation of ϵ_0 and ϵ_∞.

In order to analyze the dielectric data, it is necessary to evaluate the limiting values of ϵ^* at low and high frequencies, i.e., ϵ_0 and ϵ_∞, respectively. The most straightforward approach to this problem is to carry out measurements over a sufficiently wide frequency range so as to encompass the dispersion in question. Because of the breadth of relaxations in polymers, such measurements have only rarely been performed.[13] If ϵ' and ϵ'' are determined as functions of temperature, the expression $\epsilon_0 - \epsilon_\infty = A/T$ is valid over the temperature range of the relaxation, and the activation energy is independent of temperature, then $\epsilon_0 - \epsilon_\infty$ can be evaluated from the expression[2]

$$(\epsilon_0 - \epsilon_\infty)T_{\max} = 2E_a\left(\pi R\int_0^\infty \epsilon'' d(1/T)\right) \tag{3}$$

where E_a is the activation energy, R is the gas constant, and $T_{\max}$ refers to the ϵ'' peak maximum for the relaxation. Unfortunately, many sub T_g relaxations have an ϵ_0 which increases with temperature, including the γ relaxations of the Hy-PP-CN's. Also, relaxations associated with T_g usually exhibit temperature-dependent E_a's of the WLF type.[2] E_a is generally evaluated from the slopes of plots of log frequency vs. $1/T$ which can also lead to error as will be discussed subsequently. Because of these difficulties, the application of eq 2 for the determination of ($\epsilon_0 - \epsilon_\infty$) is semiquantitative at best. An alternative method for determining ($\epsilon_0 - \epsilon_\infty$) is through the use of Cole–Cole plots.[2] The values so obtained are dependent on the magnitude of the distribution parameter β because the geometric parameters of the resulting semicircle are functions of ϵ_0, ϵ_∞, and β. Therefore, ($\epsilon_0 - \epsilon_\infty$) will be model dependent, a different value being obtained, for example, if the Davidson-Cole distribution parameter were assumed instead. As a result of these considerations, all the ($\epsilon_0 - \epsilon_\infty$) values quoted in this study were obtained by direct inspection of the ϵ' dispersion as illustrated in Figure 5. The single relaxation in sample D, which shows a very small ϵ_0 temperature dependence, was analyzed by the method of eq 3 as well yielding identical results to the direct inspection method.

Table VI collects the experimentally determined values of ϵ_0 and ϵ_∞ for all the samples. In the semicrystalline polymers, ϵ_0 is the value of ϵ' taken at a temperature above the β relaxation (or α if it is present) and ϵ_∞ is the value of ϵ' taken at temperatures below the γ relaxation. The connection between ($\epsilon_0 - \epsilon_\infty$) and the concentration and magnitude of the dipoles participating in the relaxation process for liquids is given by the Onsager equation.[2]

$$N\mu^2 = 9kT/4\pi[(2\epsilon_0 + \epsilon_\infty)/\epsilon_0]\,[(\epsilon_0 - \epsilon_\infty)/(\epsilon_\infty + 2)^2] \tag{4}$$

where N is the number of dipoles per cubic centimeter and μ is the magnitude of the dipole moment in debyes. The

Table VI
Constants Relevant to Understanding the Relationship between ϵ_0 and ϵ_∞

Polymer	Sample	ϵ_0	ϵ_∞	$(\epsilon_0 - \epsilon_\infty)$	Temp, °C	f_a	$E' \times 10^{-7}$, dyn cm^{-2} (110 Hz)
PP-CN (7.4)	A	3	2.3	0.7	−30	3.8	86
Hy-PP-CN (7.4)	B	2.4	2.0	0.4	90	3.8	101
Hy-PP-CN (7.4)	C	2.6	2.1	0.5	90	3.2	59
PP-CN (20)	D	5.5	2.5	3.0	−10	2.6	4.9
Hy-PP-CN (20)	E	3.2	2.0	1.2	70	3.6	24
Hy-PP-CN (20)	F	3.6	2.1	1.5	70	3.1	19

equation is assumed to hold for the case where no orientational correlations are present between the dipoles which should certainly be true for the polymers of the present study. Anticipating the results we define a quantity f_a as follows

$$f_a = \frac{4\pi N\mu^2}{9kT}\,[\epsilon_0/(2\epsilon_0 + \epsilon_\infty)][(\epsilon_\infty + 2)^2/(\epsilon_0 - \epsilon_\infty)] \qquad (5)$$

If the system obeys the Onsager equation, f_a will be unity. In the present study it is assumed that all of the dipoles, that is, the CN groups, participate in the single β relaxation of samples A and D and contribute to the sum of the two amorphous phase relaxations, the γ and β, in samples B, C, E, and F. Thus N can be calculated from the known chemical composition

$$N = N_A\rho/M \qquad (6)$$

where N_A is Avogadro's number, ρ is the density, and M is the molecular weight of the polymer repeat unit. In the semicrystalline samples B, C, E, and F, the actual value of N is slightly less than that calculated due to the incorporation of a small quantity of CN groups into the crystal lattice. μ was taken to be 4.0 D for all samples which is the quoted value for cyanopropane.[14] Using the values for ϵ_0, ϵ_∞, N, and μ, determined as described above, the application of eq 5 results in the values of f_a collected in Table VI. Inspection of Table VI reveals that f_a varies from 2.6 to 3.8, indicating that the Onsager equation does not apply to these polymers. The simplest way to account for these results is to assume that the inapplicability of the Onsager equation arises from the fact that in these systems elastic restoring forces act on the dipoles, thus reducing their degree of alignment with the electric field compared to the case of a viscous liquid where no such forces exist. The greater the restoring force acting, the greater should be f_a. Table VI also lists E' (the storage modulus) values at the temperature at which ϵ_0 was determined. E' may be taken as a rough indication of the magnitude of the elastic restoring force. Table VI shows that there is indeed a correspondence between E' and f_a, the samples with greater values of f_a also exhibiting greater values of E'. It should be stressed that up to this point the concept of an elastic restoring force influencing the value of ϵ_0 is model independent, being a necessary consequence of the fact that the "relaxed" state in these polymers is rubber-like rather than viscous liquid like. It is not related to the nature of the relaxation processes leading to the rubber-like state.

Several models have been proposed to account for the relaxation process.[2] Yamafuji and Ishida[15] derived eq 5 by applying the diffusion equation to a polymer having small rigid dipoles attached to a polyethylene backbone, as part of a more general treatment. They label f_a as (Γ_a/kT) and interpret it as a complex function of molecular force constants arising from different types of molecular interactions occurring during the relaxation accompanying the glass transition. It is noteworthy that this theory predicts that below T_g, $(\epsilon_0 - \epsilon_\infty)$ increases with temperature while above T_g, $(\epsilon_0 - \epsilon_\infty)$ decreases with temperature. This behavior is observed in the case of the PP—CN and Hy—PP—CN polymers of the present study as well as in the chlorinated polyethylenes,[5] and many other substituted polyethylenes.[15] The site model of Ishida and Yamafuji,[16] which is a barrier theory applicable to a system of nonrigid dipoles attached to a polyethylene backbone, predicts that $(\epsilon_0 - \epsilon_\infty)$ will deviate from the Onsager value since the energy barriers restrict the dipole motion to a certain region of space. Matsuoka et al.[5] used the two-site model to explain the observed increase of ϵ_0 with temperature in the γ relaxation region in chlorinated polyethylenes. In the same system these workers applied the Onsager equation to the combined γ through α relaxations which led to a value of $N\mu^2$ as much as 40% low assuming that all of the dipoles participated in these combined relaxations. This discrepancy is easily understood in light of the above discussion as due to the elastic restoring force influencing the value of ϵ_0.

It remains to discuss the α, β, and γ relaxations from the mechanistic point of view. The essential features of these relaxations have been presented in the results section.

The γ relaxation in polyethylene and its substituted derivatives has been postulated to arise in part from motions occurring in both the amorphous and crystalline phases.[17] Considerable experimental evidence exists indicating the correctness of this assertion.[1,18-20] The present study serves to further reinforce this conclusion. That is, the mechanical γ relaxation occurs at considerably lower temperatures and is much broader than the dielectric γ relaxation in the Hy-PP-CN samples (B, C, E, F), in accordance with the idea that the crystalline γ relaxation occurs at lower temperatures than the amorphous γ relaxation and that the CN groups are largely excluded from the crystal lattice. In the case of samples A and D, a very small mechanical γ relaxation exists but there is no evidence for a dielectric γ relaxation. The mechanism of the crystalline γ relaxation has been postulated to involve local motions of chain ends present in the crystal lattice as defects,[17] while that of the amorphous γ has been postulated to involve conformational changes involving sequences of only a few bonds (crankshift motions).[21] Recently, conformational calculations have been performed[22] which indicate that the Schatzki crankshift mechanism (involving five bonds between stem bonds) is probably not operative but that the Boyer crankshaft mechanism[23] (involving three bonds between stem bonds) is responsible for the amorphous γ relaxation.

Because ϵ_0 can vary quite markedly with temperature, E_a is best obtained from experiments in which the frequency is varied at constant temperature rather than the reverse which is the procedure used here. The results must be viewed with some caution because of this. In general, the E_a's for the dielectric γ relaxations of the Hy—PP—CN samples (B, C, E, F) are less than those for their mechanical counterparts (Tables III and IV), and are comparable to results obtained for other substituted polyethylenes. They are considerably greater than the theoretical value of Boyd and Breitling[22] of 8.3 kcal/mol for the Boyer crankshaft mechanism. Nevertheless, the qualitative trend is consistent with the Boyd–Breitling predictions.

The β relaxation in the PP—CN samples (A, D) is clearly associated with motions accompanying the glass transition, as already mentioned in the results section. As a consequence, the E_a's of the β relaxation of these polymers should exhibit a WLF type temperature dependence. Unfortunately, it was not possible to carry out dielectric measurements over a sufficient frequency range to observe this effect. Both the dielectric and mechanical β relaxations in the Hy—PP—CN samples (B, C, E, F) exhibit behavior closely analogous to the corresponding relaxation in the hydrogenated polypentenamers.[1] This serves to reinforce the interpretation presented that the β relaxation in these polymers is also associated with motions accompanying the glass transition.

The α relaxation in polyethylene[17] and in the hydrogenated polypentenamers[1] has been assigned to motions occurring within the crystal phase. The virtual absence of a dielectric α relaxation in the Hy—PP—CN samples together with the small concentration of CN groups present in the crystal lattice provides strong support for this mechanism.

Conclusion

1. In the Hy—PP—CN samples, the CN groups are largely excluded from the polyethylene crystal lattice.

2. The Onsager equation cannot be applied even to the PP—CN samples indicating that dipole reorientation cannot be completely free. The probable cause of this is the presence of an elastic restoring force after the relaxation process has occurred.

3. The dielectric and mechanical relaxation behavior is generally analogous to that observed in the hydrogenated polypentenamers and other substituted polyethylenes. The γ relaxation consists of both an amorphous and crystalline component. The behavior of the amorphous component is consistent with the mechanism of Boyd and Breitling.[22] The β relaxation arises from microbrownian segmental motions accompanying the glass transition and the α relaxation arises from motions in the crystalline phase.

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References and Notes

(1) K. Sanui, W. J. MacKnight, and R. W. Lenz, *Macromolecules*, **7**, 101 (1974).
(2) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.
(3) G. P. Mikharlon, S. P. Kabin, and T. A. Krylova, *Sov. Phys. Tech. Phys. (Engl. Transl.)*, **2**, 1899 (1957).
(4) P. J. Phillips, G. L. Wilkes, B. W. Delf, and R. S. Stein, *J. Polym. Sci., Part A-2*, **9**, 499 (1971).
(5) S. Matsuoka, R. J. Roe, and H. F. Cole, "Dielectric Properties of Polymers", F. Karasz, Ed., Plenum Press, New York, N.Y., 1972, p 255.
(6) K. Sanui, W. J. McKnight, and R. W. Lenz, *Macromolecules*, **7**, 952 (1974).
(7) K. Sanui, W. J. MacKnight, and R. W. Lenz, *J. Polym. Sci., Polym. Lett. Ed.*, 11, 427 (1973).
(8) L. Mandelkern, R. R. Garrett, and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 3949 (1952).
(9) K. W. Scott, private communication.
(10) G. Natta, I. W. Bassi, and G. Fayherezzi, *Eur. Polym. J.*, **5**, 239 (1969).
(11) A. Kutner and D. S. Breslow, *Encycl. Polym. Sci. Technol.*, 384 (1967).
(12) I. Sanchez and R. K. Eby, *J. Res. Natl. Bur. Stand.*, in press.
(13) E. A. Nicol, B. E. Read, and G. W. Chantry, *Br. Polym. J.*, **5**, 379 (1973).
(14) R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", National Bureau of Standards, 1967.
(15) K. Yamafuji and Y. Ishida, *Kolloid Z. Z. Polym.*, **183**, 15 (1962).
(16) Y. Ishida and K. Yamafuji, *Kolloid Z. Z. Polym.*, **177**, 97 (1961).
(17) J. D. Hoffman, G. Williams, and E. Passaglia, *J. Polym. Sci., Part C*, **14**, 173 (1966).
(18) K. H. Illers, *Kolloid Z. Z. Polym.*, **250**, 426 (1972).
(19) L. W. McKenna, T. Kajiyama, and W. J. MacKnight, *Macromolecules*, **2**, 58 (1969).
(20) S. Lee and R. Simha, *Macromolecules*, **7**, 909 (1974).
(21) T. F. Schatzki, *J. Polym. Sci., Part C*, **14**, 139 (1966).
(22) R. H. Boyd and S. M. Breitling, *Macromolecules*, **7**, 855 (1974).
(23) R. F. Boyer, *Rubber Chem. Tech.*, **34**, 1303 (1963).