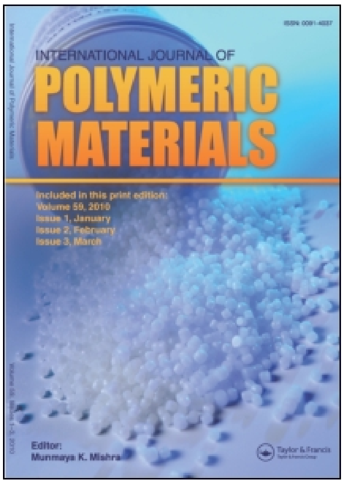

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Cryogenic Relaxations in Tough Amorphous Polymers

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Cryogenic Relaxations in Tough Amorphous Polymers

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The dynamic mechanical behavior of five phenyl containing polymers was studied at temperatures from 4.2 to 300°K using a free oscillating torsional pendulum. Polycarbonate (PCA) was found to have two relaxations γ and δ at 165 and 40–50°K, respectively. Orientation increases the temperature of the PCA γ relaxation from 165 to 170°K and crystallization causes a decrease in the intensity of the γ relaxation, but neither of these forms of molecular organization seem to affect the δ relaxation to any great extent. In addition to the previously reported γ relaxation at 300°K, melt cast polyphenylene oxide (PPO) has δ and ϵ relaxations at 75 and 12°K respectively. Residual solvent in PPO cast from $CHCl_3$ changes its mechanical spectra drastically, shifting the γ relaxation from 300 to 250°K, splitting the δ relaxation into two processes having maxima at 120 and 45°K and shifting the ϵ peak from 12 to 15°K. Amorphous poly(cyclohexylene dimethylene terephthalate) (CHDMT), whose mechanical spectra is previously unreported, has a very intense (Δ = 0.195) γ relaxation at 205°K which decreases in intensity when the polymer is crystallized. Below 80°K the internal friction of CHDMT is very weak with only a slight shoulder at 50°K and a small increase in intensity as the temperature drops from 20 to 4.2°K. The Polyimide (Kapton) has a low level of damping at all temperatures below room temperature with only one small (Δ = 0.020) relaxation at 180°K.

INTRODUCTION

For many years noncrystalline polymers were primarily characterized by their glass transition temperature, above which they were believed to be tough and below which brittleness was expected. More recently polymers have been synthesized which have phenyl rings in the main chain and which are tough below T_g. Investigation of these materials by dynamic mechanical and dielectric techniques has shown that some have rather extensive relaxation processes below the glass transition.[1–4]

It is the purpose of this paper to report the internal friction spectra and shear modulus of four tough amorphous polymers in the temperature range 4–300°K. In a rather extensive study of PET, Armeniades[4] has shown that its mechanical spectra is strongly sensitive to physical processing history. In order to determine the general nature of this behavior, the effect of solid state organization on the internal friction behavior of polycarbonate, and polyphenylene oxide has also been studied.

EXPERIMENTAL

Dynamic mechanical measurements were made on an inverted torsional pendulum constructed by Armeniades and described in detail elsewhere.[4] This equipment was designed especially to measure low level damping ($\Delta > 10^{-4}$) in thin polymer films. The strain of the specimen is measured by an optical system which is capable of determining angular displacement to $\pm 1\%$, and the read out is equipped with a counter timer which times oscillations to 0.05 seconds automatically. A dual thermocouple system accurate to better than ±0.5°K throughout the temperature range 4–300°K is used to monitor the temperature of the system and a heater surrounding the sample area makes it possible to hold temperature drifts to ±0.5°K during a single measurement.

The modulus and logarithmic decrement are calculated on an 1108 Univac Computer which is programmed to take into account effects due to tension in the sample, thermal expansion of the sample and viscous drag of the helium atmosphere.

The polymers used in this work are summarized in Table I.

RESULTS AND DISCUSSION

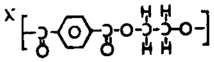
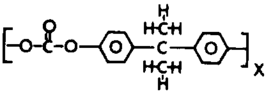
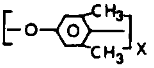
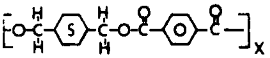
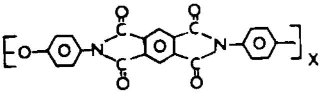
a) PCA

Shear modulus and internal friction were determined for PCA using specimens which had three different physical histories. The amorphous PCA was as-received melt quenched film, which showed neither orientation by birefrigence nor crystallinity by X-ray diffraction. Specimens of 28% crystallinity were prepared by exposing the amorphous film to acetone vapors at room temperature for 24 hours. Oriented specimens were prepared by drawing the amorphous film to 220% elongation at 151°C. These conditions were selected because drawing just above the glass transition temperature gives the maximum orientation with uniform extension.

Figure 1 shows the internal friction and shear modulus of amorphous PCA

TABLE I

Polymeric materials used in this work

PET	Amorphous poly(ethylene terephthalate) —  Melt cast commercial film, M_n = 15,000 with 1% low molecular weight (xylene extractable) species and no crystallinity by x-ray diffraction.	(a)
Mylar A (d)	Oriented and heat set PET	(a)
PCA	Bisphenol A polycarbonate —  Melt cast commercial Lexan (e) film Amorphous: As received Lexan film Crystalline: Crystallized by exposure to acetone vapor for 24 hours at room temperature. 28% crystalline by x-ray diffraction. Oriented: Drawn 220% at 151°C.	(b)
PPO (e)	Polyphenylene oxide —  Melt cast: Molded from powder at 300°C and rapidly cooled. Solvent cast: Received as film cast from $CHCl_3$ and contained 0.5% residual solvent.	(b)
CHDMT (d)	Poly(1,4-Cyclohexylene dimethylene terephthalate) —  Received as molding pellets with M_w = 24,000. Samples molded at 310°C and cooled at various rates.	(c)
Kapton (d)	Polyimide: Received and tested as 5 mil film — 	(a)

(a) Received from E. I. duPont de Nemours and Co.
(b) Received from G.E.
(c) Received from Eastman Kodak Co.
(d) Trade mark of DuPont
(e) Trade mark of G.E.

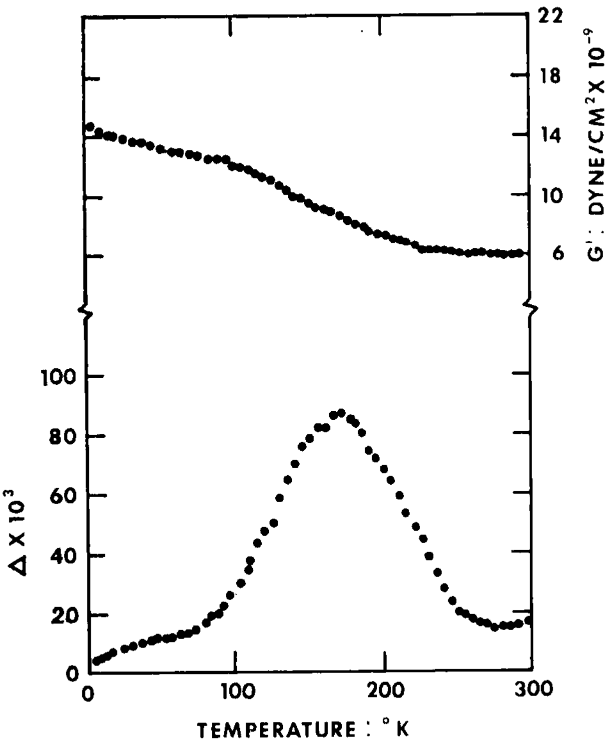


FIGURE 1 Shear modulus and logarithmic decrement of amorphous polycarbonate as a function of temperature.

from 4.2 to 300°K. The large γ relaxation at 165°K has been reported by several other authors.[5-8] Matsuoka[8] has found a large dielectric loss for PCA in the temperature region of the γ relaxation, which indicates that the relaxation is due at least in part to movement of the dipole in the carbonate group. In 1961 Reding[7] studied a series of polycarbonates which were modifications of the bisphenol A and found that the temperature of the γ relaxation did not shift appreciably unless groups were added in the positions ortho to the carbonate group. Substitutions of four chloro groups in the ortho positions caused a shift of the γ relaxation from $-110°C$ to $+80°C$ which further substantiates that the relaxation is related to motion of the carbonate group. NMR data by Matsuoka shows that the γ relaxation also involves the onset of some phenyl ring motion.

PCA also has a small rather broad δ relaxation which appears as a shoulder at 40–50°K. At the present time the molecular origin of this relaxation is unknown but it is likely due to vibration or rotation of the methyl groups which are attached to the central carbon. Other polymers such as polypropylene and poly α-methyl styrene have δ relaxations in the 20–40°K range and these relaxations have been attributed to methyl group motion.[9] The δ relaxation in PCA may occur at a slightly higher temperature due to greater hinderence to motion of these groups.

Internal friction and shear modulus of amorphous, crystalline and oriented PCA are compared in Figure 2. Orientation shifts the γ relaxation from 165 to 170°K which may be caused by an increase in activation energy which results from greater order in the oriented polymer. The γ relaxation is slightly less intense in the crystallized sample indicating that the process involves molecular motion within the amorphous phase.

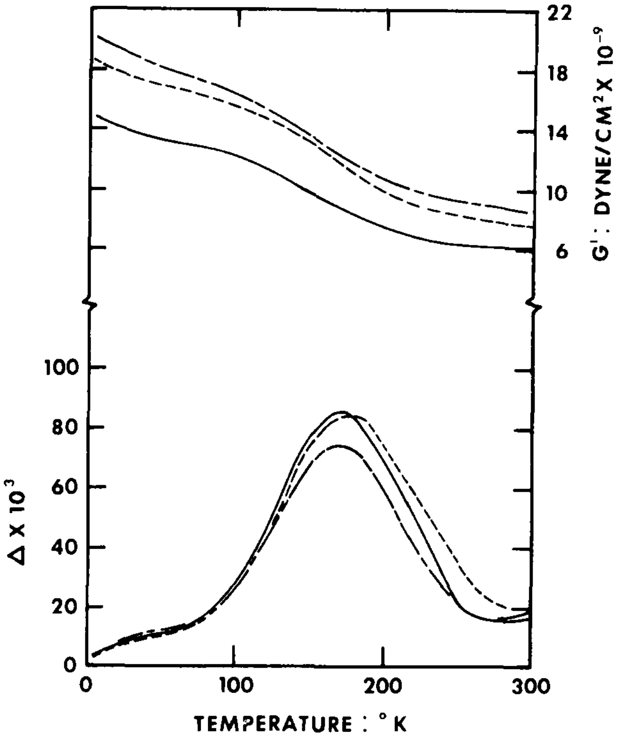


FIGURE 2 Shear modulus and logarithmic decrement of polycarbonate as a function of physical process history.

———— Amorphous
——–—— Crystallized 28%
- - - - - - - Oriented 220% at 151°C

As a comparison, Figure 3 shows the internal friction spectra and shear modulus which Armeniades[4] found for PET. Orientation and crystallization

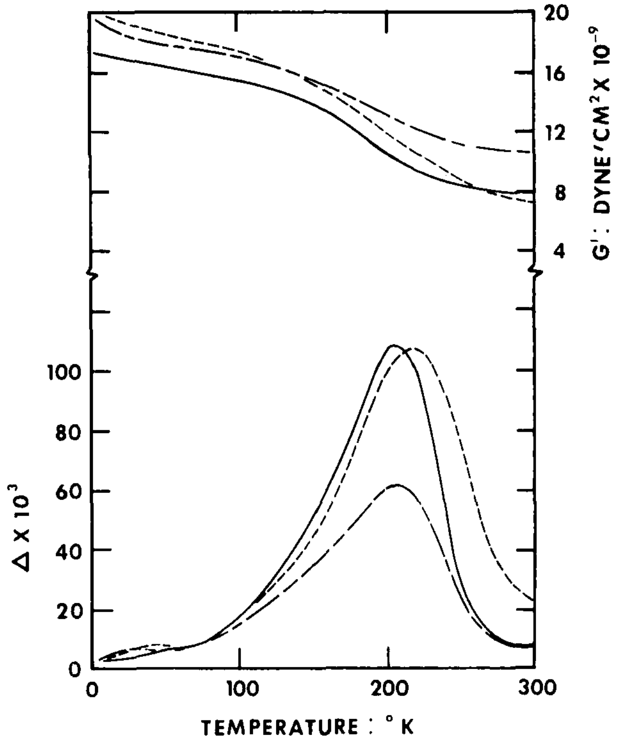


FIGURE 3 Effect of molecular organization on the shear modulus and internal friction of PET.

———— Amorphous
- - - - - - - Oriented 500%
—— - —— Crystallized 59%

affect the γ relaxation of PCA and PET in a similar manner but the effects are smaller in PCA because it can be crystallized or oriented to a lesser extent.

In PCA the temperature of the δ relaxation is unaffected by either crystallization or orientation and its magnitude is only slightly changed. This is in sharp contrast to the large effects found in PET. Again this may be due to differences in amounts of orientation or crystallization.

The modulus of PCA (Figure 2) decreases continuously throughout the temperature range 4.2 to 300°K with the sharpest drop in the region of γ relaxation. For PCA the total modulus defect (percentage modulus decrease from 4.2–300°K) is about 60%. This rather large modulus defect may be due to the comparatively large damping in PCA even at very low temperatures. Neither crystallization nor orientation greatly affect the shape of the modulus temperature curve for PCA.

b) PPO

The shear modulus and internal friction of two PPO specimens with widely varying physical histories are shown in Figure 4. The melt cast PPO specimens were compression molded at 300°C from dried powder. Solvent cast specimens were made by casting a film from a $CHCl_3$ solution and contained 0.5% residual solvent.

Three relaxations (γ, δ and ϵ) were found for melt cast PPO at 300, 70 and 12°K respectively. Heijboer[5] has previously reported relaxations in PPO at 300 and 160°K but has indicated that the 160°K peak may be due to water. The absence of this peak in the present work confirms the conclusion that the 160°K peak may be due to impurities.

Baccaredda *et al.*[10] have examined several modified polyphenylene oxides and have found that the position of the γ relaxation was a function of the groups attached to the phenyl ring. This evidence suggests that the γ relaxation in PPO may be due to motion of the phenyl ring.

Below the γ relaxation, PPO has a rather high background damping which seems to be initiated by the δ relaxation at 70°K. It is suggested that the δ relaxation may be due to oscillation of the phenyl ring and that this motion continues to absorb energy up to the γ relaxation. The low temperature ϵ peak could again be due to motion of the methyl groups.

It is known that small amounts of low molecular weight additives can greatly alter the internal friction of a polymer.[11] Solvent cast PPO is an example of such a polymer, for the residual $CHCl_3$ in the solvent cast sample changes every relaxation found in melt cast PPO. The most important change is the shifting of the γ relaxation from 300 to 250°K, for this is accompanied by a change from brittle to ductile behavior at room temperature. Other changes include splitting of the δ relaxation into two peaks at 45 and 120°K and the shifting of the ϵ peak from 12 to 15°K. The exact cause of these shifts is unknown but it is possible that $CHCl_3$ is hydrogen bonded to the PPO.

The shear modulus of PPO shown in Figure 4 decreases in an almost linear fashion from 4.2 to 300°K with no indication of a relaxation and with a modulus defect of only 37%, which is low for a tough polymer. Solvent cast PPO has a 30% higher modulus than that of the melt cast sample. This modulus increase may be caused by greater order in the solvent cast film.

c) CHDMT

In Figure 5 are shown the shear modulus and internal friction which were found for amorphous and crystalline CHDMT. The amorphous film was made by compression molding at 310°C and quenching directly into cold water. Crystalline specimens were made by heating the amorphous film to just below the melting point and cooling slowly to room temperature.

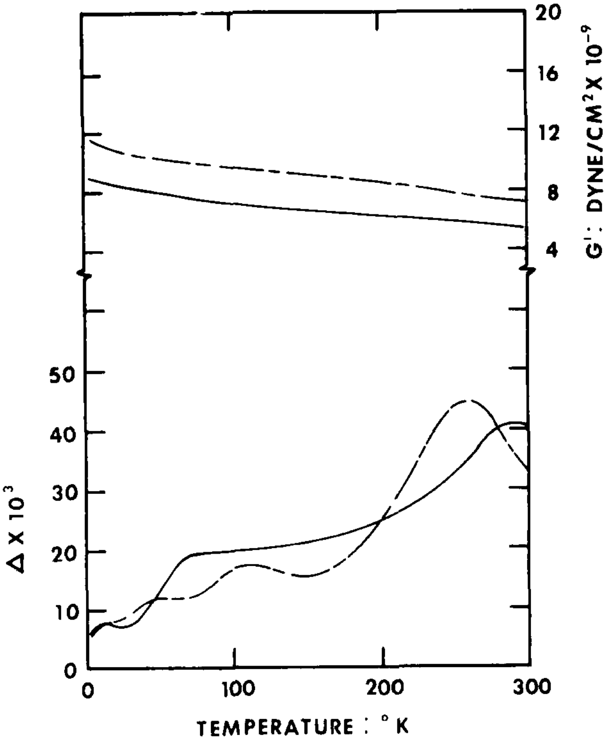


FIGURE 4 Shear modulus and logarithmic decrement of PPO as a function of casting technique.

— —— — Solvent cast from $CHCl_3$
——————— Melt cast

Amorphous CHDMT, of which the mechanical spectra has not previously been reported, has a very intense relaxation ($\Delta = 0.195$) at 205°K. Since this relaxation occurs at about the same temperature as the γ relaxation in PET, it is suggested that both relaxations may involve the —C(=O)—O group. However, the relaxation in CHDMT is nearly 80% larger than the PET γ relaxation, which indicates that the cyclohexane ring also may be contributing to the process. From the work of Turley,[13] it is known that the cyclohexane ring has a relaxation process in this temperature region.

Compared to PET (Figure 3) CHDMT has a very low level of damping below 80°K. There is only a small shoulder at 40 to 50°K and a slight increase in damping as the temperature drops from 20 to 4.2°K. The difference in low temperature damping in PET and CHDMT may indicate that the low temperature damping in PET may involve the small O—CH_2CH_2—O group.

As in both PET and PCA, crystallization of CHDMT decreases the magnitude of the γ relaxation. In addition, crystallization seems to move the

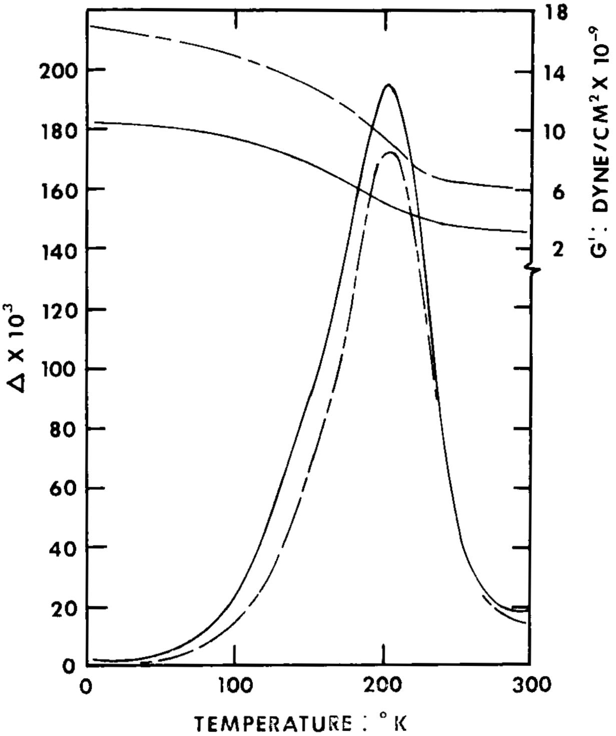


FIGURE 5 Shear modulus and logarithmic decrement of CHDMT as a function of physical history.

——— Amorphous
— — — Crystalline

γ relaxation to a slightly higher temperature and decreases the size of the low temperature peak at 50°K.

The shear modulus of CHDMT (Figure 5) drops continuously from 4.2 to 300°K, with a very sharp drop in modulus in the temperature region of the γ relaxation. The total modulus defect is 71% and 65% for amorphous CHDMT and crystalline CHDMT, respectively. This difference is to be expected, for the amorphous CHDMT has the larger γ relaxation.

d) Polyimide (Kapton)

The internal friction and shear modulus of as-received amorphous Kapton film are shown in Figure 6. The Polyimide Kapton has a very low level of damping throughout the temperature region of 4.2–300°K, with only one small relaxation process at about 180°K. Since this is in the same temperature

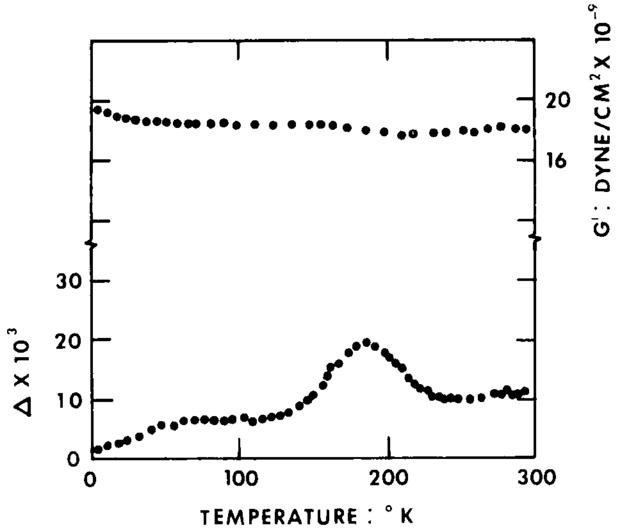


FIGURE 6 Shear modulus and logarithmic decrement of Kapton.

region as the transition in PET, this relaxation may also be due to —C(=O)— motion.

The shear modulus of the Polyimide (Kapton) behaves in an erratic manner due to error caused by having a sample which was too thin. Armeniades[4] has cautioned against the use of thin samples, but it is not possible to prepare Polyimide (Kapton) films thicker than 5 mil.

e) Correlation of Shear Modulus with Transition

Table II shows the existence of from one to four relaxations in each of the polymers studied. Since the logarithmic decrement can be measured only

TABLE II
Summary of the low-temperature relaxations

Material	γ peak °K	$\Delta \times 10^3$ at peak	δ peak °K	$\Delta \times 10^3$ at peak	ϵ peak °K	$\Delta \times 10^3$ at peak
PCA	165	83	40–50	11	—	—
PET[a]	200	110	50	6	—	—
PPO[b]	290–300	—	—	—	—	—
PPO (MC)	290	42	75	19	12	8
PPO (SC)	250	45	120	18	15	8
			45	12		
CHDMT	205	195	50	4	—	—
Kapton	180	20	—	—	—	—

[a] Armeniades[4]
[b] Heijboer[5]

down to 4.2°K, another method must be sought to determine the presence of relaxation processes at still lower temperatures. The third law of thermodynamics demands that at absolute zero the modulus of a system must approach a constant. Therefore, it has been suggested that relaxations below 4.2°K can be detected by plotting shear modulus as a function of log temperature.[12] From Figure 7 it can be seen that crystalline polymers such as PE and POM do not have relaxations below 4.2°K for $dG'/dT \to 0$ as $T \to 0$. Amorphous polymers such as PPO and PS have a finite change in modulus in the 1°K to 4°K range and therefore may have relaxation processes occurring even below 4.2°K.

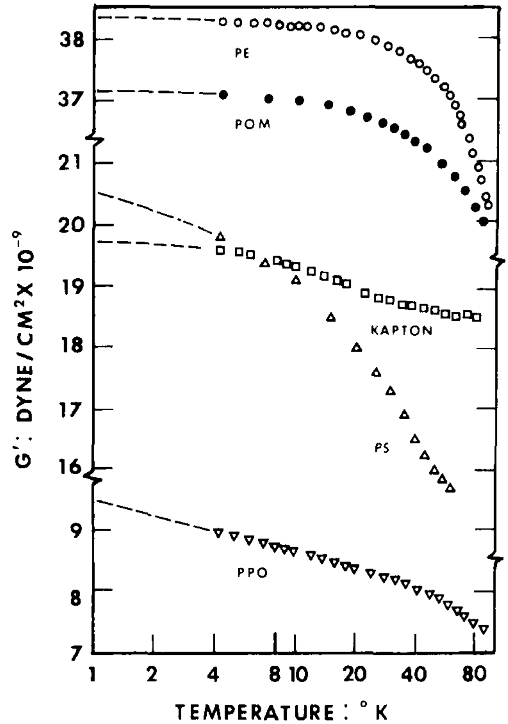


FIGURE 7 Shear modulus of various polymers plotted as a function of logarithmic temperature.

When CHDMT is amorphous, dG'/dT is nearly constant (see Figure 8) and negative from 35 to 4.2°K indicating that a relaxation is occurring and continuing below 4.2°K. This relaxation is also indicated by the low temperature damping (Figure 5) which is increasing as the temperature drops from 20 to 4.2°K. Crystallization decreases the low temperature damping in

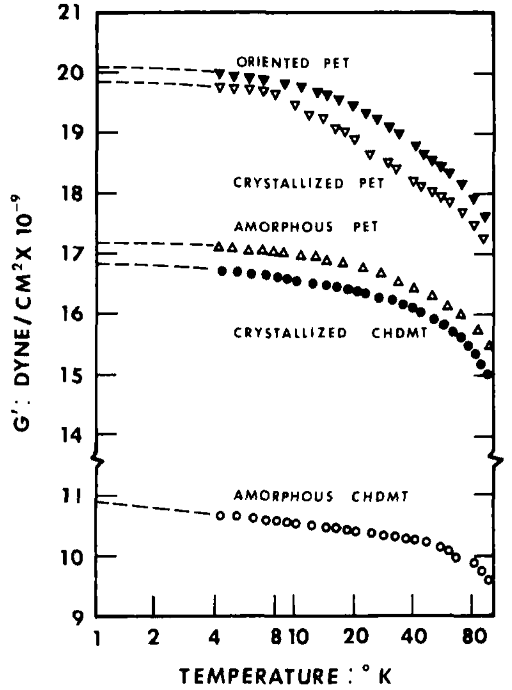


FIGURE 8 Effect of crystallinity and orientation on the shear modulus of PET and CHDMT.

CHDMT and also decreases dG'/dT as the temperature approaches absolute zero, indicating that crystallization hinders molecular motion and lessens the intensity of the relaxation process. Crystallization does not cause a similar change in low level modulus behavior of PCA (Figure 9), possibly because PCA is unable to crystallize to a great extent. From Table III it can

TABLE III

Correlation between low temperature damping and derivative of shear modulus at 1°K

Material	$(dG'dT)/G'$ at 1°K	$\Delta \times 10^3$ at 4.2°K
PE[a]	$< 1 \times 10^{-3}(°K)^{-1}$	0.8
POM[a]	$< 1 \times 10^{-3}(°K)^{-1}$	1.8
Kapton	$< 1 \times 10^{-3}(°K)^{-1}$	1.5
CHDMT (Crystalline)	$2 \times 10^{-3}(°K)^{-1}$	1.5
CHDMT (Amorphous)	$7 \times 10^{-3}(°K)^{-1}$	2.0
PCA	$9 \times 10^{-3}(°K)^{-1}$	4.0
PS[b]	$13 \times 10^{-1}(°K)^{-1}$	5.0
PPO	$18 \times 10^{-3}(°K)^{-1}$	5.0

[a] Y. S. Papir (private communication)

[b] C. D. Armeniades (private communication)

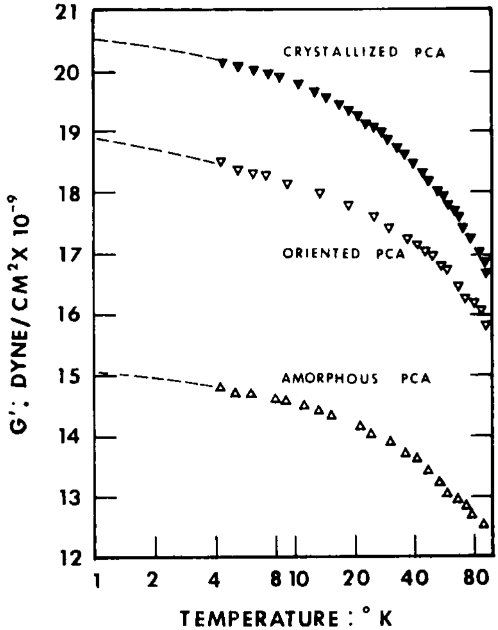


FIGURE 9 Shear modulus of PCA as a function of orientation and crystallization.

be seen that dG'/dT can be correlated with damping at 4.2°K for most polymers.

CONCLUSIONS

In addition to the previously reported γ relaxation at 165°K, PCA has a small δ relaxation at 40–50°K. Orientation shifts the γ relaxation from 165 to 170°K and crystallinity decreases its intensity but these effects are less pronounced than those found in PET. Neither crystallization nor orientation seem to affect the δ relaxation. The greater effects seen in PET may be due to its greater orientation and crystallization.

Melt cast PPO has two unreported relaxations δ and ϵ at 75 and 12°K respectively as well as the γ relaxation at room temperature. In solvent cast PPO, the residual $CHCl_3$ has a pronounced effect on the low temperature transitions. Both the intensity and temperature of the γ relaxation are changed, the δ relaxation is split into two peaks with maxima at 45 and 120°K and the ϵ relaxation is shifted from 12 to 15°K. The shift of the γ relaxation from 300 to 250°K results in solvent cast PPO being ductile at temperatures at which melt cast PPO is brittle.

Previously uninvestigated CHDMT has a very intense relaxation ($\Delta = 0.195$) at 205°K. Below 80°K the internal friction of CHDMT becomes very low with only a very weak relaxation appearing as a shoulder at 50°K and a slight increase in damping as the temperature drops from 20–4.2°K. Crystallization of CHDMT causes a decrease in its γ relaxation intensity indicating that the γ process may involve motion within the amorphous phase.

Although the Polyimide (Kapton) is a tough polymer at low temperatures, it has a low level of damping from 4.2 to 300°K with only a single weak relaxation at 180°K.

In some amorphous polymers, the modulus does not approach a constant value as the temperature approaches 0°K indicating the presence of relaxations below 4.2°K.

References

1. L. E. Nielsen, *Mechanical Properties of Polymers* (Reinhold, 1962), p. 180.
2. C. D. Armeniades, I. Kuriyama, J. M. Roe, and E. Baer, *J. Macromol. Sci.* **B1,** 777 (1967).
3. K. H. Illers and H. Breuer, *J. Colloid Sci.* **18,** 1 (1963).
4. C. D. Armeniades, *Ph.D. Thesis* (Case Western University, Sept. 1969).
5. J. Heijboer, *J. Polym. Sci.* **C16,** 3755 (1968).
6. K. H. Illers and H. Breuer, *Kolloid-Z.* **176,** 110 (1961).
7. F. P. Reding, J. A. Faucer, and R. D. Whitman, *J. Polymer Sci.* **54,** S56 (1961).
8. S. Matsuoka and Y. Ishida, *J. Polym. Sci.* **C14,** 247 (1969).
9. J. A. Sauer and R. G. Saba, *J. Macromol. Sci.—Chem.* **A3** (7), 1217 (1969).
10. M. Baccaredda, E. Butto, V. Frosini, and S. De Petris, *Mater. Sci. Eng.* **3,** 157 (1968-69).
11. C. D. Armeniades, E. Baer, and J. K. Rieke, *J. Appl. Polymer Sci.* **14,** 2635 (1970).
12. A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses* (John Wiley and Sons, New York, 1968), p. 395.
13. S. G. Turley, quoted by R. F. Boyer, 1968 International Award in Plastics and Science Engineering lecture (New York City, May 8, 1968).