

Physical Studies of Ionically Terminated Polytetrahydrofuran Polymers. IV. Solid-State Studies

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SYNOPSIS

The object of this work was to investigate the effect of the introduction of pyridinium chain-ends in polytetrahydrofuran (PTHF) polymers on certain solid-state properties. A comparison of solid-state properties of methoxy-terminated (PTHF-OMe) with pyridinium bromide-terminated (PTHF-Py) polytetrahydrofuran polymers of virtually identical molecular weights was made. Crystallization studies and dynamic mechanical and stress-strain analyses have been undertaken. It was concluded that the introduction of the ionic pyridinium bromide groups to the PTHF polymers influenced the degree of crystallinity and this, in turn, affected other physical properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polytetrahydrofuran (PTHF) is a crystalline polymer, some of whose properties are shown in Table I. In the crystalline state, it has a planar zigzag chain conformation similar to that of polyethylene, but not fully linear. The kinetics of crystallization of PTHF polymers have been studied dilatometrically¹ and by dielectric permittivity.¹³ As usual, the introduction of comonomer units decreases the degree of crystallinity. In one study,¹⁴ 20–30% of 3-ethyl-3-chloromethyloxetane completely prevented crystallization. The isothermal crystallization of PTHF polymers has been studied¹⁵ by dilatometry, dielectric measurements, DTA, and small-angle X-ray scattering. Crystalline regions with very narrow size distributions and amorphous regions with broad size distributions are produced, consistent with a morphology of small-angle branched lamellae. During secondary crystallization, slight lamellar thickening occurs and there is an increase in the densities of both the crystalline and amorphous phases. Secondary crystallization is interpreted in terms of an increasing degree of perfection of the crystalline re-

gions with time. There is also evidence⁴ for an increase in surface free energy.

Dynamic mechanical measurements of storage and loss components of the rigidity modulus of PTHF polymers have been determined¹⁶ for several frequencies. There is a main relaxation (α -transition) region associated with the onset of micro-Brownian motion of the main chain. In the region of the melting temperature, a catastrophic drop in modulus appears. Also, a secondary mechanical (β -transition) process characteristic of motion of four or more methylene units is visible.^{4,17}

An understanding of the relations between bulk properties and molecular architecture is a major aim of polymer science research. Chemical modification of a polymer has been a powerful tool for making novel polymeric materials. Many varieties of organic ions can be incorporated into polymers, either as part of the backbone or on a side chain or even at the chain ends, imparting a wide range of properties to the resultant ion-containing polymers.

It was, therefore, of considerable interest to ascertain to what extent the properties of ion-containing polymers in the bulk are a function of the type and structure of the polymer and the ion involved. The object of this study was to investigate the effect of the introduction of pyridinium bromide end groups in PTHF polymers. This has been studied by comparing the solid-state properties of PTHF-OMe and PTHF-Py polymers of similar molecular weight.

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Table I Properties of Tetrahydrofuran Polymers

Property	Value	References
Melting temperature (°C)	42, 55, 58–60	1–6
Glass transition temperature (°C)	–86	1, 4, 7–9
Tensile strength (MN/m ²) ^a	27.6–41.4	10
Elongation (%) ^a	300–820	10
Modulus of elasticity (MN/m ²)	96.5	11
Degree of crystallinity (%)	33, 80	1, 4
Unit cell dimensions (nm)		5, 12
<i>a</i>	56.1, 54.8	
<i>b</i>	89.2, 87.3	
<i>c</i>	122.5, 120.7	
β	134°30', 134.2°	
space group	<i>C2/c</i> , <i>C2/c-C2h</i>	

^aExact value depends on molecular weight.

EXPERIMENTAL

The PTHF polymers used in this work were synthesized by anionic polymerization using a procedure that is already detailed¹⁸ in the literature. The PTHF-OMe and PTHF-Py series cover a relatively wide range of molecular weights. A previous publication¹⁹ in this series contains full characterization data.

Sheet Preparation

PTHF samples in sheet form were used to carry out the solid-state studies. These sheets were prepared by using a hot press at 60°C at a pressure of 20 tons on 4 in.-diameter ram for 5 min. A "picture-frame" mold was used. The pressure was retained during the cooling period. The samples were stored in a freezer at ca. –20°C prior to testing.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to study melting, crystallization, and the glass transition. DSC thermograms of the PTHF polymers were obtained using a Perkin-Elmer DSC-1B. Test pieces weighing approximately 20 mg were cut and sealed into aluminum pans and tested at a heating rate of 8°C/min. DSC was used to determine the

crystallinity of the PTHF polymers. The method required the measurement of the heat of fusion (ΔH_f) of the polymer and the assumption that this quantity is proportional to the crystalline content of the material. If the heat of fusion of a hypothetical 100% crystalline material is known, then the weight fraction of crystalline material in the unknown sample can be determined.²⁰

Thermal Mechanical Analysis

A Perkin-Elmer TMS-1 thermal mechanical analyzer employs two operating modes: penetration and expansion. In this study, investigations were generally performed using the former mode because of its better sensitivity. Samples, approximately 1.0 × 1.0 × 0.5 cm in dimension, were cut from the prepared sheets and tested over the temperature range –160 to 40°C at a heating rate of 5°C/min. The samples were purged with dry helium during the test.

Optical Microscopy

A Nikon Microflex model EFM optical microscope with a semiautomatic photomicrographic attachment was used. Each sample was melted and photographs were taken (18°C) over a period of time to study the crystallization process to completion.

Stress-Strain Measurements

The stress-strain behavior of a limited number of the PTHF polymers was examined (18°C) using a J. J. Lloyd tensometer. Standard dumbbell test pieces were cut from sheets of the polymers. The extension was continued to break. The strain rate was 1 cm/min in all cases.

Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties of these PTHF polymers were investigated using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA). This DMTA instrument is a nonresonance, forced vibration instrument. It is capable of operating over a wide range of temperatures from –150 to 300°C at a number of fixed frequencies. The dimensions of the test pieces were generally about 1.3 × 0.08 × 0.04 cm. Samples were scanned over the desired temperature range at a heating rate of 2°C/min at frequencies of 0.33, 1, 10, and 30 Hz.

RESULTS AND DISCUSSION

Crystallinity and Crystallization Studies

Table II shows the values of the melting points and the percentage crystallinities (standard deviation $\pm 1\%$) of the PTHF-OMe and the PTHF-Py samples. The melting point, T_m , was measured as the peak temperature of the endotherm. It can be seen that the degree of crystallinity of the PTHF-Py samples are lower than those of the PTHF-OMe samples, showing that the ionic ends do influence the degree of crystallinity. It was also noted that the magnitude of the decrease in percentage crystallinity of the low molecular weight samples A and B is higher than for the higher molecular weight samples G and H. The low molecular weight samples A and B were also more crystalline than were samples G and H. The greater number of entanglements in the higher molecular weight materials may be hindering chain motions. A second factor may be the higher viscosity of the higher molecular weight polymers. The higher molecular weight samples G and H were chosen for these solid-state studies because of their easier handling in both sheet preparation and in the application of the different techniques used.

The thermal mechanical analysis technique was also used to calculate values for the melting temperature and the glass transition temperature, T_g . Table III shows that the melting temperature values for samples G and H compare favorably with the values measured earlier by DSC. It may be noted from Table III that the glass transition temperature of sample H is lower than the value for sample G. This may be explicable in terms of the difference in degrees of crystallinity.

Isothermal crystallization was carried out on samples G and H using the DSC instrument. The

Table III Some Physical Constants of PTHF Samples Obtained from TMA

Sample	M_n	T_g (°C)	T_m (°C)
G	44,000	-75	33
H	44,100	-83	32

sample was melted at 50°C and held at that temperature for 10 min. The temperature was then rapidly reset to the crystallization temperature of -25°C. A time-base record was then obtained until the crystallization was complete. The end of crystallization was determined as the time at which the pen returned to the original base line. It was found that the crystallization times of samples G and H were 97 and 114 min, respectively. Thus, sample G not only crystallizes to a somewhat greater extent than does sample H, it also crystallizes faster.

It has been reported¹⁵ that PTHF of high molecular weight crystallizes under ambient conditions by two distinguishable processes to give an overall crystallinity of approximately 50%. The primary process concerns nucleation and radial growth of lamellae in a spherulitic regime until impingement between neighboring spherulites is complete. The secondary process increases the crystallinity by a slow isothermal thickening and increases the density of the crystalline lamellae through the removal of defects. Possibly because of the close constraints imposed on the amorphous regions by the crystallites, the amorphous phase also increases in density during the secondary crystallization process.

Samples G and H were used to monitor the crystallization process by using an optical microscope. Examination of thin sections of PTHF samples showed that spherulites grow up to diameters of a few millimeters. It was reported²¹ that the number, size, and fine structure depend on the temperature of crystallization, which determines the critical size of the nucleating center. This means that large, fibrous structures form near T_m , whereas greater numbers of smaller spherulites grow at lower temperatures. It was found that when the nucleation density is high, the spherical symmetry tends to be lost.

It was also noted that secondary crystallization takes place at a slow rate at 20°C. Even around 15 h, noticeable change is still taking place in both polymer types. It was also noted that the PTHF-OMe sample yields larger and fewer spherulites than does the PTHF-Py sample. Therefore, it can be concluded that the introduction of the pyridinium

Table II Some Physical Constants of PTHF Samples Obtained by DSC

Series	Sample	M_n	T_m (°C)	Crystallinity ^a (%)
PTHF-OMe	A	10,800	32	51
	J	24,000	32	49
	C	29,000	33	43
	G	44,000	33	42
PTHF-Py	B	10,900	31	43
	K	24,100	32	44
	D	29,100	32	39
	H	44,100	32	39

^a Standard deviation $\pm 1\%$.

bromide groups in the PTHF significantly influences the crystallization process.

Dynamic Mechanical Studies

The investigation of the dynamic modulus and internal friction over a wide range of temperatures and frequencies has proven to be very useful²² in studying the structure of high polymers and the variations of properties in relation to end-use performance. The dynamic loss modulus, or damping, is sensitive not only to many kinds of molecular motion, but also to various transitions, relaxation processes, structural heterogeneities, and the morphology of multiphase systems. Therefore, interpretations of the dynamic mechanical properties at the molecular level are of great scientific²³ and practical importance.

Some research has been done on the dynamic mechanical properties of PTHF polymers. Willbourn⁸ studied the dynamic mechanical behavior of PTHF to investigate the glass transition and the secondary dispersions of these polymers. Wetton and Williams⁴ reported dielectric loss measurements over a range of frequencies for PTHF polymers. The research carried out by Wetton and Allen¹⁶ indicated that PTHF exhibits two dispersions below 0°C. The temperature location of these two dispersions were

-120 and -84°C at 0.1 Hz. They also noted that the temperature of the lower dispersion shows the stronger frequency dependence, with the result that greater separation is achieved at lower frequencies. They concluded that the locations of these two dispersions agree with those discussed by Willbourn.⁸

The dynamic mechanical studies in this work were carried out only on samples G and H to ascertain the influence of the ionic ends. These dynamic mechanical results were compared with those of the previous research.^{4,8,16} Measurements of the dynamic mechanical storage and loss components of modulus of both samples were made at 0.33, 1, 10, and 30 Hz. Figures 1-4 show the results.

Figures 1 and 2 show that both PTHF-OMe (sample G) and PTHF-Py (sample H) have two dispersions below 0°C. The lower dispersion is a secondary β -process characteristic of motions involving four or more methylenes (i.e., the four methylene groups in the tetrahydrofuran repeat unit). The β -peak falls in the range of -140 to -124°C. Willbourn⁸ indicated that the β -relaxation in both amorphous and crystalline polymers could in many cases be attributed to a restricted motion of the main chain that required a run of at least four methylene groups. This is the crankshaft mechanism of Schatzki²⁴ and Boyer.²⁵

The α -dispersion represents the main relaxation (T_g) region arising from the amorphous regions of

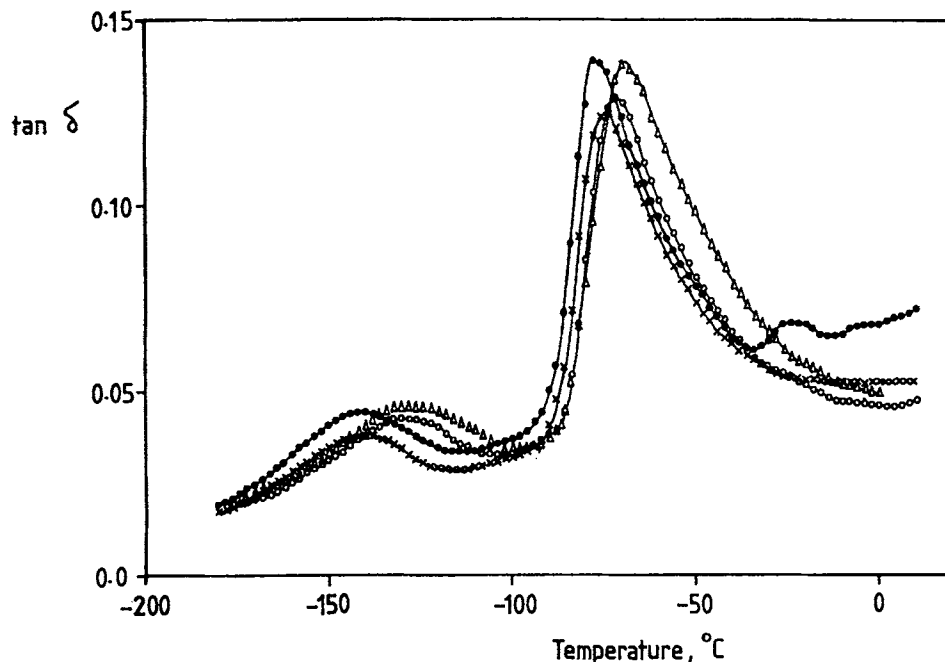


Figure 1 Tan δ -temperature plots for sample G (PTHF-OMe) at (●) 0.33 Hz, (X) 1 Hz, (○) 10 Hz, and (△) 30 Hz.

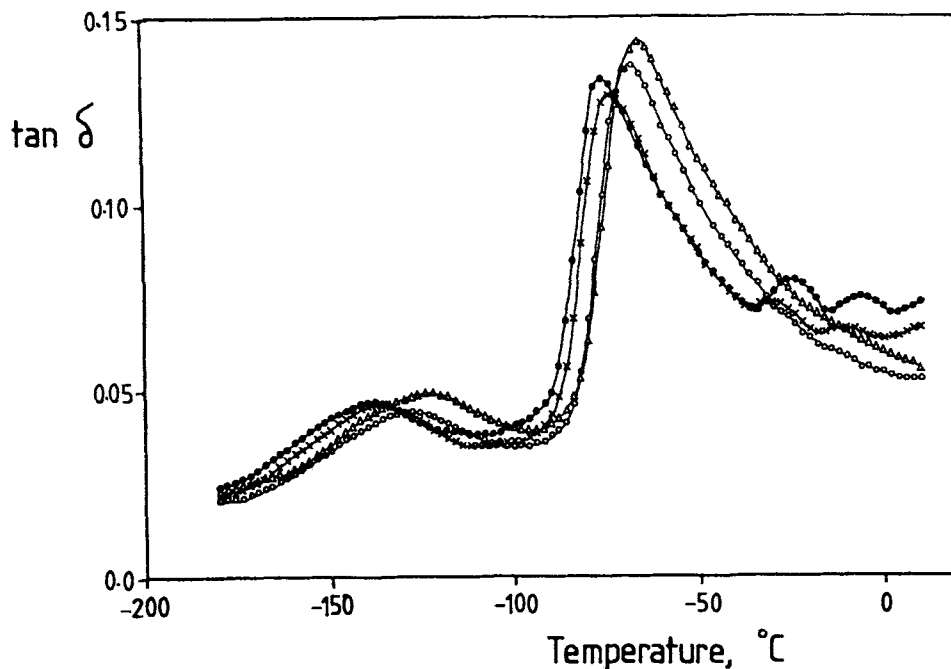


Figure 2 Tan δ -temperature plots for sample H (PTHF-Py) at (●) 0.33 Hz, (X) 1 Hz, (O) 10 Hz, and (Δ) 30 Hz.

the polymers. The glass transition temperatures of samples G and H fall between -75 to -66°C for the frequency range used.

The PTHF samples also show other tan δ loss peaks at approximately -25 and -6°C , which fall between the α -dispersion and the crystalline melting

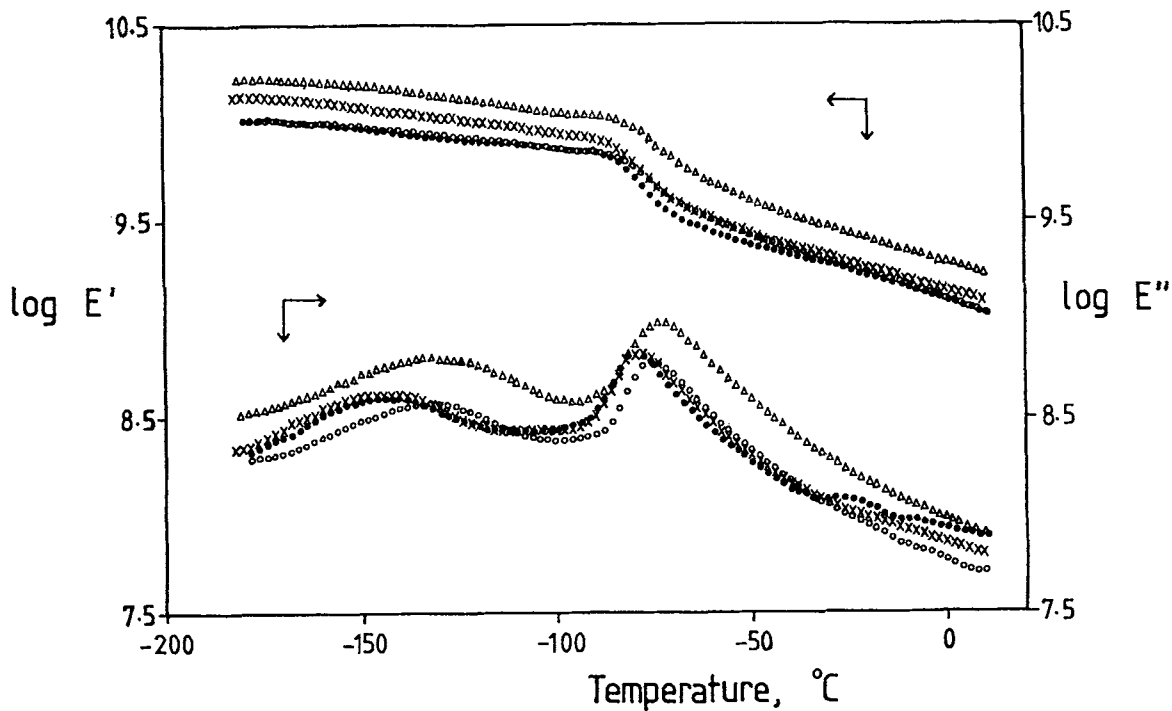


Figure 3 E' and E'' temperature plots for sample G (PTHF-OMe) at (●) 0.33 Hz, (X) 1 Hz, (O) 10 Hz, and (Δ) 30 Hz.

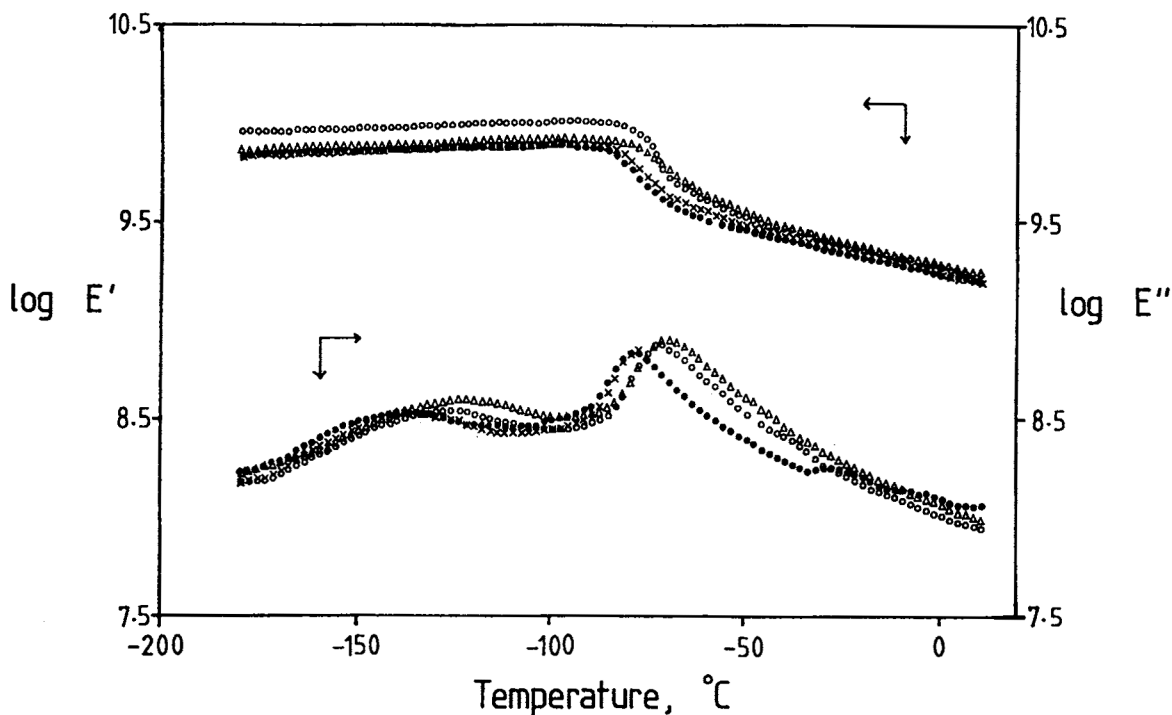


Figure 4 E' and E'' temperature plots for sample H (PTHF-Py) at (●) 0.33 Hz, (X) 1 Hz, (○) 10 Hz, and (△) 30 Hz.

temperature. These are more pronounced at lower frequencies and have also been reported by Wetton and Allen.¹⁶ This relaxation may be called the α_c -dispersion. It has been reported²³ that this process involves rotation about the chain axis of chain-folded polymers to yield a second-order expansion of the lattice parameters perpendicular to the chain direction in the crystalline phase. Takayanagi²⁶ also attributed the α_c -dispersion to molecular motion within the crystalline phase. He concluded that this crystalline dispersion was the result of the frictional

viscosity of specific crystalline planes or molecules within the crystals.

Table IV summarizes the dynamic mechanical results. Comparison of the dynamic mechanical data for the PTHF-OMe sample and the PTHF-Py sample indicates that the values of the height of the α -dispersion peak ($\tan \delta_{\max}$) of the PTHF-Py sample was larger than that of PTHF-OMe sample for most of the frequencies. This is what would be expected for a somewhat less crystalline sample.

An investigation by a cantilever vibration

Table IV Dynamic Mechanical Properties PTHF-OMe (Sample G) and PTHF-Py (Sample H)

Sample	Frequency (Hz)	α -Transition (°C)	Tan δ_{\max}	β -Transition (°C)
G	0.33	-78	0.139	-142
	1	-75	0.125	-140
	10	-72	0.129	-129
	30	-69	0.139	-127
H	0.33	-76	0.133	-140
	1	-74	0.130	-138
	10	-69	0.138	-128
	30	-66	0.144	-124

method²⁷ showed that although the α -transition (T_g) initially shifted to higher temperatures with increasing crystallinity, above a certain crystallinity, the α -transition (T_g) began to shift back. This reversal of trend was also found by Takayanagi et al.²⁸ Another detailed study by a torsion-pendulum method²⁹ of the dynamic properties of unoriented films with differing degrees of crystallinity showed that the α -peak shifted to higher temperatures for crystallinities up to 30%. At yet higher crystallinities, it shifted toward lower temperatures. Illers and Breuer²⁹ attributed this behavior to the effect of crystal size on the amorphous regions.

It was noted that the value of the dynamic storage modulus below the glass transition temperature at -150°C for the PTHF-Py sample was lower than that for the PTHF-OMe sample (Figs. 3 and 4). This was attributed to the decrease in the degree of crystallinity of sample H. Table V shows the storage modulus, E' , and the dynamic loss modulus, E'' , of both series of PTHF polymers at 10°C .

The PTHF-OMe sample was calculated to have an apparent activation energy for the glass transition temperature of 190 kJ/mol, while the PTHF-Py sample had an activation energy of 146 kJ/mol. Since the introduction of ionic pyridinium bromide groups has decreased the degree of crystallinity, the difference is explainable in those terms.

Stress-Strain Studies

An informative mechanical experiment for any material is the determination of its stress-strain curve in tension. The stress-strain curves of the PTHF-OMe and the PTHF-Py samples are presented in Figure 5. These curves were measured at 18°C , which is, of course, considerably above the T_g for

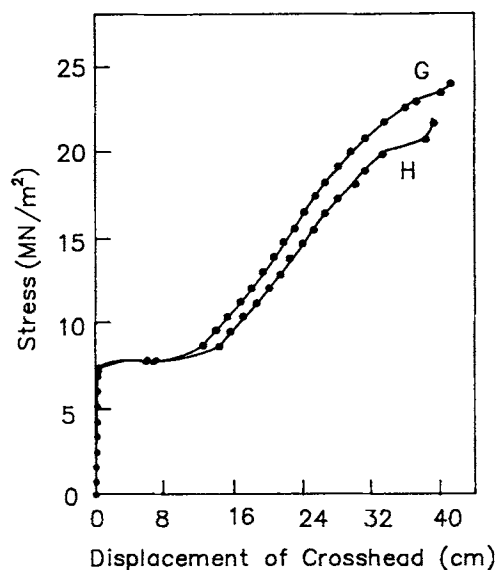


Figure 5 Stress-strain properties (18°C) for samples G (PTHF-OMe) and H (PTHF-Py).

both polymers. However, the PTHF samples both have relatively high degrees of crystallinity (see Table II).

Both samples G and H have a relatively high initial modulus. An increase in crystallinity raises the modulus of a polymer. PTHF stress-strain curves indicate that both samples show a yield point. The values of stress at yield of sample G and H are virtually the same. It is also shown that both samples are ductile and neck and cold-draw. Cold-drawing after the yield point means that there is a strain-hardening process. Strain hardening generally results from molecular orientation. However, the strain hardening of crystalline polymers might come partly from strain-induced crystallization.³⁰

In crystalline polymers,³¹ cold-drawing disrupts the crystalline morphology from that of a folded chain structure in spherulites to a fibrillar, extended-chain morphology in which the chains in the crystallites are highly oriented in the stretching direction. Peterlin³² believes that the cold-drawing of ductile, crystalline polymers, such as PTHF, consists of three stages:

- (i) Plastic deformation of spherulites with rotation of the stacks of lamellae, crystal twinning, and chain slippage.
- (ii) Discontinuous transformation of the spherulitic structure into a fibrous structure by micronecking.
- (iii) Plastic deformation of the fibrous structure with chain slippage and chain fracture.

Table V Dynamic Mechanical Data of PTHF-OMe (Sample G) and PTHF-Py (Sample H) at 10°C

Sample	Frequency (H_z)	$E' \times 10^{-9}$ (N/m^2)	$E'' \times 10^{-9}$ (N/m^2)
G	0.33	1.07	0.08
	1	1.26	0.06
	10	1.07	0.05
	30	1.66	0.08
H	0.33	1.55	0.11
	1	1.55	0.10
	10	1.70	0.09
	30	1.74	0.10

Table VI Stress-Strain Properties of PTHF-OMe (Sample G) and PTHF-Py (Sample H)

Sample	Stress at Yield, σ_Y (MN/m ²)	Extension at Yield (cm)	Tensile Strength, σ_B (MN/m ²)	Extension at Break (cm)
G	7.6	0.58	23.4	38.13
H	7.7	0.54	20.7	36.18

Table VI shows the values of stress and extension at yield, tensile strength, and extension at break for both the PTHF-OMe and the PTHF-Py samples. These values are very similar for both samples. The tensile strength of sample G (23.4 MN/m²) is significantly greater than that of sample H (20.7 MN/m²). Nielsen³¹ indicated that a decrease in crystallinity brings about a decrease in tensile strength. Since the introduction of the ionic pyridinium groups has decreased the degree of crystallinity of the PTHF polymers, the difference in the values of the tensile strengths of samples G and H is attributed to the effect of the ionic pyridinium bromide groups on the crystallinity of the PTHF-Py polymer.

CONCLUSIONS

Crystallization studies and dynamic mechanical and stress-strain analyses were used to compare certain solid-state characteristics of PTHF-OMe with PTHF-Py polymers of virtually identical molecular weights. It was concluded that the introduction of ionic end groups resulted in a decrease in the degree of crystallinity.

REFERENCES

- G. S. Trick and J. M. Ryan, *Polym. Prepr.*, **7**, 92 (1966).
- J. Furukawa and T. Saegusa, *Polymerisation of Aldehyde and Oxides*, Interscience, New York, 1963.
- A. C. Farthing, in *Polyethers. Part 1, Polyalkylene Oxides and Other Polymers, High Polymers*, N. G. Gaylord, Ed., Interscience, New York, 1963, Vol. XIII, Chap. V.
- R. E. Wetton and G. Williams, *Trans. Faraday Soc.*, **61**, 2132 (1965).
- M. Cesari, G. Perego, and A. Mazzei, *Makromol. Chem.*, **83**, 196 (1965).
- W. R. Sorenson and T. W. Campbell, *Preparative Methods in Polymer Chemistry*, Interscience, New York, 1961, p. 225.
- M. P. Dreyfuss and P. Dreyfuss, unpublished data.
- A. H. Willbourn, *Trans. Faraday Soc.*, **54**, 717 (1958).
- J. Brandrup and E. H. Immergut, *Polymer Handbook*, Interscience, New York, 1966, pp. 111-80.
- P. Dreyfuss and M. P. Dreyfuss, *Fortschr. Hochpolym. Forsch.*, **4**, 528 (1967).
- R. C. Burrows, *Polym. Prepr.*, **6**, 600 (1965).
- K. Imada, T. Miyakawa, Y. Chatani, H. Tadakoro, and S. Murahashi, *Makromol. Chem.*, **83**, 113 (1965).
- G. S. Fielding-Russell and R. E. Wetton, *J. Polym. Sci. (B)*, **5**, 761 (1967).
- A. I. Marei, E. A. Sidorovish, G. E. Novikova, and E. I. Rodina, *Vysokomol. Soedin.*, **10A**, 542 (1968).
- P. F. Warner, D. S. Brown, and R. E. Wetton, *J. Chem. Soc. Faraday Trans. I*, **72**, 1064 (1976).
- R. E. Wetton and G. Allen, *Polymer*, **7**, 331 (1966).
- K. Bak, G. Elefante, and J. E. Mark, *J. Phys. Chem.*, **71**, 4007 (1967).
- A. V. Cunliffe, D. B. Hartley, S. B. Kingston, D. H. Richards, and D. Thompson, *Polymer*, **21**, 101 (1981).
- S. A. M. Ali and D. J. Hourston, *J. Appl. Polym. Sci.*, **43**, 1503 (1991).
- A. P. Gray, *Instrum. News*, **20**, 8 (1969).
- J. M. G. Cowie, *Polymers: Chemistry & Physics of Modern Materials*, Intertext Books, London, 1973, p. 197.
- T. Murayama, *Dynamic Mechanical Analysis of Polymeric Material*, Elsevier, New York, 1978, Chap. 1.
- L. Holliday, Ed., *Ionic Polymers*, Applied Science, London, 1975, Chap. 3.
- T. F. Schatzki, *J. Polym. Sci.*, **57**, 496 (1962).
- R. F. Boyer, *Rubber Rev.*, **34**, 1303 (1963).
- M. Takayanagi, *Mem. Fac. Eng.*, **23**(1) (1963).
- T. Kawaguchi, *J. Polym. Sci.*, **32**, 417 (1958).
- M. Takayanagi, M. Toshino, S. Minami, *J. Polym. Sci.*, **61**, 171 (1962).
- K. H. Illers and H. Breuer, *J. Colloid Sci.*, **18**, 1 (1963).
- I. M. Ward, *Mechanical Properties of Solid Polymers*, Interscience, New York, 1971.
- L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974, Vol. 2, Chap. 5.
- A. Peterlin, *J. Mater. Sci.*, **6**, 490 (1971).

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