Copolyester Studies. VI. Melt Spinning and Mechanical Properties of Tetramethylene Terephthalate–Poly(tetramethylene Oxide) Random Block Copolymers

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Synopsis

Fibers were prepared from tetramethylene terephthalate–polytetrahydrofuran (PTHF) random block copolymers, containing the latter in the range of molecular weights 1000–5000 with up to 30% by weight incorporation, using a conventional melt spinning technique. The spinnability of the copolymer and the mechanical properties of these undrawn fibers were evaluated. The changes in mechanical properties brought about by the incorporation of PTHF groups in 4GT units were related to the PTHF block size and content in the copolymer. X-ray diffraction data are also discussed briefly in terms of the structural differences.

INTRODUCTION

In a previous paper[1] we reported the preparation of polytetrahydrofuran polymers of different molecular weights and their use as the diol component in the preparation of random block copolymers of tetramethylene terephthalate and polytetrahydrofuran. The polymers were characterized by NMR, thermal methods, and dynamic mechanical studies. We now report the evaluation of the mechanical properties of fibers melt spun from these polymers together with data obtained from wide-angle x-ray examination.

EXPERIMENTAL

Melt Spinning

The polymers were prepared and characterized as previously reported.[1] The polymers were converted into fibers using a rod-spinning apparatus. Polymer chips (75 g dried at 100°C/1 mm Hg for 16 hr) were fed into the cylinder of the rod spinner and were candled for 15 min. This process is necessary before extrusion in order to remove the entrapped air bubbles which cause oxidation of the polymer and possible discontinuities in the extruded filaments. The upper and lower parts of the cylinder were heated by separately controlled heaters so that the polymer was subjected to a minimum residence time at the extrusion temperature which is shown in Table II.

Mono- or multifilaments were obtained from a spinneret having either a single

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TABLE I
Representation of the X-Ray Data From Microdensitometer

Copolymer code	Height of the peak, cm
4GT/PTHF 1000 10%	15.2
4GT/PTHF 2000 10%	13.7
4GT/PTHF 3000 10%	12.5
4GT/PTHF 4000 10%	12.2
4GT/PTHF 5000 10%	10.8

central hole (0.55 mm in diameter) or five holes equal in diameter (0.2286 mm). The mono- or multifilament spinning threadline converged several feet below the spinneret (approximately 10 ft) and the filaments were collected on a bobbin which was surface driven at the lowest practical speed so that little orientation was induced in the fiber.

Mechanical Properties Measurements

The spun fibers were stored in a constant temperature/humidity room (20°C/65% R.H.) for at least seven days before testing. The deniers of the undrawn fibers were determined by accurately weighing 9 m of the monofilament. The load/extension curves of the fibers were obtained using a bench-model Instron tensile testing machine. A standard gauge length (5 cm) and testing speed (5 cm/min) were used throughout. Initially, 25 samples were chosen at random and tested. From the results, the number of samples (n) required in order that the average of the test results would be within 2% of the mean 95% of the time was evaluated.[2] The addition tests required ($n - 25$) were performed and the

TABLE II
Melt Spinning Conditions and Fiber Properties

Copolymer code[a]	Copolymer composition, wt % PTHF	Intrinsic viscosity[b]	$\overline{M}_n$[b]	Spinning temperature, °C	Fiber denier
4GT/PTHF 1000	10	0.96	17,800	230	146
4GT/PTHF 1000	20	0.95	16,600	228	102
4GT/PTHF 1000	30	1.02	18,800	225	122
4GT/PTHF 2000	10	1.12	23,600	240	142
4GT/PTHF 2000	20	0.77	13,100	235	82
4GT/PTHF 2000	30	1.09	23,400	230	97[c]
4GT/PTHF 3000	10	0.87	14,300	235	88
4GT/PTHF 3000	20	1.10	22,500	[d]	—
4GT/PTHF 3000	30	0.79	13,500	[d]	—
4GT/PTHF 4000	10	0.81	13,800	238	78
4GT/PTHF 4000	20	0.90	16,100	[d]	—
4GT/PTHF 4000	30	1.04	21,100	[d]	—
4GT/PTHF 5000	10	0.83	16,000	245	86
4GT/PTHF 5000	20	0.99	18,800	[d]	—
4GT/PTHF 5000	30	0.82	15,300	[d]	—

[a] Diol component in melt-phase polymerization was butane diol and hydroxyl-ended poly(tetramethylene oxide) PTHF of the molecular weight specified.[1]

[b] See ref. 1.

[c] Spun as a multifilament. The denier refers to a monofilament.

[d] Could not be spun as a mono- or multifilament under conditions employed in this study.

mean, standard deviation, and coefficient of variation for n tests were calculated. However, during tensile testing, slippage of the fiber in the clamps may occur so that the nominal gauge length is not the effective gauge length.[3] Corrections for slippage were made according to the relevant standard.[4]

X-Ray Diffraction Measurements

These were made using a cylindrical Shearle camera with radius $r_f = 30$ mm using nickel-filtered monochromatic CuK_α radiation. All measurements were carried out at room temperature, the exposure period being $\frac{1}{2}$ hr.

A frame was designed for holding strands of about 20 fibers perpendicular to the incident x-ray beam. The developed films of the copolymers containing 10% by weight PTHF, where there was no evidence of PTHF crystallinity and the changes in intensity of the polyester rings were not easily discernible, were scanned using a Joyce–Loebl microdensitometer. A relative measure of the degree of crystallinity of the polyester phase was obtained from the height of the peak arising from a Bragg spacing of 3.88 Å (Table I) relative to the background. With those polymers which did not give satisfactory filaments, lengths could be formed adequate for x-ray examination.

RESULTS AND DISCUSSION

The spinning conditions used and typical properties of the as-spun fibers are shown in Table II. Note is also made of those copolymers which failed to spin either as mono- or as multifilaments, even though several spinning temperatures were employed.

Spinning was carried out using the rod spinner described elsewhere. The melt temperature employed was in the range of 10–20°C higher than the melting point of the polymer, the temperature being chosen to give a viscosity suitable to produce coherent filaments.

Not all the polymers studied could be transformed into filaments since the

TABLE III
X-Ray Analysis of Fiber Samples

Sample	Polyester	Polyether
4GT/PTHF 1000 10% Monofil	present	—
4GT/PTHF 2000 10% Monofil	present	—
4GT/PTHF 3000 20% Monofil	present	—
4GT/PTHF 4000 10% Monofil	present	—
4GT/PTHF 5000 10% Monofil	present	—
4GT/PTHF 2000 20% Monofil	present	—
4GT/PTHF 3000 20% Monofil of poor quality	present	present
4GT/PTHF 2000 30% Multifilaments	present	present
4GT/PTHF 3000 30% Monofil of poor quality	present	present
4GT/PTHF 4000 30% Monofil of poor quality	present	present
4GT/PTHF 5000 30% Monofil of poor quality	present	present

threadline could not in some samples be sustained by the weight of the falling filament. Some fibers could only be formed as multifilaments, i.e., using spinneret orifices of smaller diameter. Under these circumstances, the cooling rate of the thread was faster. The ability of the copolymers to form fibers decreased with increasing polyether content. This may arise from two causes. By analogy with the corresponding copolymers which contained poly(hexamethylene terephthalate) 6GT, increases in the polyether content reduced the rate of crystallization presumably because of the decreasing molecular length of the polyester segments.[5] In addition, the strength of the fibers dramatically decrease with increase in the polyether content for the same reason.[6]

The situation is somewhat counterbalanced when the molecular weight of the polyether is increased for samples which have the same weight percentage of polyether; with these samples, there is an increase in the D.P. of the polyester segments and hence an increase in the rate of crystallization of the polyester as well as the crystallization of the polyether and a resultant increase in the modulus of the fiber. Nevertheless, the strength of the filaments were not found to be adequate for satisfactory fibers to be formed.

X-Ray Diffraction Measurements

Polytetrahydrofuran (PTHF) exhibits eight well-pronounced diffraction rings, and 4GT, 11. All the samples examined which were in fiber form showed polyester spacings, whereas those with polyether of molecular weight of not less than 3000 and concentrations greater than 20% showed the presence of crystalline polyether, as indicated in Table III.

On cooling the block polymers, the polyester crystallizes faster than the polyether[7]; the polyether segments which are located in the amorphous regions are restricted in their motion and hence their crystallization is hindered. These restrictions do not apply to blends of materials.[8] Moreover, crystallization occurs more readily if the crystallizable polyester matrix is replaced by an analogous amorphous material.[9] Provided the polyether blocks are large enough,[10] the ability of the polyester to crystallize will also depend on the rate at which the polyester crystallizes and hence on the manner in which the sample is formed. It is interesting that the sample which exhibits exceptional behavior in the above table, namely, 4GT/PTHF 2000, 30%, which by analogy to the 6GT system is not expected to crystallize, is the one which could be spun only in the form of multifilaments. Under such circumstances, the cooling was rapid, and hence the polyether phase would have the opportunity to crystallize. It may be noted[1] that thermal analysis using melt-pressed films did not show an endotherm attributable to the melting of the polyether phase in samples whose polyether component had a molecular weight of 2000 or less. Presumably when the polyether has molecular weight in excess of this, the chains are sufficiently mobile to crystallize, as has been suggested by other workers for analogous systems.[11,12]

These observations are in line with those of Goodman et al.[6] who showed in an examination of polymers prepared from PTHF and 6GT containing 50% by weight of polyether that the ability of the former to crystallize is not apparent until a molecular weight of 3000 is reached. It is interesting also to note that increasing the size of the polyether block at constant weight percent incorporation

TABLE IV
Parameters of Undrawn Fibers[a]

Polymer code	wt % of PTHF	Initial modulus, g/denier	Yield stress, g/denier	Breaking strength, g/denier	Yield strain, %	Breaking extension, %
4GT	—	14.7 (0.05)	0.32 (0.03)	0.69 (0.05)	2.34 (0.03)	602 (4)
4GT/PTHF 1000	10	8.2 (0.03)	0.22 (0.02)	0.54 (0.04)	3.44 (0.04)	598 (4)
4GT/PTHF 1000	20	4.0 (0.05)	0.13 (0.02)	0.53 (0.05)	11.90 (0.06)	659 (5)
4GT/PTHF 1000	30	2.2 (0.04)	0.11 (0.01)	0.36 (0.03)	19.50 (0.06)	788 (8)
4GT/PTHF 2000	10	8.7 (0.04)	0.24 (0.03)	0.55 (0.09)	2.67 (0.05)	595 (5)
4GT/PTHF 2000	20	7.3 (0.01)	0.19 (0.02)	0.54 (0.08)	6.00 (0.02)	682 (7)
4GT/PTHF 2000	30	5.5 (0.02)	0.18 (0.02)	0.37 (0.06)	16.40 (0.07)	813 (6)

[a] Figures in brackets refer to mean deviation of each value.

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TABLE V
Parameters of Undrawn Fibers[a]

Polymer code	wt % of PTHF	Initial modulus, g/denier	Yield stress, g/denier	Cold-draw stress, g/denier	Breaking strength, g/denier	Yield strain, %	Breaking strain, %	Natural draw ratio
4GT/PTHF 1000	10	8.2 (0.03)	0.22 (0.02)	0.18	0.53 (0.05)	3.44 (0.04)	598 (4)	2.79
4GT/PTHF 2000	10	8.7 (0.04)	0.24 (0.04)	0.21	0.55 (0.09)	2.67 (0.05)	595 (5)	3.20
4GT/PTHF 3000	10	15.0 (0.02)	0.29 (0.02)	0.26	0.55 (0.02)	2.42 (0.07)	581 (2)	3.25
4GT/PTHF 4000	10	16.2 (0.01)	0.30 (0.02)	0.27	0.58 (0.08)	2.38 (0.02)	495 (6)	3.36
4GT/PTHF 5000	10	17.9 (0.05)	0.32 (0.06)	0.28	0.63 (0.06)	2.28 (0.07)	581 (2)	3.15

[a] Figures in brackets refer to mean deviation of each value.
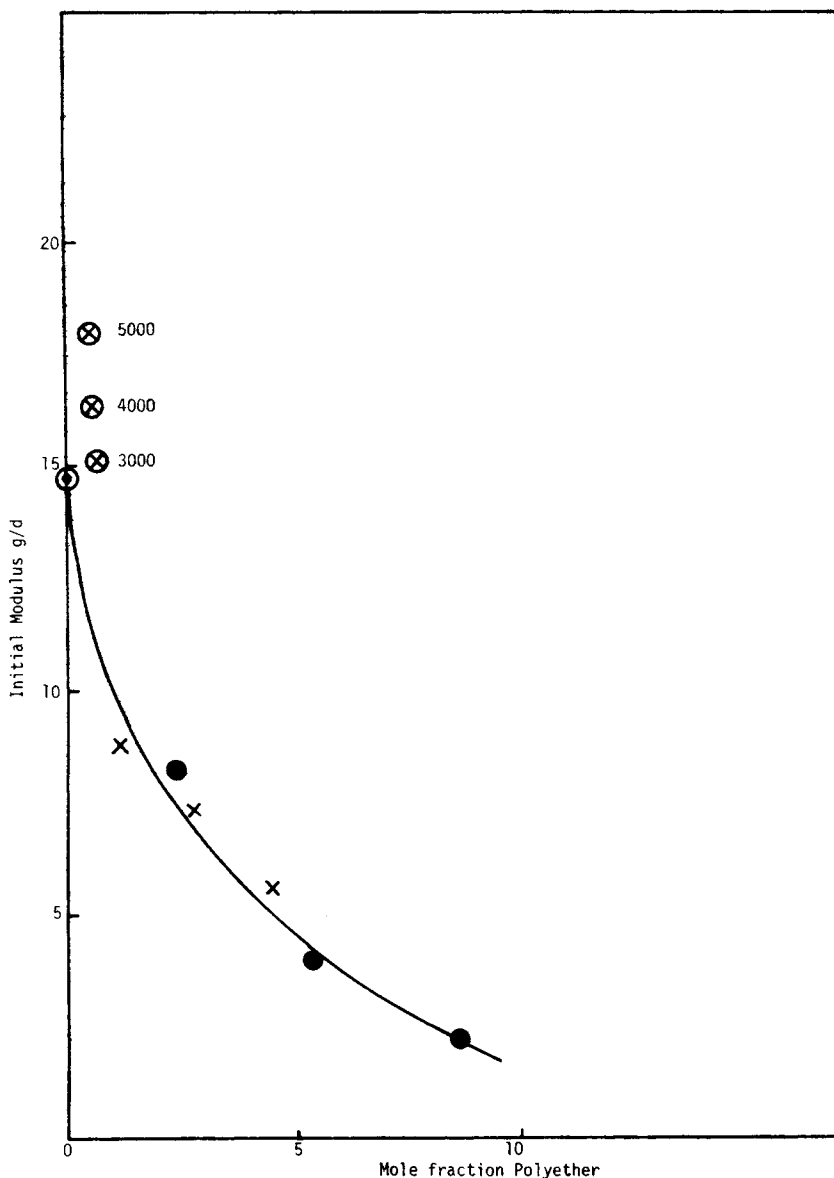
Fig. 1. Correlation of initial modulus with mole fraction: (●) PTHF 1000; (X) PTFH 2000; (⊗) PTHF of specified molecular weight; (○) 4GT.

also decreases to a small extent the ability of the polyester to crystallize, as shown in Table I.

Mechanical Properties

In order to fix a convenient testing speed, preliminary studies using undrawn fibers of 4GT/PTHF 1000 containing 10% by weight PTHF were performed at different speeds from 2.5 to 100 cm/min using a nominal gauge length of 5 cm. Both yield and drawing stress increase with increasing extension rate up to a value
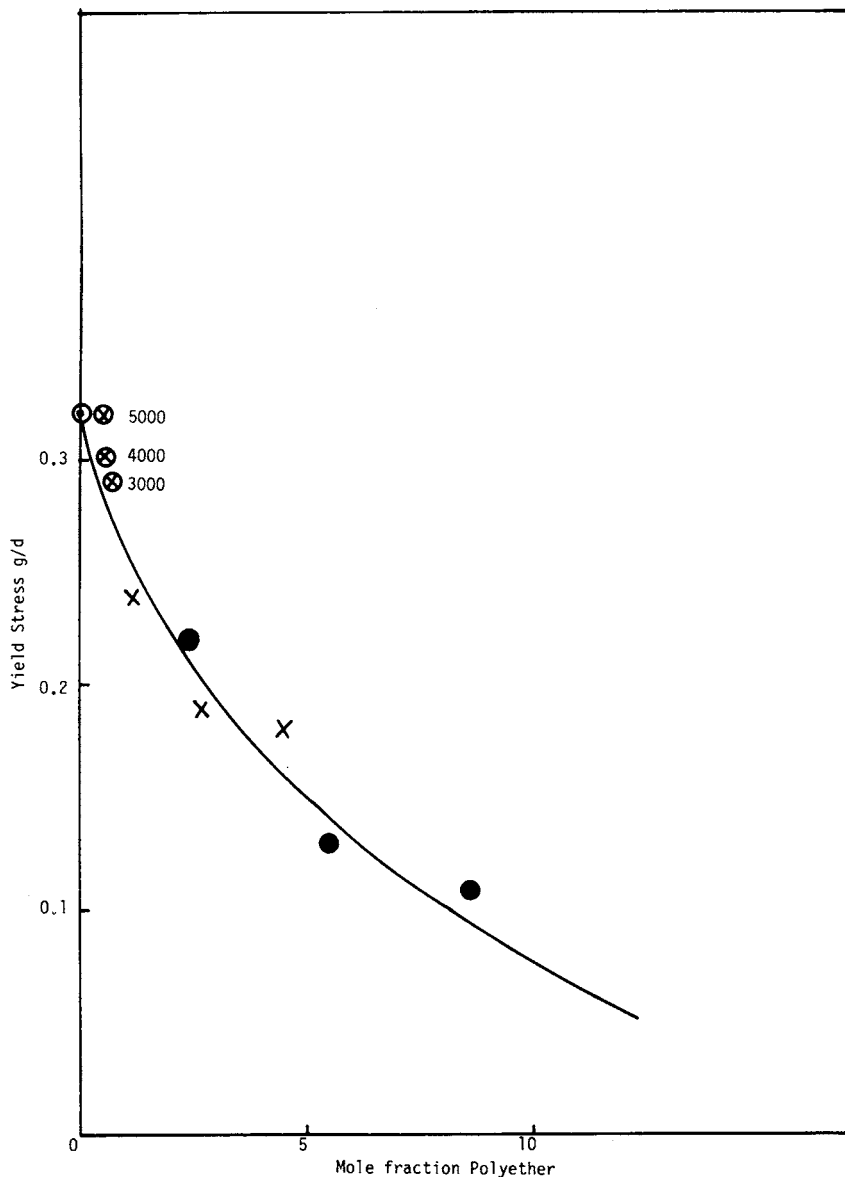
Fig. 2. Correlation of yield stress with mole fraction: (●) PTHF 1000; (X) PTHF 2000; (⊗) PTHF
of specified molecular weight; (⊙) 4GT.

of 10 cm/min; further increases in rate resulted in a decrease in both. This de-
crease at the high rates presumably arises because of conduction of heat from
the yielded portion of the neck to the unyielded. Moreover, at speeds of 10 and
20 cm/min the fibers showed a lacunose effect,[11,13,15] i.e., the Instron trace took
the form of a sawtooth once an extension of 60% was exceeded. As a result of
the above examination, a rate of extension of 5 cm/min was chosen for the data
given in Tables IV and V.

In the series containing 10, 20, and 30% polyether of molecular weight 1000
and 2000, there is a decrease in initial modulus and yield stress as the concen-
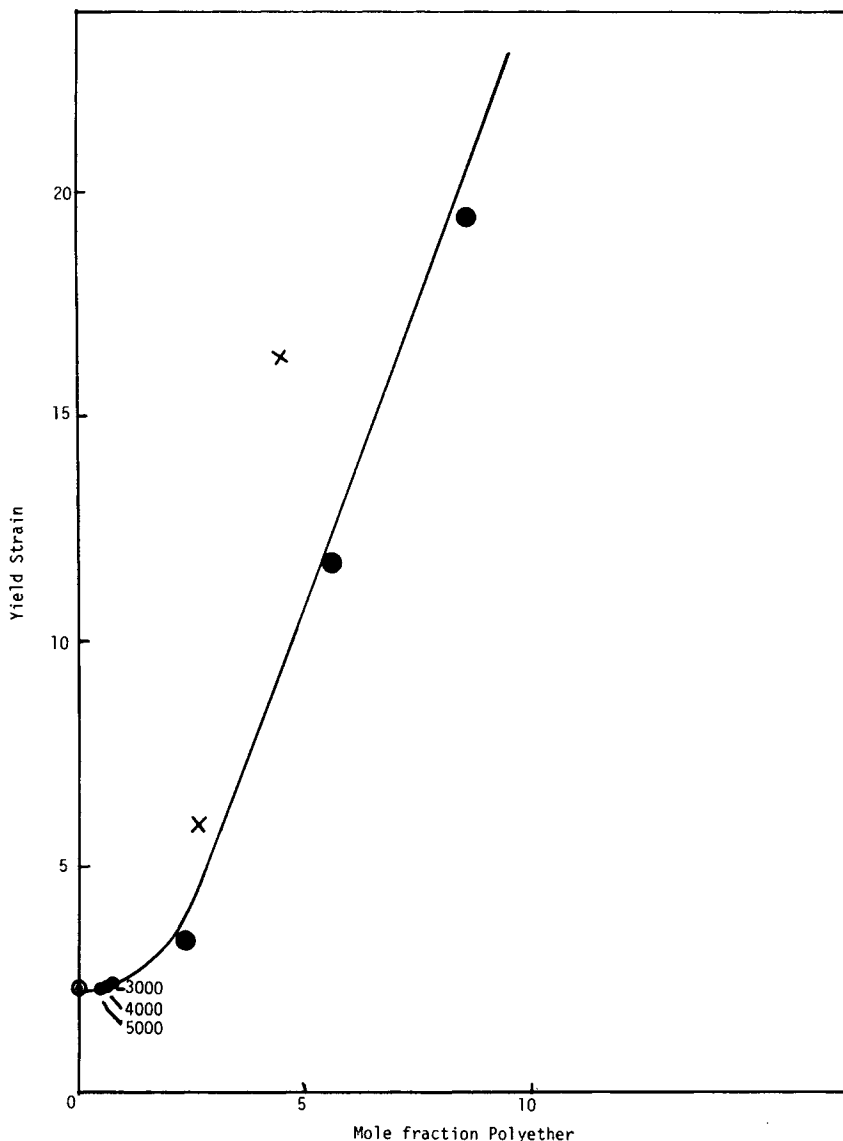
Fig. 3. Correlation of yield strain with mole fraction: (●) PTHF 1000; (Χ) PTHF 2000; (⊗) PTHF of specified molecular weight; (⊙) 4GT.

tration of polyether is increased: these decreases are similar in character to those found in other systems (6GT with polyethylene oxide and 6GT with PTHF).[5,6] However, when the polyether component does not crystallize, these mechanical properties are expected to depend on the strength of the polyester matrix. A measure of the latter will be given by the mole fraction of the polyester or, what amounts to the same thing, the mole fraction of the polyether. Confirmation of this point is shown when the properties of the samples containing PTHF 1000 and 2000 are plotted against mole fraction (Fig. 1), when a single curve is obtained. The data for those samples which crystallize (samples containing polyether of molecular weights 3000, 4000, and 5000 at a concentration of 10%) lie in higher positions, suggesting that the modulus is augmented.

Analogous considerations relate to the yield stress (Fig. 2), but here the increase in stress of the polyether samples containing crystallizable polyether is small, suggesting that it is the breakdown of the polyester matrix which occurs in the main at yield. This latter point is confirmed by the correlation of the yield strain with mole fraction of the polyether where the data for all samples fall clearly on a single line (Fig. 3).

A model for the structure is thus one in which the polyether forms regions interspersed in the polyester matrix; the changes in initial modulus suggest that these regions cause a reduction in the tie molecules holding the polyester matrix together. This latter point is emphasized in such systems since a significant proportion of the polyether molecules will form chain ends.

On stretching the fibers to break, it is noticeable that over the range of concentrations studied the variations of both breaking strength and strain are very small, suggesting again that the fundamental properties are connected with the polyester matrix.

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