Poly(7-oxabicyclo[2.2.1]heptane-*co*-tetrahydrofuran): Polymerization, polymer characterization and spinning

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A high-yield cationic copolymerization of 7-oxabicyclo[2.2.1]heptane (OBCH) and tetrahydrofuran (THF) was developed to yield high molecular weights, the mechanism being deduced from product and kinetic studies. The monomer ratios were varied to arrive at a range of products melting at various temperatures. The crystallization rate was influenced by copolymerizing minor amounts of a third monomer—ethylene oxide (EO). Spinning experiments were carried out mainly on a miniature spinning apparatus, enabling ram extrusion from an evacuated chamber heated only in the lower part. Polymers and yarns were characterized by solution viscosities, nuclear magnetic resonance (proton and carbon) spectra, gel permeation chromatography, wide-angle and small-angle X-ray scattering, hot-stage microscopy, interference microscopy and thermal scan wide-angle X-ray scattering. Rheology characterization was attempted using the miniature spinning device with wide 'spinning holes'. Copolymerization proceeds in a truly random fashion; molecular weight is regulated almost exclusively by precipitation. The viscosity of the polymer melt, very high at rest, drops to a fairly low level upon shearing and the shear stress seems to be essentially independent of the shear rate. The OBCH/THF copolymers show thermotropic liquid-crystalline behaviour with as little as 30 wt% of the rigid monomer, OBCH. High molecular orientation is easily achieved in as-spun yarn. Poor drawdown ratios, no higher than 2.4, can be reached. No high-modulus or high-tenacity yarns are accessible with the present copolymer system. The poor extensibility of the spinning thread seems to point to extensive chain folding in the (imperfect) lamellae in the liquid-crystalline state.

(Keywords: thermotropic aliphatic polyether; cationic polymerization; isomorphous substitution; evacuated miniature spinning machine)

INTRODUCTION

In recent years, much effort has been directed at the production of high-modulus, high-tenacity yarns by melt spinning. The only routes that showed some success feature extensive (hot) aftertreatments of the yarns: thermotropic polyesters, the most successful example being the material developed by workers at Celanese[1]. Pitch-derived carbon fibres in fact fall into this category as well[2]. The long aftertreatment is a grave economic disadvantage; it must be considered impossible to circumvent when one uses stiff chain polymers made thermoplastic by the incorporation of stiff but asymmetric or 'wrong-sized' comonomers[3]. Only after crystallinity is developed can attractive tenacities be reached.

An alternative way to arrive at thermoplastic behaviour of polymers consisting mainly of stiff chains is the incorporation of flexible elements[4]. Striving for isomorphicity of the flexible with the stiff elements, with high crystallization rates as the result (in contrast with the thermotropic polymers employing stiff, ill-fitting comonomers) seemed a worthwhile idea.

Model studies suggest that tetrahydrofuran (THF) fragments may well be isomorphous with 7-oxabicyclo[2.2.1]heptane (OBCH) derived fragments in a polymer[5]; OBCH in fact is inspired by cellulose (*Figure 1*). Thus, we studied the OBCH/THF copolymer system; this entailed the development of a monomer synthesis applicable to fairly large-scale work as well[6], since the monomer is commercially available in very small quantities only[7].

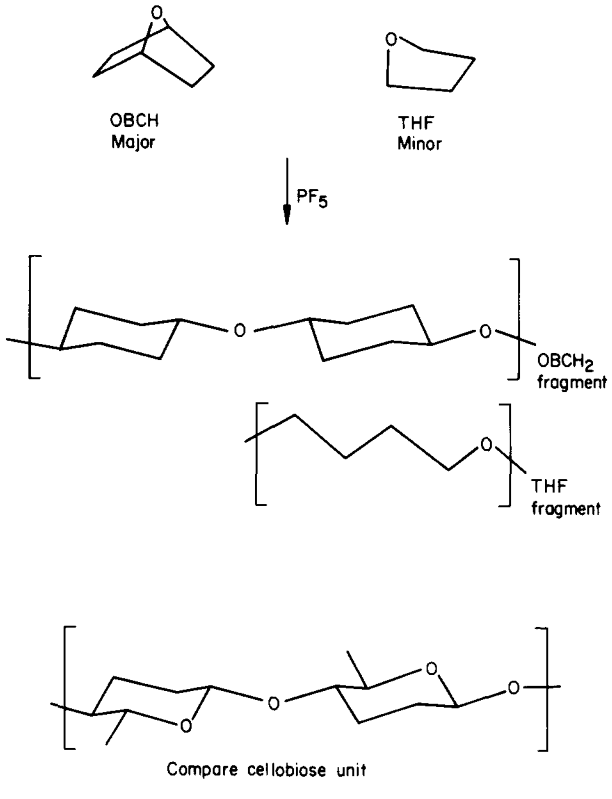

Figure 1 Comparison of OBCH and cellulose

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OBCH is mentioned in the literature as a model (co)monomer in cationic (co)polymerization work directed at thermodynamic and kinetic subjects[8]. Work focused on the polymer as such is reported with poor yields of low molecular weight polymers using complicated initiator systems[9]. Depressing the high melting point of poly(OBCH) by copolymerization with THF was also reported earlier[9], although no further polymer characterization or utilization seems to have been attempted.

EXPERIMENTAL

Reagents

1,2-Dichloroethane (DCE) (Merck, reinst) and 7-oxabicyclo[2.2.1]heptane (OBCH) (ref. 6, >99.8%, < 0.2% 5-hexenal) were stored under dry nitrogen over 3A molecular sieves activated at 280°C. Tetrahydrofuran (Baker) was dried over activated 3A molecular sieves and distilled from sodium hydride, and stored over activated 3A sieves, under dry nitrogen. Ethylene oxide (EO) and boron trifluoride (Fluka), PF_5 (Air Products), $SbCl_5$ and SO_2 (Baker), and PCl_5 (Merck) were used as received. 1,2-Dichlorobenzene and nitrobenzene (Janssen, 99%) were dried over activated 3A molecular sieves; diethyl ether (Baker) was dried over activated3A sieves and stored over sodium hydride.

Polymerization apparatus

All parts of the mini-plant (*Figure 2*) were dried in an oven at 115°C, assembled while hot, and cooled in a stream of nitrogen dried over activated 3A sieves in a column (*Figure 2*: 13). The various parts of the mini-plant were interconnected by glass piping with ball-and-socket joints sealed with Viton O-rings. The cocks were of the Teflon screw type, and enabled isolation of parts that occasionally had to be dismantled for cleaning or modification; on such occasions the remainder of the installation would not contact outside air. Monomers and solvent could be moved through the piping with nitrogen pressure, controlled by a mercury-filled safety valve (*Figure 2*: 14). The whole mini-plant was protected from contact with outside air (i.e. moisture) by sweeping with a slow flow of dried nitrogen. Accidental entry of air by unintentional generation of a vacuum in the installation was safeguarded by the drying column (*Figure 2*: 12) near the oil-filled outlet bubble counter.

Typical polymerization run

DCE (800 ml) from the 35 kg drum (1) was placed in the double-walled reactor provided with an anchor shaped, oil-sealed stirrer (8). Via a calibrated 700 ml cylindrical funnel (6), 475 ml (460.8 g, 4.702 mol) of OBCH from (5) was added. THF (102 ml) (90.0 g, 1.250 mol) from (4), distilled through a 45 cm Vigreux column and jacketed coil condenser (3), was added via a 100 ml graduated funnel (7). The reactor contents were cooled with stirring to −11.5°C by means of cold ethanol in the reactor jacket, supplied by a cooling machine. Then 35.4 ml of a 0.7074 M PF_5 solution, prepared by absorbing PF_5 into a diethyl ether/DCE 1/3 mixture, was collected from (11) and introduced into the reactor within 2 min by means of

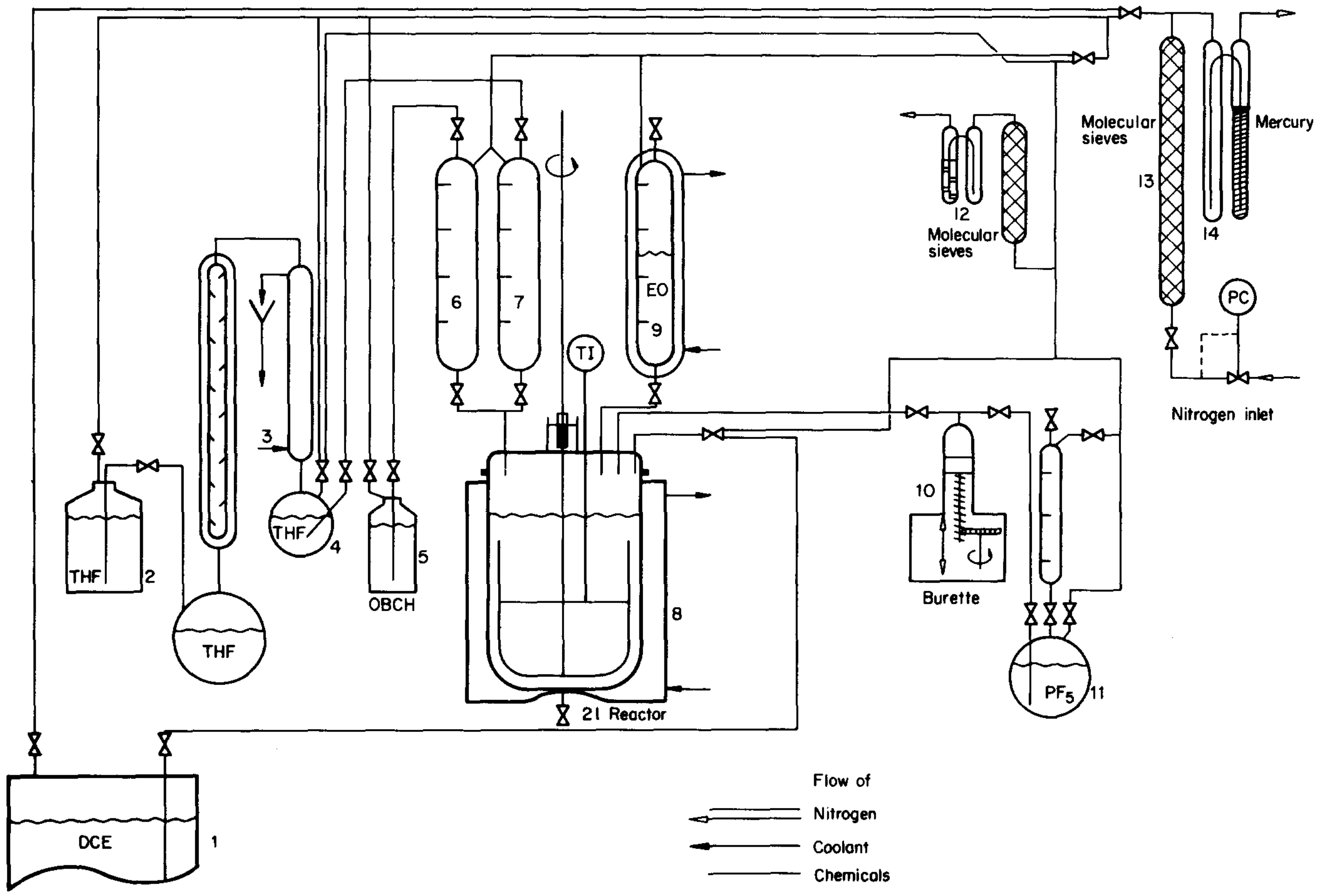

Figure 2 Polymerization mini-plant

a motor-driven burette (10). During the addition of initiator the reaction mixture temperature increased to −10.7°C; 10 min after starting the initiator addition, a slight turbidity (temp. −11.1°C) indicated the first precipitation of polymer. After 2.5 h, a solution of 14.0 g of EO in 54 ml of DCE, totalling 70 ml and cooled to −20°C, started to be added very slowly from a graduated double-wall dropping funnel (9) (temperature of reaction mixture stable at −11°C). The EO addition took 36 h, during which time the reaction mixture became very opaque; the slurry became slightly viscous, necessitating occasional stirrer speed correction. After completion of the EO addition the reaction mixture was stirred for an additional 9.5 h at −11.6°C. Then the slightly coloured slurry was discharged through the bottom valve of the reactor and terminated with about 500 ml of ethanolic ammonia by stirring for 1 h. This changed the colour to white. The polymer was collected on a sintered glass filter and washed with three to five 500 ml portions of water, until neutral as judged by the filtrate, plus one portion of ethanol to facilitate drying: 80°C, 16 h, 20 mbar.

Yield: 545.5 g (96.6%) of perfectly white copolyether powder, η_{rel} 2.751 (1% in *m*-cresol, 25°C).

RESULTS AND DISCUSSION

Polymerization

Expanding on earlier work[8,9] OBCH-*co*-THF polymerization is conveniently performed with PF_5 initiator and 1,2-dichloroethane (DCE) as solvent; 40 vol% of monomers in the batch. A mini-plant was constructed (*Figure 2*) facilitating work at exceedingly low water levels by eliminating any contact with outside air after purification of the materials used. PF_5 proved superior to $SbCl_5$ used in early explorations of this polymerization (cf. runs 18 and 19, *Table 1*). Initiating systems of the type BF_3 + epoxide, very effective for the

Table 1 Polymerization (1.5 litre scale) at 40 vol% concentration of combined monomers OBCH/THF(/EO) in DCE with 0.40 mol% of PF_5

Run no.	Polymer compos. (mol%)	Reaction temp. (°C)	Reaction time (h)	η_{rel} (1% in *m*-cresol)	Yield (wt%)	Comments[a]
1	80/20	0	22.5	2.631	76.4	
2	80/20	0–15	22.5	2.320	88.9	5 h, 0°C
3	80/20	5	22.5	2.434	84.1	
4	80/20	10	22.5	2.256	85.7	
5	80/20	15	22.5	2.068	84.0	
6	80/20	−5 to 22	22.5	2.070	70.0	1 h, −5°C; max. 34°C
7	80/20	0	166.5	2.628	94.0	[b]
8	80/20	0	142	2.577	96.7	[b,c]
9	80/20	−5	165	2.795	94.3	[b]
10	80/20	−11	164	3.225	95.6	[b]
11	80/20	−21	360	3.704	87.7	[b]
12	80/20	0–15	167	1.936	34.5	[b,d]
13	80/20	0–15	94	–	–	3 × 0.4% BF_3/PCl_5 init.
14	80/20	0	888	2.325	11.8	0.8% Meerweins salt[e]
15	80/20	−11	96	3.610	47.3	0.24% PF_5
16	80/20	−11	96	2.978	93.5	0.5% PF_5 gas
17	80/20	−11	96	2.913	92.8	0.5% PF_5 gas
18	80/20	−11	96	2.379	35.3	0.4% $SbCl_5$
19	80/20	−11	215	2.509	46.8	0.4% $SbCl_5$; yellow polymer
20I	80/20	0	48	2.667	90.8	Filtration experiment
20II	80/20	0	116	2.536	95.2	Mother liquor of 20I used
21	80/20	−22	168	2.020	7.8	Solvent sulphur dioxide
22	80/20	−11	165	2.992	93.0	Solvent *o*-dichlorobenzene
23	80/20	0–3	164	2.684	97.7	Solvent nitrobenzene
24	75/25	0	47.5	2.888	91.0	Stirrer stoppage
25	75/25	−11	240	3.454	98.4	[b]
26	70/30	0	73	3.055	90.1	Stirrer stoppage[f]
27	70/30	−11	163	3.528	96.0	Stirrer stoppage[f]
28	60/40	0	50	2.895	86.7	Stirrer stoppage
29	84/8/8	−11	96	2.264	91.8	
30	83/16/1	−11	96	3.104	84.3	Transfer 2nd reactor
31	80/17/3	−11	96	2.817	95.5	Transfer 2nd reactor
32	79/19/2	−11	96.5	2.964	89.9	
33	80/17/3	−11	96	2.836	89.6	0.25% PF_5
34	79/17/4	−11	115.5	2.731	98.4	
35	75/20/5	−11	48	2.751	96.6	
36	75/20/5	0	48	2.499	96.2	
37	75/19/6	0	24	2.437	95.5	
38	75/20/5	0	24	2.267	95.8	0.8% PF_5

[a] *Termination:* ethanolic KOH; from no. 14, ethanolic ammonia; nos. 18 and 19, sodium sulphide

[b] Samples were taken from the reaction mixture for kinetic analyses

[c] After 47 h, 0.04% PF_5 extra

[d] 2 × 0.4% Meerweins salt[e]

[e] Triethyloxonium tetrafluoroborate

[f] 35 vol% concn of monomers

polymerization of THF[10], gave very low conversions in early explorations; triethyloxonium tetrafluorborate proved to be somewhat more effective but still poor (runs 12 and 14). Combinations of BF_3 and PCl_5 gave no polymer at all (run 13).

Gas chromatographic analysis of filtrates showed that OBCH and THF are consumed without preference in the polymerization.

Changing the monomer ratios to 'softer' compositions than the 80/20 OBCH/THF used as the standard in early work aimed at finding a convenient procedure, required special attention to stirring in the later phase of the reaction. The softer products precipitate with more absorbed solvent, making the precipitate somewhat cheeselike. At 70/30 we could not keep the stirrer in action towards the end of the polymerization in spite of somewhat lower polymer concentration (runs 26 and 27). Work-up of the product (deactivation with ethanolic KOH, later ammonia; washing with ethanol and water) proved troublesome in the case of compositions softer than 70/30. Washing and filtering at higher temperature (about 80°C) more or less solved the problem.

The possibility of initiating the polymerization in the elaborate mini-plant reactor, then transferring the reaction mixture to a simpler reactor for stirring over a prolonged period (i.e. a high production capacity of the present mini-plant) was demonstrated (runs 30 and 31), as well as succesful recycle of filtrate containing some residual monomer, with polymerization of that monomer without work-up (runs 20-I and -II).

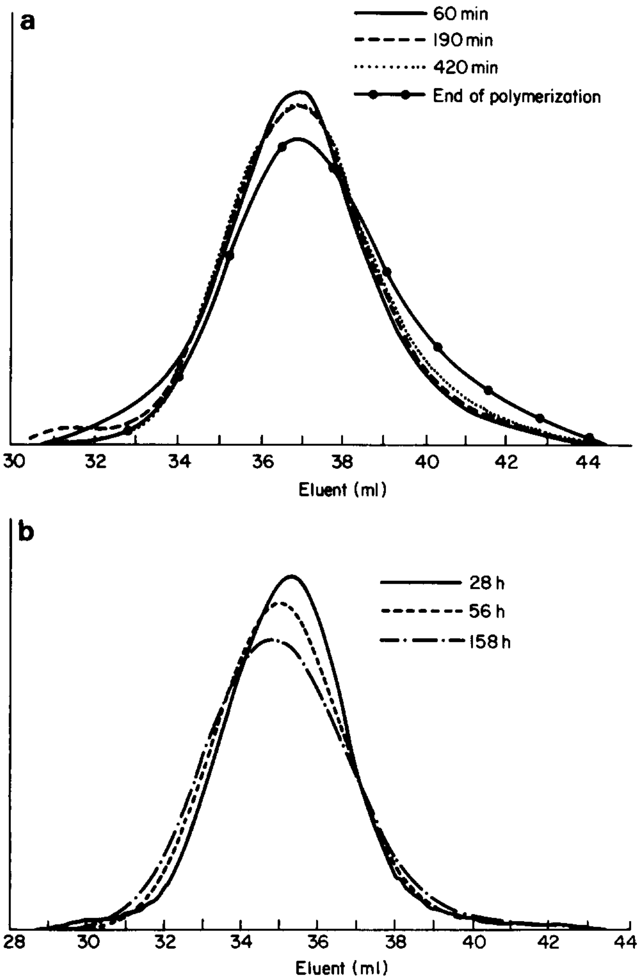

Figure 3 Molecular weight determination by g.p.c. in 15/85 *m*-cresol/dichloromethane. Styracel/Microgel column and RI Knauer detector. 80/20 OBCH/THF copolymer. (a) Polymerization temperature 0–5°C. (b) Polymerization temperature – 21°C (*Table 1*, run 11)

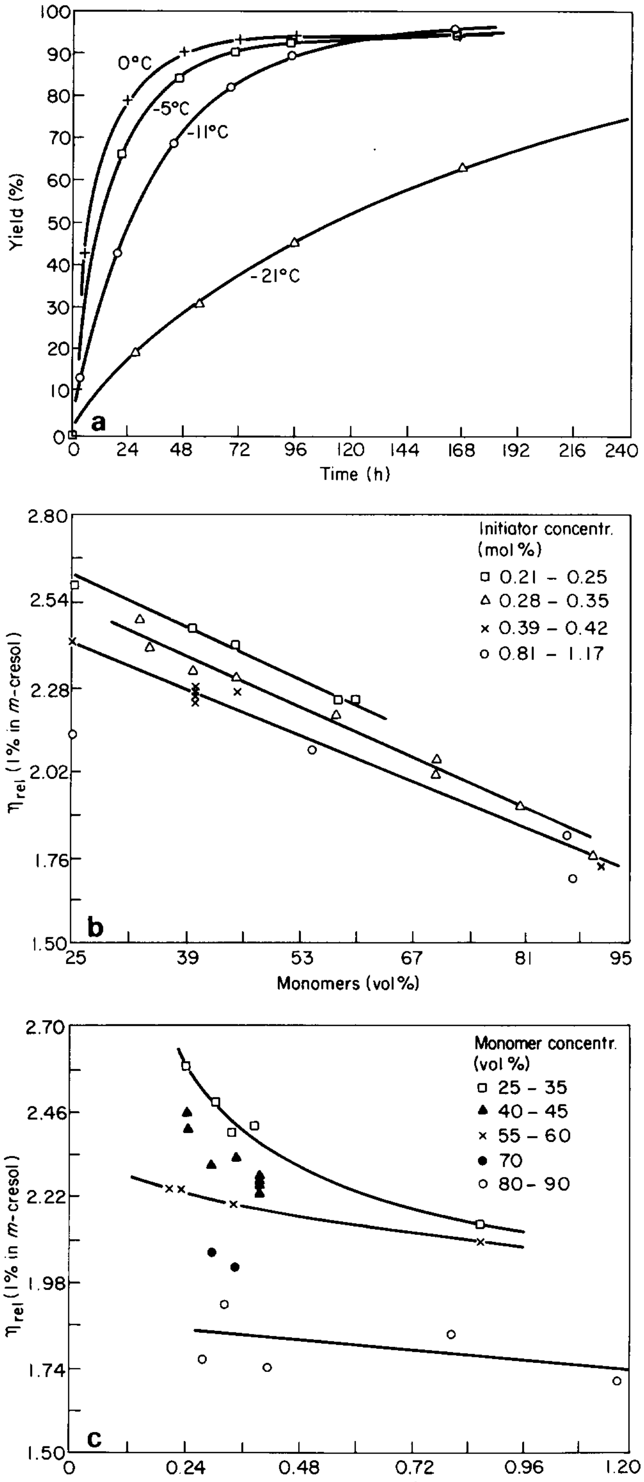

Figure 4 (a) Yield of 80/20 OBCH/THF copolymer as a function of time and temperature. (b) Solution viscosity vs. monomer content for 80/20 OBCH/THF copolymer, for polymerization at 0°C. (c) As (b) but as function of initiator content

Gaseous PF_5 instead of its etherate, the gas being deemed more convenient for larger-scale operations, was used with no adverse effects in runs 16 and 17.

The question of molecular weight control was addressed as follows. *Figures 3* and *4* show that the MW is controlled by polymer solubility; the initiator concentration has only a minor influence. In the precipitate—which starts to form within 5 min after initiation—no further growth is observed in experiments at 0–5°C. Increasing the reaction temperature to obtain better solubility proved to result in lower MW material; lowering the temperature gave higher molecular weights. It was shown that at -5 and -10°C precipitation likewise resulted in termination of growth; at -20°C some further MW increase was observed in the solid phase, comparing precipitate collected earlier and later during the reaction (*Figures 3b* and *5*). These observations suggest an inverse solubility–temperature relationship. Better solvents than DCE were sought. No solution viscosities appreciably higher than those routinely obtained in DCE were found in experiments in *o*-dichlorobenzene or nitrobenzene. The latter solvent proved unusual in that polymer growth in the precipitate occurred, although the reaction temperature was relatively high (0°C at the start, 3°C towards the end of the reaction) (runs 22, 23, *Table 1*).

Kinetic work is summarized in *Figure 6*, with $d[\text{monomer}]/dt = -k'[\text{monomer}]$. At the higher temperatures, the apparent rate constant falls off with time, at -11°C it is practically constant, and at -20°C it increases. $E_a = 58.3\ \text{kJ mol}^{-1}$, $\Delta H^* = 56.1\ \text{kJ mol}^{-1}$ ($13.4\ \text{kcal mol}^{-1}$), $\Delta S^* \sim -63.8\ \text{J mol}^{-1}\ \text{K}^{-1}$ (-15.3 eu). Since the apparent rate constant is actually a measure of the number of growing chains, it is in fact a probe of the relative rates of initiation and termination. The sharp drop very early in the reaction may support a higher order in PF_5 in the initiation mechanism, such as has been suggested in the literature[11].

These data relating to the polymerization mechanism seem to fit best the following model: Initiation is slow compared to propagation (precipitation of high MW polymer begins at an extremely low conversion; note that the solution viscosity passes through a maximum at about 80–90% conversion (*Figure 5*), suggesting that the initiator approaches exhaustion later than the monomer. No significant transfer reactions are expected since protonic acids were found to be unable to initiate; low conversions are found in poor solvents; molecular weight distributions are not unduly wide, at M_w/M_n 1.6–1.9 at -20°C; 2.2–2.6 at 0–5°C (*Figure 3*). Termination reactions are probably unimportant in the liquid phase, judging by the high conversions of precipitated, high MW polymer reached at temperatures below about $+20$°C. In the precipitate, propagation is expected to be slow; at temperatures above -20°C termination is much faster; at -20°C propagation can compete to some extent with termination.

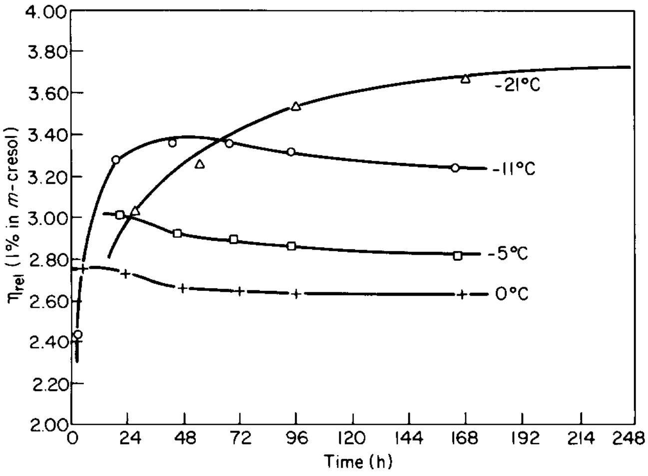

Figure 5 Solution viscosity of polymer samples isolated during prolonged polymerization runs

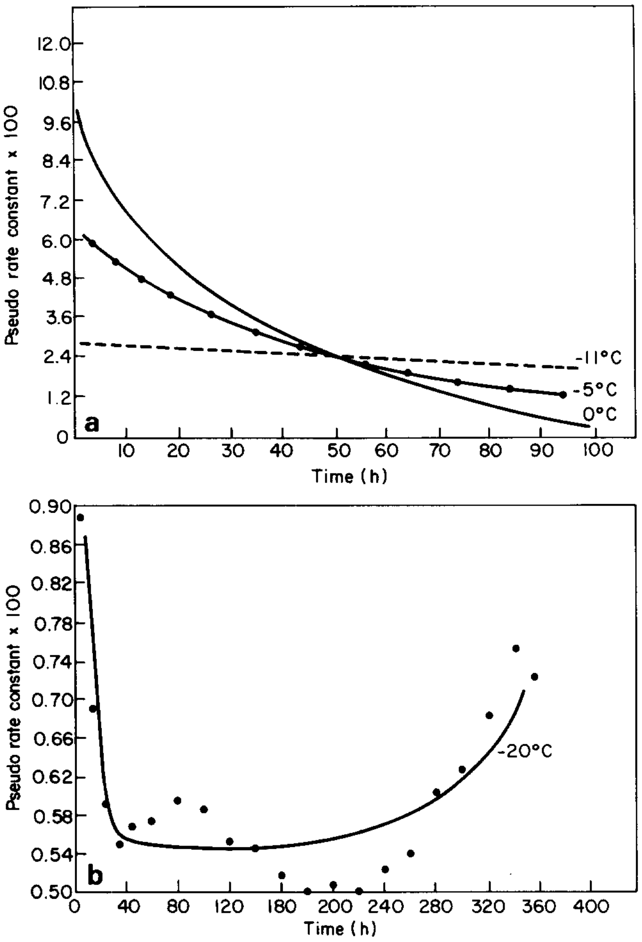

Figure 6 Kinetic analysis of 80/20 OBCH/THF copolymerization runs

Note that ethylene oxide greatly enhances initiation, as expected: higher production rates and lower solution viscosities at a given PF_5 concentration were recorded; see, for example, runs 24 vs. 37, and 15 vs. 33 in *Table 1*.

N.m.r. data on both the copolymers (*Figure 7*) and terpolymers (*Figure 8*) with ethylene oxide used in small amounts to influence the crystallization rate support fully random copolymerization. This suggests nucleophilic attack of an ether on the oxonium ion to be rate-limiting in the propagation, rather than the ring-opening process proper—i.e. a mechanism with an early transition state, resembling the initial state more closely than the product state—assuming similar ring-opening mechanisms for OBCH and THF (*Figure 9*).

Polymer characterization

The polymers are isolated as white powders which melt to give liquid-crystalline melts; in the case of sufficiently 'soft' compositions, isotropic melts may be observed before the onset of thermal degradation. Note that d.s.c. measurements gave no useful information on the crystalline–liquid crystal transition; liquid crystal–isotropic melt transitions could be observed in the 'softer' grades (cf. *Figure 10*). An endotherm at ~100°C was shown by WAXS to correspond to an increase of the spacings in the crystal, which seems to maintain its character and integrity otherwise. *Figure 11* shows a

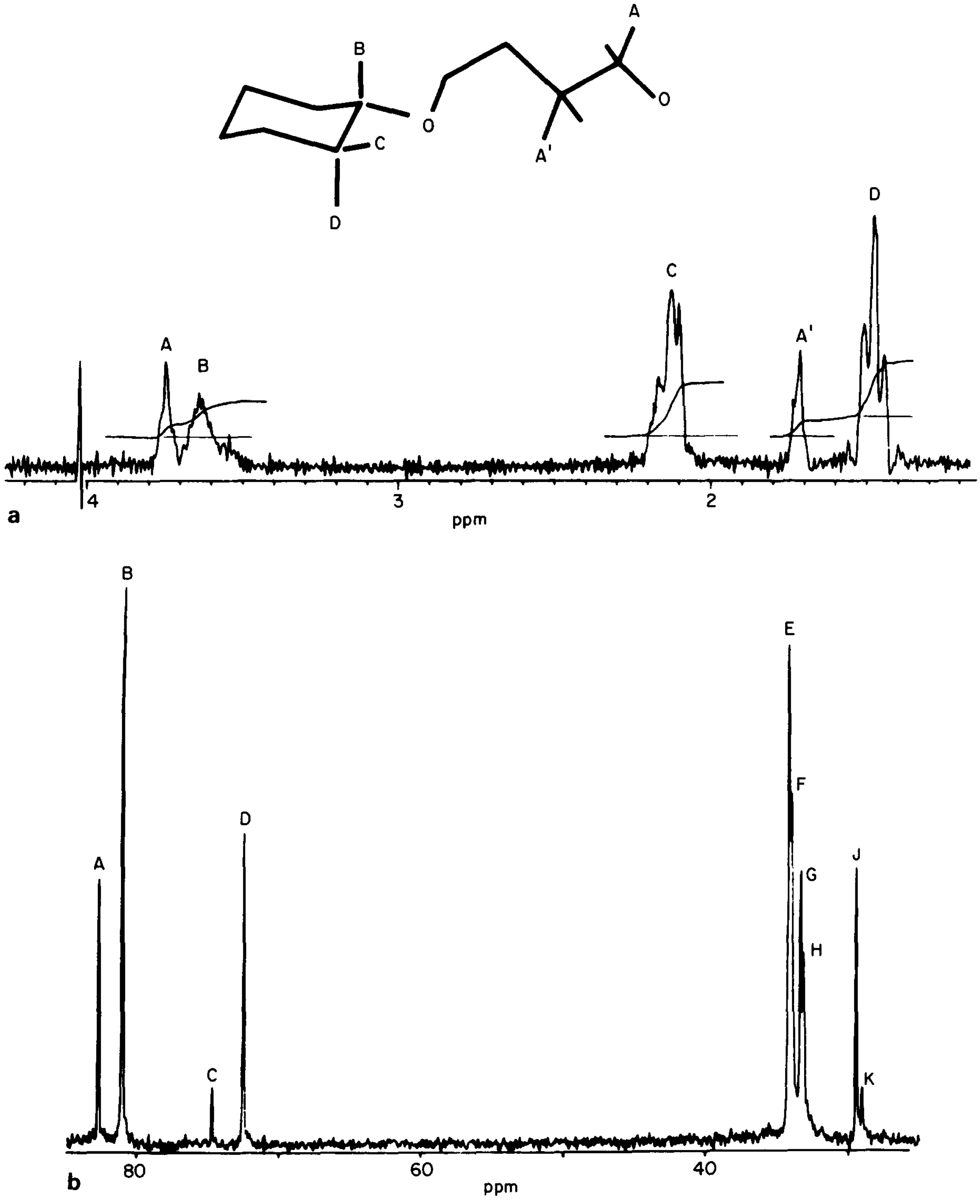

Figure 7 (a) Proton n.m.r. spectrum of the product from run 1, *Table 1*: 80/20 OBCH/THF copolymer. (b) ^{13}C n.m.r. spectrum of the product from run 1, *Table 1*: 80/20 OBCH/THF copolymer. A = methine cyclohexyl C neighbouring a THF derived fragment; B = methine cyclohexyl C in OBCH 'block'; C = oxygenated carbon in THF fragment, in THF 'block'; D = ditto carbon, neighbouring OBCH derived fragment; E = methylene cyclohexyl carbon in OBCH 'block'; F = C(3) methylene cyclohexyl carbon neighbouring THF derived fragment; G = C(2) ditto (i.e. nearer to the THF fragment than 'F'); H = C(2) ditto however neighbouring a THF 'block'; J = THF non-oxygenated carbon neighbouring cyclohexyl fragment; K = ditto carbon in THF 'block'

phase diagram depending on copolymer composition. Isomorphous behaviour of THF is supported by the very fast crystallization observed both in hot-stage microscopy (small undercooling possible) and in WAXS at variable temperature (*Figure 12*), where well defined and sharp reflections are regenerated upon quenching. Spinning attempts characterized by fast cooling, if not proper quenching, gave rise to isotropic sharp crystalline WAXS patterns (*Figure 13*).

Rheology measurements utilizing a Goettfert ram extruder were unsuccessful owing to oxidative polymer degradation in the instrument where air cannot conveniently be excluded (80/20 copolymer, 300°C). Measurements on a miniature spinning machine (*Figure 15*), featuring melting under vacuum, showed extrusion pressures independent of extrusion rate at shearing rates between about 800 and 4000 s^{-1}. Pressure instabilities, notably at longer residence times, which we ascribe to an onset of polymer degradation, render detailed and quantitative interpretation of the data questionable (75/20/5 OBCH/THF/EO; 300°C). A representative extrusion pressure would be 10 MPa, or melt viscosities of 200–1000 Pa s at the above shear rates.

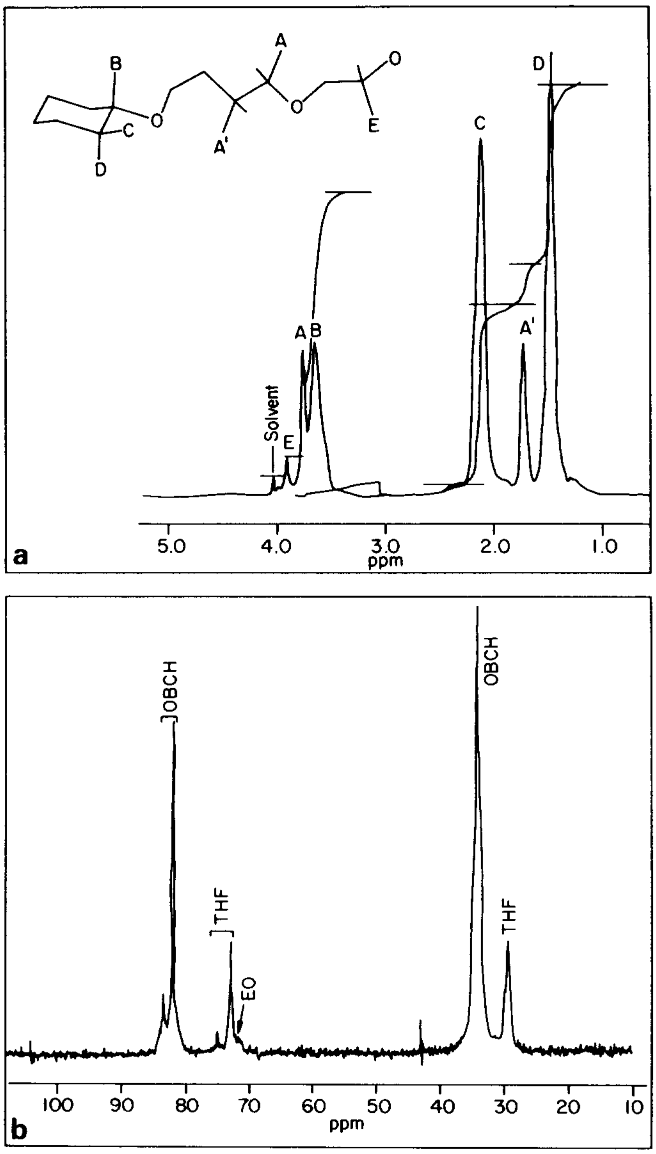

Figure 8 (a) Proton n.m.r. spectrum of terpolymer sample 34 (*Table 1*), trifluoroacetic acid solution. (b) ^{13}C n.m.r. spectrum of terpolymer sample 34 (*Table 1*), trifluoroacetic acid solution

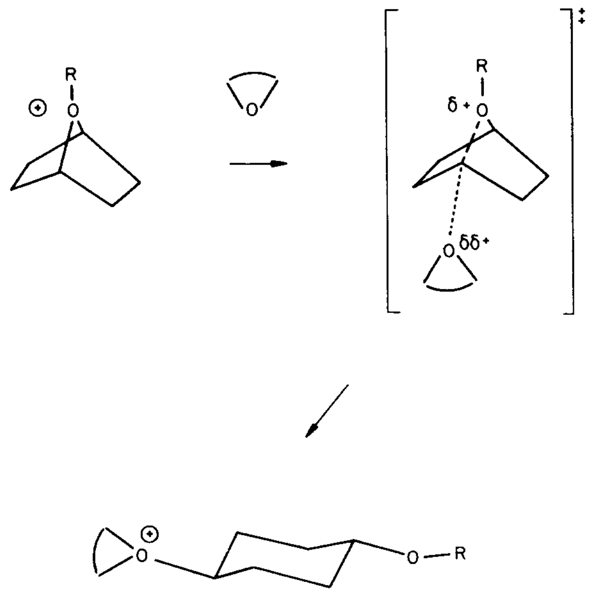

Figure 9 Propagation mechanism: transition state resembles educts more than adduct

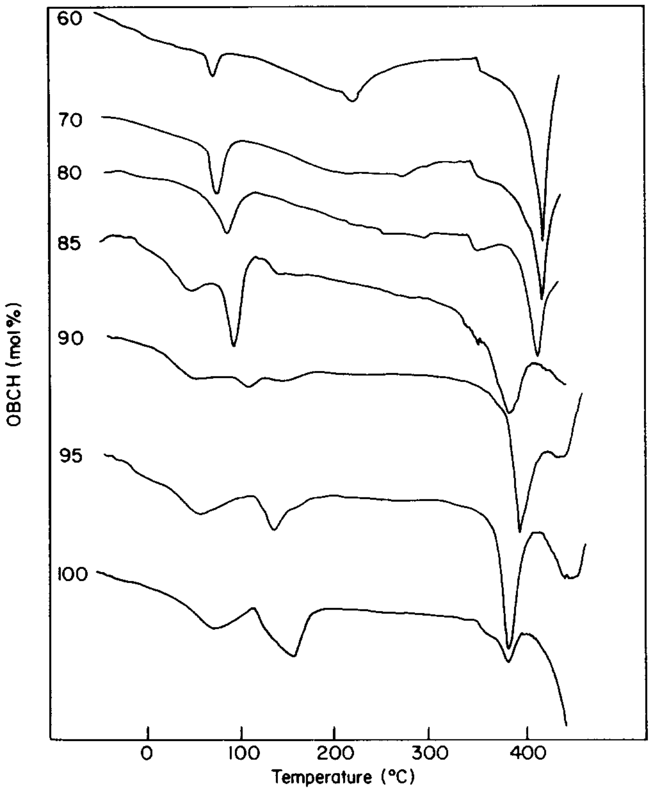

Figure 10 D.s.c. traces (20°C min^{-1}) of OBCH/THF copolymers made in bulk at 0°C ($SbCl_5$/pentane initiation)

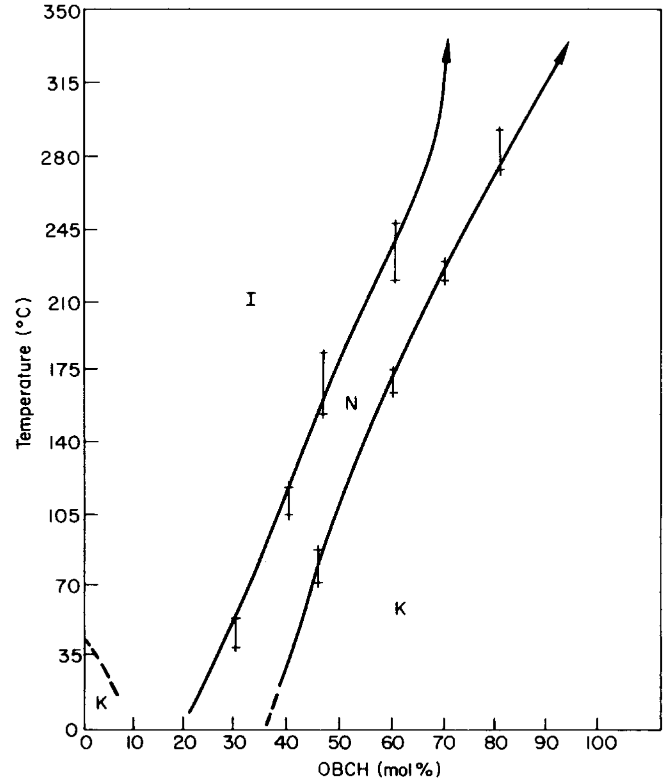

Figure 11 Phase diagram: K, crystalline solid; N, nematic liquid; I, isotropic liquid

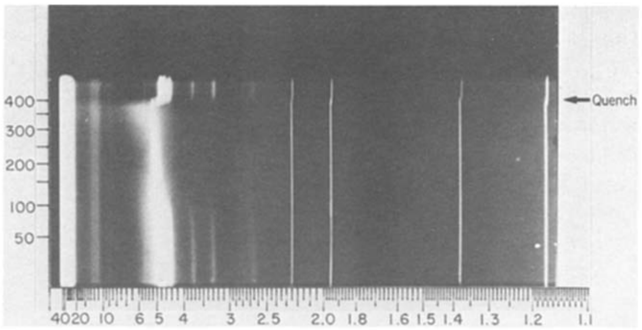

Figure 12 X-ray diffraction photograph of a sample of 80/20 OBCH/THF copolymer being heated, then quenched

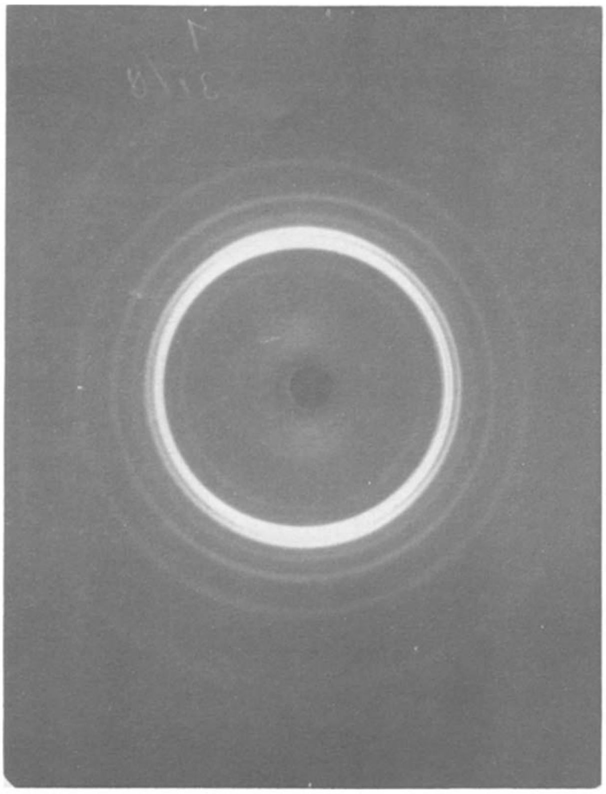

Figure 13 X-ray diffraction photograph of an 80/20 OBCH/THF copolymer sample rapidly cooled from the melt in a spinning attempt

Spinning

Early spinning attempts with 80/20 copolymer, using a small extruder spinning machine, showed troublesome feeding owing to the powder character of the product. Since liquid-crystal melts are difficult to deaerate in an extruder, we used an evacuated hopper; an experiment with a nitrogen-flushed hopper gave a yarn rich in bubbles. A few of the extruder experiments are described in *Table 2*. We soon switched to a piston-type miniature spinning machine, illustrated in *Figure 15*, featuring heating *in vacuo*, to eliminate feeding and melt deaeration problems.

The product crystallized within millimetres below the spinneret (judging by its becoming white and opaque) and would break a few millimetres below the spinneret if drawn down forcibly. Increasing the extrusion rate did not improve matters; neither did the use of a separately heated spinning plate at temperatures far above the extrusion temperature of 300°C—cf. experiments 1–3, *Table 2*. The 70/30 copolymer was much easier to spin and handle. A high level of rigid comonomer, implying a melting point quite near to the spinning temperature, seemed to require a crystallization retarder to enable significant drawdown during spinning.

Therefore, a series of terpolymers was prepared, including material with as high as 84% of rigid monomer, which could be spun into highly oriented yarn (experiment no. 7A, *Table 3* and *Figure 14*), although it resisted drawing down by ratios exceeding about 1.5 and proved too rigid to be taken up on a godet.

The terpolymers incorporating 1–5% of EO showed crystal–nematic transitions 10–20 K below the related copolymers (*Table 4*), and allowed substantial undercooling (hot-stage microscopy: as much as 35 K with EO vs. ~7 K without EO) in the nematic state. Spinning experiments were performed using the miniature spinning machine illustrated in *Figure 15*.

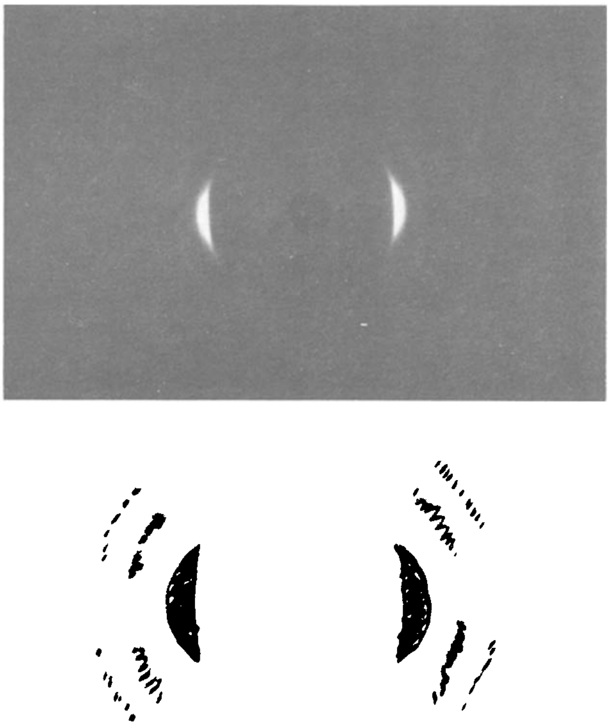

Figure 14 WAXS photograph of yarn from spinning experiment no. 7A (84/8/8 terpolymer)

Table 2 Spinning experiments of 80/20 OBCH/THF copolymer (η_{rel}2.5) on an extruder spinning machine with evacuated hopper, spinneret 10 × 200 μm

Run no.	Spinneret temp. (C)		Spinning velocity (m min^{-1})	Draw-down[b]	WAXS orientation of spun copolymer[c]
		Plate[a]			
1 A	324	320	9.6	+	–
B		340	9.6	+	
2 A	293	320	30	0	
B		320	96	+	0/–
3 A	307	315	9.6	0	0/–
B		315	28.7	0	–
C		330	9.6	0	0
D		330	23.9	0	–

[a] Temperature of separately heated spinning plate
[b] + = small drawdown ratio (not measured; 0 = no drawdown possible
[c] Gradation of orientation: 0 = slight, = none

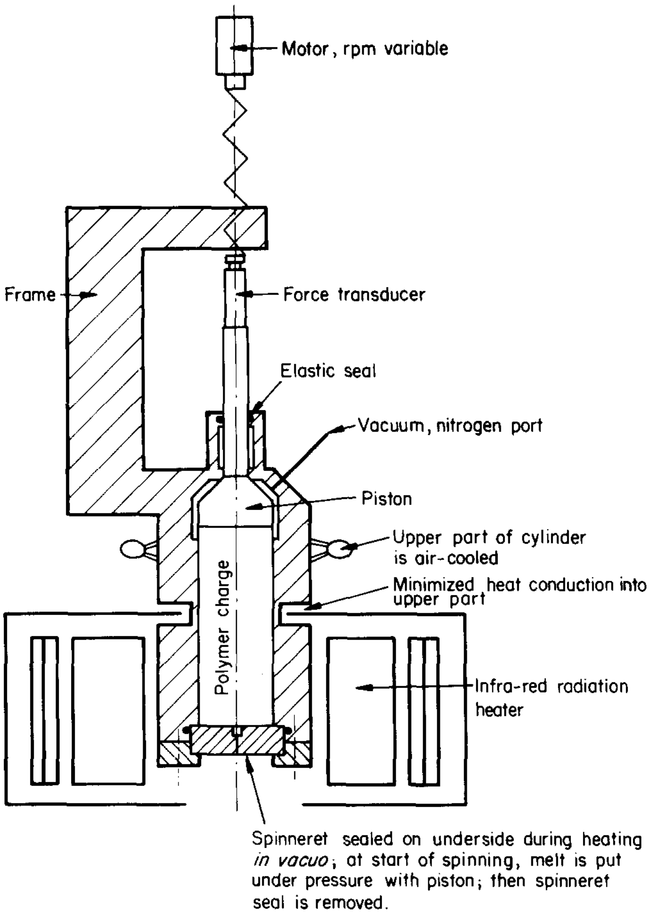

Figure 15 Miniature spinning machine

In all cases, drawdown was limited to <2.4, independent of extrusion rate, spinning temperature, or the use of a hot air zone below the spinneret at temperatures up to 400°C. In fact, whereas highly oriented materials (WAXS) were obtained in many cases, the use of a hot air tube resulted in destruction of such orientation (*Table 3*). Note that the 'softer' 70/30 and 60/40 two-component copolymers could be extruded into highly oriented materials as well. The 60/40 material allows experiments both in the nematic and in the isotropic liquid phase. Experiments 5 and 6 (*Table 3*) show nearly unlimited melt extensibility in the isotropic phase, but a maximum drawdown of 1.9 in the liquid-crystalline phase. At about the nematic–isotropic transition, a drawdown of

Table 4 Comparison of phase transition temperatures of some co- and terpolymers

Copolymer composition OBCH/THF/EO	K→N (°C)	N→I (°C)
80/20	270–290	>330, d
80/17/3	260–270	>330, d
79/17/4	259–273	>330, d
84/8/8	270–290	>330, d
75/20/5	231–256	>330, d
75/25	250–258	>330, d
70/30	220–230	>320, d
60/40	165–178	220–250
46/54	70–90	153–187
40/60	<25	104–120
30/70	<25	38–55

Table 3 Spinning experiments of copolymer OBCH/THF(/EO) on a piston extrusion spinning machine with evacuated chamber

Run no.	Polymer compos. OBCH/THF/(/EO)[a]	η_{rel}	Spinneret		Hot air tube (°C)	Spinning velocity (m min^{-1})	Drawdown	WAXS orientation of spun copolymer[b]	Comments[c]
			Hole diam. (μm)	Temp. (°C)					
4 A	70/30I	3.53	1×250	270	–	8.1	2.4	+ +/+ L	A
B				280	–	4.1	2.0	0 P	
C						13.0	1.6	0 P	B
D						72.5	1.3		
5 A	60/40I	2.90	1×250	270	–	13.0	14.3		
B						5.1	36.5	+ P	
C						22.9	8.1	+ P	
6 A	60/40I	2.90	1×250	210	–	13.0	1.6	+/+ L	C
B						7.1	1.9		D
C				220	–	7.1	2.3		
D				230	–	7.1	5.0	0 P	E
E						22.9	2.7		
7 A	84/8/8	2.26	1×250	300	–	70.7		+ L	[d]
8 A	80/19/1	2.64	1×250	300	–	32.1	1.4	+ +/+ L	
9 A	79/20/1	3.08	1×250	300	310	22.9	1.6	–	
B					310	64.5	1.4	0/–	
10 A	80/17/3	2.73	1×250	300	–	32.8	1.4	+ + L	F
11 A	80/17/3I	2.82	1×250	305	310	13.0	1.7		
B					310	32.8	1.6	–	[e]
C					310	52.7	1.2	+ +/+ L	
12 A	80/17/3I	2.73	1×250	305	310	13.0	1.8		
B					400	32.8	1.2		[e]
13 A	75/20/5	2.71	1×250	288	–	22.9	1.6	+ + L	G
14 A	75/20/5I	2.71	2×200	305	–	10.2	2.1		
B					–	33.4	1.3		
15 A	75/20/5I	2.71	3×150	305	–	18	2.2	–	
B					–	64	1.5	0/–	

[a] I = addition of 0.5% of phenolic antioxidant (Ionox 330)

[b] Gradation of orientation: + + = sharp, + = normal, 0 = slight, – = none. Direction of orientation to the yarn: L = longitudinal, P = perpendicular

[c] A–G For yarn tensile properties, see *Table 5*

[d] Yarn too rigid to be taken up on a godet

[e] Rough yarn

Table 5 Yarn tensile properties of some copolymers OBCH/THF(/EO) spun on a piston extrusion machine, spinneret 1 × 250 μm

Sample[a]	Polymer composition OBCH/THF/EO	Spinning Temperature (°C)	Spinning Velocity (m min^{-1})	Drawdown	Tenacity (cN/tex)	Elongation (%)	Modulus (max. 2%) (cN/tex)
A	70/30	270	8.1	2.4	16.4	1.4	1358.5
B	70/30	280	13.0	1.6	5.1	0.7	772.9
C	60/40	210	13.0	1.6	16.7	6.1	510.4
D	60/40	210	7.1	1.9	14.1	5.8	494.6
E	60/40	230	7.1	5.0	2.2	2.3	130.6
F	80/17/3	300	32.8	1.4	2.8	0.9	326.8
G	75/20/5	288	22.9	1.6	2.5	0.9	243.2

[a] See comments to *Table 3*

5 proved the maximum. The material spun in the isotropic phase showed orientation of the polymer chains perpendicular to the yarn.

A number of yarns collected were evaluated (cf. *Table 5*). They show properties not even satisfactory for clothing yarns.

This experience at first seemed very puzzling: a liquid-crystalline polymer, exhibiting shear thinning, that can be highly oriented, stubbornly resists drawdown—unless it is heated further to the isotropic phase. The yarns resist hot or cold drawing at temperatures below the melting point. In the literature, LC behaviour is suggested to aid high-performance fibre preparation[12]—see, however, results showing no benefit at all from LC behaviour in work with poly(phenylene terephthalamide)[13]. The following reasoning appears to resolve the perceived contradictions.

Viewed on the 10–100 nm scale, arrays of macromolecules that consist of relatively rigid sequences interspersed with flexible units are likely to be organized into structures analogous to the lamellae encountered in the usual polymer crystallite: in regions where the interchain alignment begins to degrade, the flexible units allow chain folding. Although poly(THF) crystallizes with an extended chain zig-zag conformation, high temperatures favour *gauche* conformers by an entropy term of $RT \ln 2$. Such chain folding decreases the concentration of tie molecules interconnecting the primary domains of aligned macromolecules. It is precisely these tie molecules that one needs to transfer the forces for drawdown, and, ultimately, to build the high-tenacity yarn envisioned.

A lamellar structure of the yarns produced is supported by a sharp two-point SAXS pattern observed in the highly oriented yarn from experiments 10A and 8A, proving a highly regular periodicity of denser and more tenuous regions in the yarn direction, with a wavelength of 23.6 and 18.6 nm, respectively—substantially less than the estimated chain contour lengths. The tenuous regions define the mechanical properties in such a series, irrespective of the (very high) orientation of the chains in the dense, crystalline, regions.

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