

# ***In Situ* Polymerization in Binary Polymer/Monomer Mixtures: A Novel Route to Polymeric Composites**

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## **Synopsis**

The formation of a polymer/polymer composite by solid-state polymerization of trioxane (TOX) crystals grown within binary trioxane/polycaprolactone or trioxane/poly(oxyethylene) mixtures is reported. At present, such composites have been formed with trioxane-rich (hypoeutectic) mixtures. It is observed that in this composition range, much higher yields are obtained through thermal orientation of the TOX crystals which result in very highly ordered systems as revealed by optical and electron microscopy. These POM-rich composites were not, however, amenable to mechanical testing.

## **INTRODUCTION**

Well-known problems with processing and fabrication of filled systems, in particular fiber-filled systems, encountered in the manufacture of some types of conventional composites have led to the search for a material that can be processed as a homogeneous melt and further reinforced by an oriented fibrous component which comes into existence only after the processing step, once the object has been given its final shape.

The previous approach to this problem has involved the *in situ* crystallization of a component which is soluble in the polymer melt but precipitates out at some temperature greater than  $T_g$  of the matrix polymer.<sup>1-4</sup> Siegmann et al. have added 2,4,5,6-tetrachloroxyethylene or 1,2,4,5-tetrachlorobenzene to ordinary and high-impact polystyrene.<sup>1,2</sup> They observed that the additive precipitated in three different morphologies depending on crystallization temperature: regular needles with aspect ratio of approximately 10, dendritic structures, and tiny crystallites as crystallization temperature decreased. Although their primary interest was the production of a fine and uniform dispersion of an additive (e.g., a fire retardant) in a desired morphology, they noted that crystallization under shear could produce oriented needles of the additive and suggested that the mechanical properties of such an anisotropic system might be of interest.

Joseph, Kardos, and Nielsen added acetanilide or anthracene to styrene-acrylonitrile copolymers.<sup>3</sup> They also observed large, regular needles and dendritic structures at high and medium crystallization temperatures; but at the lowest temperature they found very long, thin needles. They suggested that at the lowest crystallization temperatures, due to high viscosity of the matrix polymer, crystallization is sufficiently slow that there is no need to form dendritic structures to dissipate heat. Mechanical testing revealed no reinforcement ef-

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fect, and they concluded that since organic crystals are held together by the same weak van der Waals forces that hold together the glassy polymer matrix, there is *a priori* no reason to hope for reinforcement by an organic crystalline additive. In another work, Kardos et al. deliberately used a low modulus matrix (lightly crosslinked butadiene-acrylonitrile rubber) so that the reinforcing effect of the *in situ* grown crystals could be observed.<sup>4</sup> In this case, their goal was not to produce a high-performance composite but to test various equations predicting the effects of filler size, shape, and loading and also phenomena occurring at the filler-matrix interface.

Stiffening of rubber is known to occur by the addition of small amounts of phenyl- $\beta$ -naphthylamine if the additive crystallizes in the needlelike or dendritic form.<sup>5</sup>

Our approach to the problem is similar in concept to previous work, in that the first step involves the *in situ* crystallization of an additive. However, as pointed out in ref. 3, there is no hope of obtaining a high-performance composite if one stops here, and the novelty is the solid-state polymerization of the additive after crystallization. Thus, the additive is actually a monomer, and the final reinforcing component is a fibrous polymer held together by covalent bonds rather than van der Waals forces.

It is interesting to note in passing that some work has already been done on solid-state polymerization of (eutectic) mixtures, in which, however, both components were monomers, in an attempt to obtain copolymers.<sup>10</sup> In most cases, the product was either a single homopolymer or a mixture of homopolymers. To our knowledge, this procedure has not been proposed as a route to unusual composites.

Previous work has shown that binary mixtures of trioxane (TOX) with polycaprolactone (PCL)<sup>6</sup> or poly(oxyethylene) (PEO)<sup>7</sup> form eutectic systems. Our approach can be understood by referring to Figure 1, which depicts a schematic phase diagram of a TOX/polymer eutectic system. If, starting with a molten

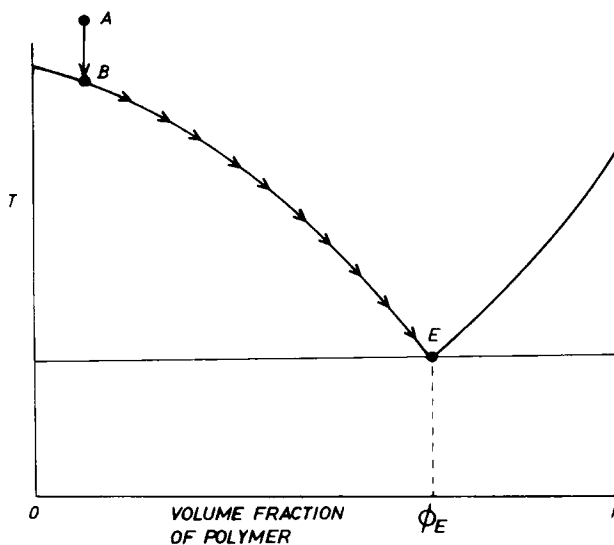


Fig. 1. Schematic phase diagram of a trioxane/polymer eutectic mixture. Arrowheads show cooling of a hypoeutectic melt.

hypoeutectic (TOX-rich) mixture at point A, one cools this melt to the TOX liquidus line at point B, pure TOX starts to crystallize out. Further cooling causes crystallization of needles of pure TOX and consequently a shift in the composition toward the polymer-rich side, following the TOX liquidus line B-E. When point E is reached, which is the eutectic composition, further cooling causes the eutectic to solidify to a physical mixture of TOX and polymer crystals with a composition  $\phi_E$ . Our hope was to "in situ polymerize" TOX needles grown in this way in the solid state via  $\gamma$ -irradiations,<sup>8</sup> to form fibrous poly(oxyethylene) (POM) which would reinforce the polymer matrix. The fate of the TOX remaining in the solidified eutectic matrix was an open question; we thought it unlikely that it would polymerize to any great extent, since eutectics are generally composed of tiny crystals of the pure components<sup>9</sup> and work with pure TOX reported in ref. 21 has shown that POM yield decreases with size of the parent TOX crystals.

### EXPERIMENTAL

A technique for producing appropriate amounts of purified TOX has been described in detail previously.<sup>21</sup> In brief, it involves sublimation in a poor vacuum using a stream of ultradry nitrogen to entrain the TOX vapor.

The polymers used were poly(ethylene oxide) (Carbowax 6000, Union Carbide Co.) and commercial polycaprolactone (Aldrich Chemical Co.), stored in a vacuum desiccator over phosphorous pentoxide.

TOX and polymer were blended in glass bulbs (sealed to prevent sublimation of the TOX) by holding them for 2-3 h at 90°C, to obtain homogeneous solutions. After cooling to room temperature, the solidified mass was rapidly transferred to 5 mm i.d. sample tubes. Thermal orientation of the TOX needles was achieved by pulling the sample tubes through the temperature gradient oven described in ref. 21, as in a "one-pass zone refining."

Polymerization in the solid state was achieved by  $\gamma$ -irradiation followed by postpolymerization under standard conditions:  $5 \times 10^5$  rad, 12 h at 50°C (in some cases 100-150 h at 33°C). Measuring the conversion of TOX to POM within the binary mixtures requires knowledge of the amounts of (a) residual trioxane and (b) either matrix polymer (PEO or PCL) or POM formed. The amount (and percentage) of residual TOX was determined by weighing pieces of the polymerized material before and after sublimation of that residual TOX. The amount (and percentage) of matrix polymer (PCL or PEO) in the remaining polymer/polymer mixture was then derived from appropriate DSC melting endotherms (scan speeds of 4, 8, and 16°C/min).

An internal check of this procedure and of sample homogeneity is provided by the comparison of initial TOX content with that of the residual TOX plus converted TOX (i.e., POM). An additional check of the precision and reliability of the procedure can be obtained by determining the amount of POM also, with the help of the DSC melting endotherms. This determination is, however, lengthy and was not used routinely. The heat of fusion  $\Delta H_f$  of PEO, PCL, and POM obtained by solid-state polymerization of pure TOX were determined in a Perkin-Elmer DSC-1B calibrated with indium and are summarized in Table I.

The results thus obtained with both *in situ*-polymerized PCL-POM and

TABLE I

Sample	cal/g	Heat of fusion, cal/mol repeat unit
PCL (first melting run)	23.3	2656
PCL (subsequent melting runs with same recrystallized sample)	16.7	1903
PEO	41.6	1830
POM (first melting run)	62.3	1870
POM (subsequent melting runs with same recrystallized sample)	35.5	1066

PEO-POM mixtures are collected in Table II and indicate that, with one exception, the precision is better than 3% (compare total weights in the first and last columns). We consider this agreement as strong support for the implicit assumption made in our usual procedure to determine conversion during *in situ* polymerization, i.e., that  $\Delta H_f$  of the matrix polymer remains unchanged.

Some additional information can be gleaned from Table II, and from a comparison with the melting behavior of pure solid-state-polymerized POM and physical mixtures of POM with PCL or PEO (as distinguished from *in situ*-polymerized POM). While these observations are not directly relevant to the reliability of the experimental method, they are worth mentioning in view of their intrinsic interest as follows:

The melting temperature of POM depends both on thermal history and environment. Thus for pure POM, the melting temperature obtained during the first run is 463–469 K, while subsequently, fusion occurred at 449–451 K. This is in agreement with Amano et al.<sup>11</sup> and corresponds to a difference in melting point between the nearly 100% crystalline solid-state-polymerized POM and melt crystallized POM of lower crystallinity. A similar phenomenon is observed for the *in situ*-polymerized POM, however, the melting temperatures are depressed even further by the presence of the molten matrix polymer (column 2, Table II) to 457.5–459.5 K and 445–447.5 K for the first and subsequent runs, respectively. The crystallization temperature interval was not affected, being 416.5–418 K both for POM obtained from pure TOX and *in situ*-polymerized POM, nor was  $\Delta H_f$ , as pointed out above.

The *in situ*-polymerized POM/PCL system showed a systematic decrease in POM content for repeated fusions (column 8, Table II), whereas *in situ*-polymerized POM/PEO did not, suggesting some degradation of the POM provoked by the presence of PCL. Pure POM showed no degradation for the same cycle of three fusions, nor did a physical mixture of POM/PEO. Oddly, a physical mixture of POM/PCL showed no degradation either, indicating that the very intimate contact of the PCL with the *in situ*-polymerized POM fibrils plays a role in this degradation process.

## RESULTS

Formation of a polymeric composite by solid-state polymerization of trioxane crystals grown within a molten matrix was achieved, but at present only for hypoeutectic (TOX-rich) TOX/PCL and TOX/PEO binary mixtures. Hayashi et al. observed a similar effect in monomer/monomer mixtures of TOX/3,3-

TABLE II

Sample	T <sub>m</sub> or T <sub>c</sub> °K	Rate °K/min	Range	Chart speed cm/min	Peak area cm <sup>2</sup>	Wt. Matrix Polymer mg.	Wt. POM mg.	Total Wt. mg. (% error)
POM/PCL 10.78 mg.	336.5	+8(1 <sup>st</sup> )	16	2.5	5.63	6.21		
	333	+8(2 <sup>nd</sup> )	8	2.5	7.94	6.11		
	332	+4	4	1.25	8.65	6.65		
	333	+8	4	2.5	17.50	6.73		
	335.6	+16	8	5	18.0	6.92		
						6.52±.35	3.74	10.26 (-4.8%)
	459.5	+16(1 <sup>st</sup> )	16	2.5	9.07		3.74	
	417	+16	16	2.5	3.49		2.51	
	445.5	+16(2 <sup>nd</sup> )	16	2.5	3.20		2.30	
	417.5	+16	16	2.5	2.81		2.02	
445.5	+16	15	2.5	2.86		2.06		
POM/PCL 10.87 mg.	336.5	+8(1 <sup>st</sup> )	8	2.5	10.41	5.74		
	333	+8(2 <sup>nd</sup> )	4	2.5	15.55	5.98		
	332	+4	4	1.25	7.47	5.75		
	333.5	+8	4	1.25	8.31	6.40		
	335	+16	8	5	7.61	5.85		
						5.94±.27	4.65	10.59 (-2.6%)
	460	+16(1 <sup>st</sup> )	16	2.5	11.27		4.65	
	417.5	+16	16	2.5	4.53		3.26	
	446.5	+16(2 <sup>nd</sup> )	8	2.5	8.80		3.16	
	417.5	+16	16	2.5	3.70		2.66	
446.5	+16	8	2.5	7.74		2.78		
POM/PCL 12.85 mg.	337	+8(1 <sup>st</sup> )	16	2.5	5.50	6.07		
	333	+8(2 <sup>nd</sup> )	4	2.5	16.17	6.22		
	332.5	+4	4	1.25	8.15	6.27		
	333	+8	4	2.5	16.04	6.15		
	335	+16	8	5	16.90	6.50		
						5.24±.16	6.61	12.85 (0%)
	459.5	+16(1 <sup>st</sup> )	16	2.5	16.00		6.61	
	417	+16	16	2.5	6.66		4.79	
	447.5	+16(2 <sup>nd</sup> )	16	2.5	6.25		4.50	
	416.5	+16	16	2.5	5.64		4.06	
447	+16	16	2.5	5.63		4.05		
POM/PEO 7.76 mg.	338.5	+8	16	2.5	8.95	5.54		
	337	+4	8	1.25	8.42	5.20		
	340.5	+16	32	5	8.95	5.54		
						5.43±.19	2.25±.20	7.68 (-1.0%)
	458	+16(1 <sup>st</sup> )	32	2.5	2.37		1.95	
	417	+16	8	2.5	6.41		2.30	
	447	+16(2 <sup>nd</sup> )	8	2.5	6.93		2.49	
	417.5	+16	8	2.5	6.09		2.19	
	447	+16	8	2.5	6.45		2.32	
POM/PEO 9.00 mg.	338	+8	16	2.5	10.24	6.33		
	341	+16	16	5	19.65	6.08		
						6.21	2.72±.13	8.80 (-2.2%)
	457.5	+16(1 <sup>st</sup> )	16	2.5	6.79		2.80	
	418	+16	16	2.5	3.86		2.78	
	447	+16(2 <sup>nd</sup> )	8	2.5	7.74		2.78	
	418	+16	8	2.5	6.91		2.48	
	447.5	+16	8	2.5	7.64		2.75	
POM/PEO 8.33 mg.	339	+8	16	2.5	9.62	5.95		
	337.5	+4	8	1.25	9.18	5.68		
	342	+16	16	5	19.10	5.90		
						5.84±.14	2.37±.11	8.21(-1.4%)
	457.5	+16(1 <sup>st</sup> )	32	2.5	2.78		2.29	
	418	+16	8	2.5	6.83		2.46	
	447	+16(2 <sup>nd</sup> )	8	2.5	6.88		2.47	
	418	+16	8	2.5	6.14		2.21	
	447	+16	8	2.5	6.66		2.40	

bis(chloromethyl)oxetane, which forms an eutectic at approximately 30 mol % TOX.<sup>12</sup> Only in TOX-rich mixtures containing 70–100% TOX could POM be isolated. However, it is not clear whether the failure in their case to obtain POM for TOX concentrations less than 70% was due to morphological factors or to the low postpolymerization temperatures (<25°C) imposed by the phase diagram (which is not the case in either of our systems).

In addition to composition, we also observed a very pronounced influence of

thermal orientation of the TOX needles in a temperature gradient on the degree of conversion to POM. For the TOX/PCL mixtures with a nominal content of 80–85 wt %, thermal orientation at 0.785 mm/min resulted in yields of approximately 34%; and at 6.6 mm/min, it gave approximately 35%, while unoriented samples gave yields on the order of 8.5%. For the TOX/PEO mixtures with similar TOX content, the thermal orientation at the same rates gave yields of approximately 21 and 19%, respectively, while unoriented samples gave approximately 11%. Thus, yields were higher in the PCL matrix than in PEO, whereas they increased markedly by thermal orientation in both cases, though no significant change could be observed for an eight-fold change in the rate of crystallization. Finally, they were considerably lower than yields obtained in pure TOX polymerized under similar conditions (approximately 37% unoriented, approximately 45% at 0.785 mm/min, and 50% at 6.6 mm/min, see Kiss et al.).<sup>21</sup> Note that for both of these binary systems the melting point of the eutectic is well below the postpolymerization temperature used (50°C); thus polymerization of the pure TOX crystals actually took place within a bath of molten eutectic mixture.

In the above averages, only those results were included for which the internal check of the initial TOX concentration gave results within several percent of the nominal concentration. The internal check revealed that the samples were rather inhomogeneous and that there was a correlation between low initial trioxane concentration and low polymer yield.

Experiments on 60% mixtures of TOX/PCL and TOX/PEO thermally oriented at 6.6 mm/min gave yields of approximately 6 and 0%, respectively. For these experiments, the depression of the TOX melting point in the vicinity of the eutectic composition ( $\phi_E$ ) required the use of a lower postpolymerization temperature (33°C) for longer times (100–150 h). The yields were very low, even in comparison to pure TOX polymerized under the same conditions, and therefore even farther from its melting point.

Both the pronounced effect of the thermal orientation and the very low yields of the 60% mixtures reinforce the conclusion reached in ref. 21 that the morphology of the parent TOX crystal has a marked influence on the POM yield. In the case of thermal orientation of hypoeutectic mixtures, very highly ordered systems result giving rise to a morphology favorable to polymerization. Figures 2 and 3 show the oriented 80% PCL/TOX and PEO/TOX mixtures. In these photographs, the viewing direction is almost parallel to the thermal gradient (and hence to the trioxane needle axis). Some slight deformation incurred during sample preparation is visible. Note that the striations in both matrix polymers perpendicular to the voids left by the sublimated TOX needles are not due to epitaxial crystallization of the matrix polymers onto the TOX needles; epitaxy occurs in the case of TOX/PCL but not for TOX/PEO.<sup>6,7</sup> More likely they are due to crystallization phenomena peculiar to the thermal orientation technique, possibly even stick-slip as the sample tube is pulled out of the temperature gradient oven, although it was not observed in all samples.

On the other hand, in the case of the very low yields obtained upon approaching the eutectic concentration, it is clear that the closer to the eutectic concentration the TOX starts to crystallize, the less TOX will be able to crystallize before the eutectic concentration is attained. Thus, the pure TOX crystals grown out of such a solution will be smaller, and a greater fraction of the total TOX content

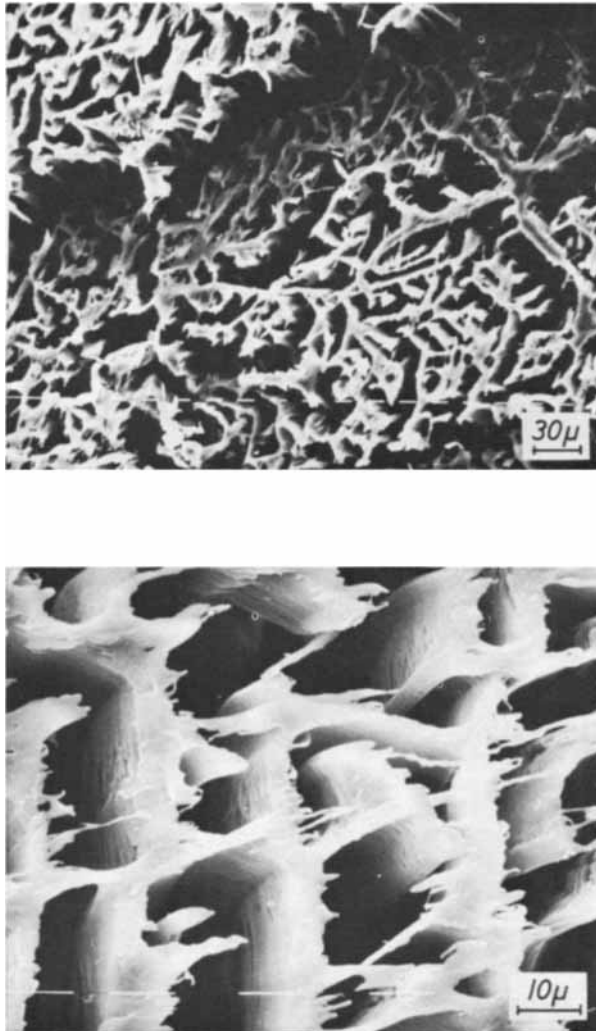


Fig. 2. Polycaprolactone (PCL) matrix after sublimation of trioxane (TOX) from a thermally oriented 80% TOX/PCL mixture, viewed approximately parallel to the thermal orientation direction.

will be incorporated into the eutectic. Both of these situations are unfavorable for conversion to POM, and low yields result.

The observation made in ref. 21 (and by previous investigations) that morphological features of the parent TOX crystals translate directly to the morphology of the resulting POM is also borne out by this work. Figure 4 shows a section of a thermally oriented mixture of TOX/PCL after polymerization and removal of the residual TOX (the original cylindrical specimen was spread laterally for clarity). It can be seen to be composed of long, parallel fibers, all apparently extending over the entire length of the section, as did the parent TOX crystals. Note that the specimen is almost perfectly unidirectional, as one might desire in a fiber-reinforced composite.

A closer look at the fibers reveals that the contact between the polymer matrix and the *in situ*-polymerized POM is very intimate, as POM fibrils can be seen

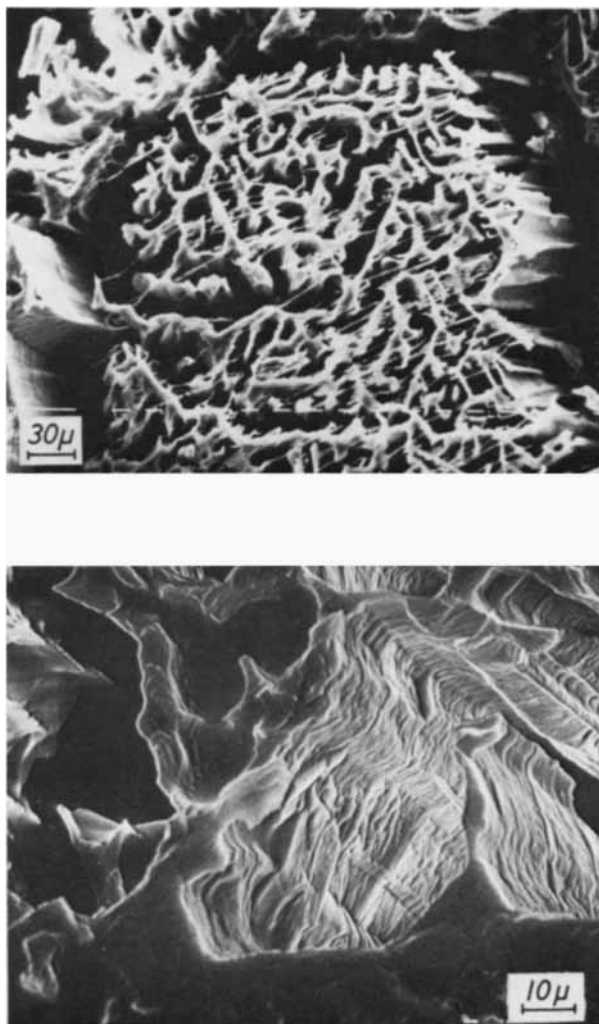


Fig. 3. Poly(ethylene oxide) (PEO) matrix after sublimation of trioxane (TOX) from thermally oriented 80% TOX/PEO mixture, viewed approximately parallel to the thermal orientation direction.

to be emerging from the matrix. This is a result of the fact that, as already noted, postpolymerization actually took place in a bath of molten eutectic ( $T_{\text{pol}} = 50^{\circ}\text{C}$ ), so that the matrix polymer (PCL or PEO) solidifies only after the formation of the POM fibers (Figs. 5 and 6). Since the interface between the reinforcing agent and the matrix is often the weak link in composites, this constitutes an advantage of the *in-situ* polymerization technique. Figures 5(b) and 6(b) show that washing away the matrix polymer reveals a "lace" morphology which we have also observed in solid-state-polymerized POM from pure TOX crystals grown from solution. The TOX needles grown from hypoeutectic mixtures are in fact solution grown, the solvent in this case being a molten mixture of TOX/matrix polymer, of ever changing composition as the crystallization proceeds. Note that dissolution of matrix polymer in Figure 6(b) may have been incomplete.

Attempts to measure the mechanical properties of the systems described above



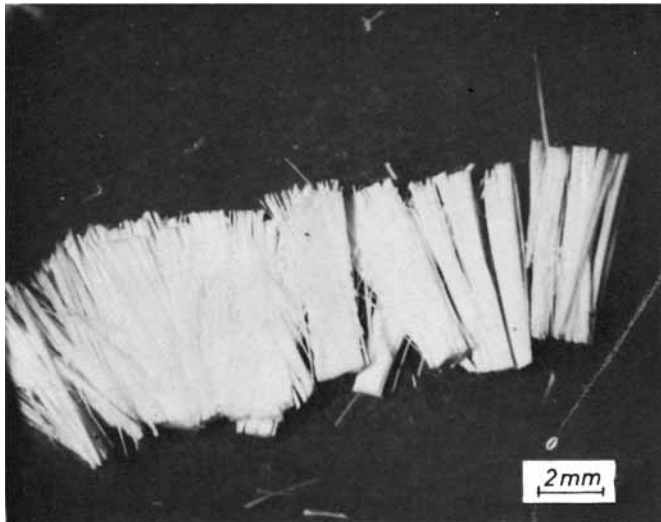


Fig. 4. Poly(oxymethylene)/polycaprolactone composite obtained by polymerization of a thermally oriented 80% TOX/PCL mixture; cylindrical transverse section spread laterally for clarity.

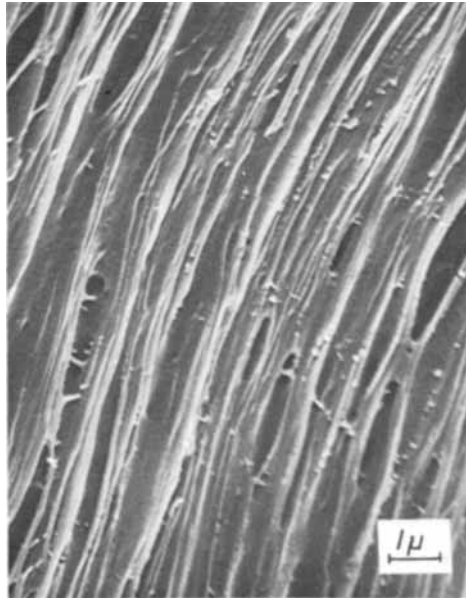
were frustrated by two obstacles. The first was the very high POM content of the composites resulting from *in situ* polymerization. Although the conversions were on the order of 20–30%, the fact that the initial TOX concentrations were 80–85% means that after removal of unreacted TOX, the composites consisted of 50% or more of POM. This very high loading made it impossible to mold suitable sample bars.

As described above, attempts to reduce the final POM loading by reducing the initial TOX concentration to 60% failed because the POM yield decreased. Further attempts to dilute the composite by the addition of pure matrix polymer were also made. It was found impossible to make acceptable test bars of either diluted composites or pure matrix polymers due to the second obstacle, that of low molecular weight of the matrix polymers, which caused cracking due to thermal stresses during cooling. Other problems in the fabrication of test bars were the formation of internal voids and the lack of consistency in the thickness of the bars. The latter is especially serious because thickness enters to the fourth power in the forced torsional oscillation of a bar of rectangular cross section, the method used for measurement of dynamic moduli. A few measurements on the best test bars resulted in wide scatter and poor reproducibility.

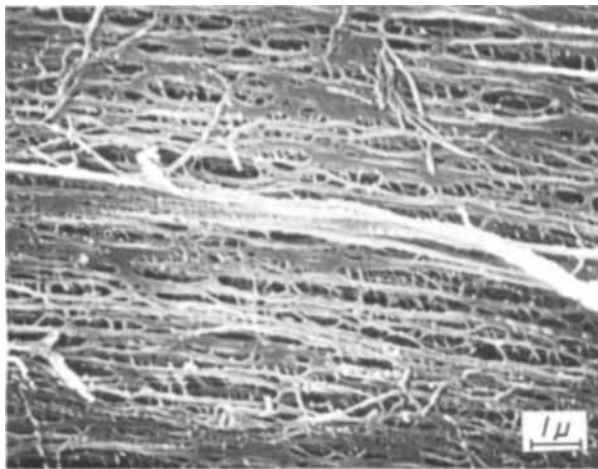
Attempts to produce samples more amenable to mechanical testing by using higher-molecular-weight matrix polymers have until now not been successful for miscellaneous reasons.

## DISCUSSION

The demonstration of the feasibility of forming a polymeric composite using *in situ* polymerization was achieved, and we were able to demonstrate the utility of thermal orientation in producing such materials in a highly anisotropic form. Thermal orientation is in fact a vital step in the *in situ* polymerization and furthermore plays a dual role. It is *desirable*, since it allows the orientation of the



(a)

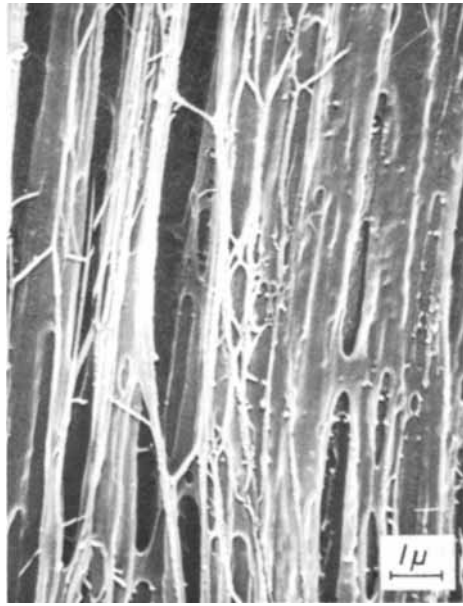


(b)

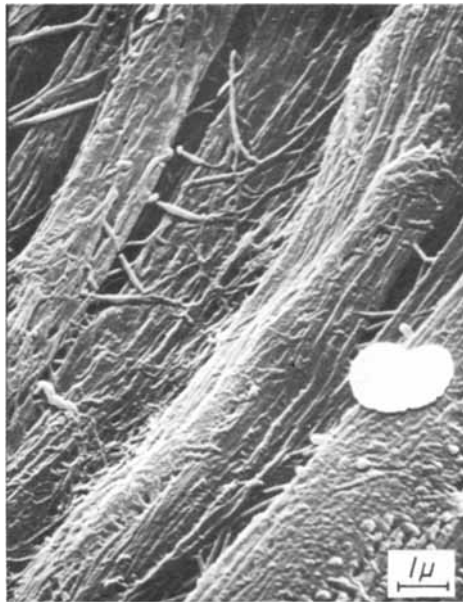
Fig. 5. (a) SEM micrograph of a poly(oxymethylene)/polycaprolactone composite. (b) POM fibrils after removal of PCL.

monomer crystals which become the reinforcing agent by polymerization. However, it is also *necessary* (at least in the case of TOX) in order to obtain monomer crystals of a morphology suitable for polymerization. As we showed in the previous report,<sup>21</sup> the morphology of the parent TOX crystal has a very significant influence on the yield of POM.

However, irrespective of possible practical applications, the *in situ* polymerization of TOX in binary mixtures has several drawbacks: polymerization only seems to be possible in mixtures with a high TOX content, leading to excessive loading of POM in the final composite; relatively low conversions leading to



(a)



(b)

Fig. 6. (a) SEM micrograph of a poly(oxyethylene)/poly(ethylene oxide) composite. (b) POM fibrils after removal of PEO.

problems with low density of the reinforcing fibers and also recycling of the unreacted TOX; POM microfibril morphology not ideally suited to formation of high-performance composites.

A propos of the last point, it was first thought that POM produced by the solid-state polymerization of TOX by irradiation formed extended chain crys-

tals.<sup>13</sup> However, it has since been demonstrated by dark-field electron microscopy that each POM microfibril contains material both in the Z-orientation (parallel to the threefold axis of the parent TOX crystal) and in the W-orientation (twinned at an angle of 76.7°).<sup>14,15</sup> Thus, Patell and Schultz<sup>16</sup> obtained lower moduli than they expected for POM fibers produced from TOX single crystals, based on a model assuming that each microfibril would contain material of only one orientation (implying that approximately 55% of the microfibrils would contain extended chain POM molecules along the fiber axis and would bear most of the load).

We were, in any case, unable to demonstrate the reinforcing action by direct measurement of mechanical properties. This was especially disappointing since one of our hopes at the outset was the exploitation of the phenomenon of epitaxial crystallization of PCL onto POM<sup>6</sup> to create intrinsically bioriented materials: thermal orientation to produce longitudinal orientation of the reinforcing agent and epitaxial crystallization to produce lateral orientation in the matrix polymer. In this way, one could partly overcome the lateral weakness that is a problem in highly anisotropic composites, and we had hoped to observe better performance in this regard for the POM/PCL system than for POM/PEO system (where epitaxy does not occur<sup>7</sup>).

Other topochemical reactions exist which might overcome the problems of the TOX polymerization. For example, some monomers with conjugated triple bonds such as di- or triacetylenes can be polymerized by UV or heat in true topochemical reactions; i.e., monomer molecules do not leave their lattice positions during the reaction, at most they undergo rotations.<sup>17,18</sup> Conversions of 100% can be achieved and fibrillar single crystals of extended chain polymer obtained, as indicated by the lack of twin structure and long period, the negative thermal expansion coefficient, and very high modulus and tensile strength.<sup>19,20</sup>

The technique of *in situ* polymerization applied to systems incorporating monomers of this type (or other which meet the criteria of very high conversion to extended chain polymer in a solid-state reaction) has the potential to generate materials that can be processed in the melt and then converted into high-performance composites after the piece has received its final shape.

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