polymer papers

Direct observation of the micromorphology of polyether polyurethanes using high-voltage electron microscopy

C. Li* and S. L. Cooper†
Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706, USA
(Received 13 October 1988; revised 6 February 1989; accepted 16 February 1989)

The micromorphology of segmented polyether polyurethanes based on poly(tetramethylene oxide) soft segments and semicrystalline methylene diphenylene diisocyanate and butanediol hard segments was examined using high-voltage electron microscopy (HVEM). Specimens for electron microscopy studies were prepared by thin-film casting and by cryoultramicrotomy of solvent cast or compression moulded bulk samples. Short cylinder or lamellar morphology was observed in the polyether polyurethanes depending on the sample's composition. Microdomain spacings measured from electron microscopy micrographs were compared to previously reported long spacings calculated from small-angle x-ray scattering data. Annealing of polyether polyurethane thin films was found to cause rearrangement of the microdomain structure.

(Keywords: high voltage electron microscopy (HVEM); segmented polyether polyurethanes; microdomain structure)

INTRODUCTION

Transmission electron microscopy (TEM) has been carried out on many polyurethane material systems. Both solvent-casting and ultramicrotomy techniques have been employed to prepare thin specimens for TEM observation[1–5]. Ultramicrotomy can provide representative thin sections of the bulk morphology of the elastomer, but the low soft segment glass transition temperature T_g requires cutting to be carried out at very low temperatures. Thin films prepared by solvent-casting techniques, on the other hand, may not represent the bulk morphology of the block copolymer because the process of phase separation depends upon the casting solvent and other conditions. Lack of mass-thickness contrast between the hard and soft segment phases can cause imaging artifacts in the electron microscope as a result of poor focusing[6]. Osmium tetroxide has been used to selectively stain chemically unsaturated moieties in order to provide contrast between the hard and soft segment phases[7]. An additional difficulty with electron microscopy of polyurethanes is that radiation damage and heating can cause the material to degrade. High voltage electron microscopy (HVEM, a TEM at 1.0 MeV accelerating potential as compared to 100 keV in conventional TEM) reduces radiation damage to the polymer specimen due to decreased electron absorption[8]. This provides the opportunity for high resolution electron microscopy of polyurethane materials.

Recently, the micromorphology of segmented polyurethanes containing polybutadiene soft segments has been studied extensively[7,10,11]. Foks and coworkers[9] have found lamellae formation in a polyester soft segment based polyurethane. Spherulitic superstructure and lamellar formation in a segmented polyether–ester material has been examined using TEM[12]. The micromorphology of commercially important polyether polyurethanes, however, has not been clearly characterized due to some of the difficulties cited above.

In this study, the micromorphology of polytetramethylene oxide (PTMO) based polyurethane block copolymers was examined. Thin film samples cast from solvent were viewed using a high voltage transmission electron microscope operated at 1 MeV to reduce electron radiation damage. The PTMO microdomains were selectively stained with ruthenium tetroxide RuO_4 to enhance electron microscopy imaging contrast[12].

EXPERIMENTAL

Segmented polyurethane block copolymers containing 2000 MW PTMO soft segments were synthesized using standard urethane chemistry in dimethylacetamide (DMAc) solvent[13]. The PTMO oligomer was first end capped with methylene diphenylene diisocyanate (MDI) and the butanediol (BD) chain extender was added in the second stage of the synthesis reaction. The hard segment weight fraction and the polystyrene equivalent number average molecular weight (measured by g.p.c.) of each of the polymer samples synthesized is shown in *Table 1*. The sample code describes the soft segment molecular weight and weight percentage of hard segment content in each material. For example, ET-2-39 indicates that the soft segment in the sample is PTMO 2000 and the hard segment content in the sample is 39% by weight.

Table 1 Composition and molecular weights of segmented polyether polyurethane samples

Sample code	MDI/BD/PTMO ratio	Hard segment content (wt%)	Molecular weight M_n
ET-2-23	2/1/1	22.9	52 750
ET-2-39	4/3/1	39.1	63 780
ET-2-50	6/5/1	49.8	39 800

* Present Address: Scientific Research Staff, Ford Motor Company, Dearborn, MI 48121, USA
† To whom correspondence should be addressed

0032-3861/90/010003-05$03.00
© 1990 Butterworth & Co. (Publishers) Ltd.

The hard segment phase volume fraction of each material was estimated by assuming complete phase separation with $0.98\,g\,cm^{-3}$ soft segment phase mass density and $1.30\,g\,cm^{-3}$ hard segment phase mass density.

Polyether polyurethane films of 0.5 to 1.0 mm thickness were cast slowly from DMAc solutions at room temperature under a dry nitrogen environment followed by vacuum drying for one week. These thick films were used as bulk samples for ultramicrotomy. Thin film specimens for HVEM were prepared by slowly casting a 0.2% polyurethane DMAc solution onto a NaCl single crystal plate. The NaCl substrate was removed by dissolving it in distilled water, such that a thin polymer film remained on the water surface. Profilometry measurements indicated that the films varied from 20 to 80 nm thick. The thin films were transferred onto 500 or 1000 mesh, gold TEM grids. The polyether polyurethane thin film specimens were placed in a vacuum chamber at room temperature for one week. To enhance the contrast, the polyurethane specimens were vapour stained with RuO_4 (from a 0.1% solution) for 10 min.

Compression moulded samples were formed in a 2.54 cm i.d. cylindrical mould in a Buehler mount press at a temperature 25°C above the hard segment melting temperature determined by d.s.c., and at a pressure of 30 MPa for 5 min. The moulds were then quenched to room temperature with ice-cooled clamps. The samples were removed from the moulds and stored at room temperature for several days prior to ultramicrotomy or other testing.

Thin sections of solvent-cast thick films (about 0.5 mm) and compression moulded bulk samples were obtained using a Reichert Ultracut E device equipped with a FC-4 Cryostage. Thin sections were cut at −90°C with either a freshly prepared glass knife or a diamond knife. Optical reflection indicated that these sections were about 40 nm thick. Thin sections were then transferred onto 1000 mesh, gold grids and stained using the same procedures as for the solvent-cast thin films.

Thin films and sections of polyether polyurethanes were viewed in the University of Wisconsin-Madison, NIH Bioresource's AEI EM7 Mk11 high voltage electron microscope[8]. All observations were at 1.0 MeV accelerating potential. The HVEM bright field images were recorded on Kodak SO-163 photographic plates through a 30 μm objective aperture with magnifications ranging from 30 000 to 125 000. To minimize the electron dose in the HEVM a low light level (silicone intensified target) video camera with a digital image enhancement/memory system, was used for all sample viewing except photographic exposure[8]. The range of electron dosage was from 1800 to 45 000 electrons nm^{-2} (ref. 8). No visible alterations in polymer structure were observed during the HVEM focusing and viewing process. Prolonged exposure of the polyurethane thin film under high beam intensity, however, resulted in specimen mass loss. Most micrographs were recorded at critical focus or very slight underfocus. The memory and differential function of the digital image processor made possible almost perfect image alignment of the same area viewed at different tilt angles[8].

RESULTS AND DISCUSSION

Figure 1 shows an HVEM micrograph of a RuO_4 stained ET-2-39 thin film cast from DMAc solution. The staining technique has been reported by Chen *et al.*[12] in a study of PTMO-based polyether–ester block copolymers. A preliminary experiment revealed that RuO_4 vapour reacts preferentially with the PTMO soft segments when the staining time remains short (less than about 20 min). The darker regions are presumably the RuO_4-stained soft segment rich microdomains while the brighter spots correspond to the unstained MDI–BD hard segment phase. The observed morphology of ET-2-39 can be described as dispersed, disordered hard segment microdomains embedded in a soft segment matrix. Alternating dark and bright short stripes are also observable in some regions. These short stripes can be the projection image of hard segment cylinders. The spacing of the phase separated structure, measured as the sum of the widths of the dark and the bright stripes, is about 11.5 nm. The size distribution of the microdomain spacings seems to be narrow. Although the MDI–BD hard segment phase is semicrystalline, no spherulitic superstructure was observed in any of the polyether polyurethane samples.

Because the hard segment content in ET-2-39 is 39 wt%, a rod-like morphology would be expected by considering the hard segment volume fraction in this sample (0.33) if the phase separation is complete. The observed morphology of ET-2-39 by HVEM imaging, however, is neither lamellar nor rod-like, but consists of short cylinders. In fact, the morphology of ET-2-39 appears somewhat similar to that of completely phase separated PBD polyurethanes with much lower hard segment content (see sample PBD-3-31 in ref. 11). The intersegmental hydrogen bonds between the urethane hard segments and the ether oxygen in the PTMO soft segments promote mixing of the hard segments into the soft-segment-rich phase. Such incomplete phase separation in polyether polyurethanes has been extensively studied and is well documented in literature[13]. The volume fraction of segregated hard segments in a partially phase mixed material is lower than that of a completely phase-separated sample. Phase mixing in ET-2-39 also reduces the imaging contrast as well as boundary sharpness of the observed microdomains from the HVEM micrograph.

Small-angle X-ray scattering (SAXS) results of a DMAc solution cast sample of ET-2-39 obtained by others showed a long spacing of 13.3 nm and a Porod inhomogeneity length of 3.8 nm[13,14]. SAXS invariant

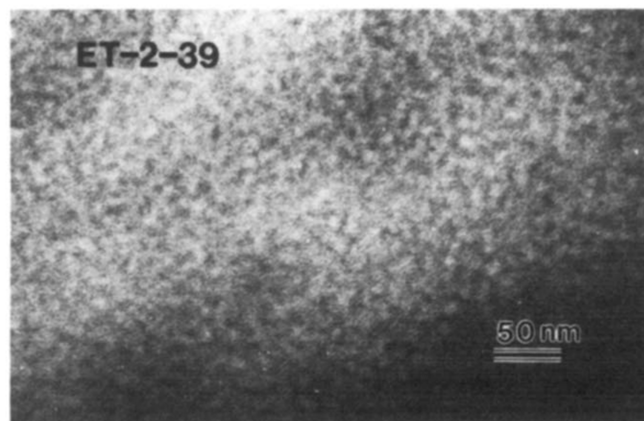

Figure 1 An HVEM micrograph of an RuO_4 stained ET-2-39 film cast from solution

data show that about 30% of the hard segments are phase mixed with the soft segments. Phase mixing occurs either in the soft segment rich phase or at the microdomain interface. The thickness of the microdomain interface, measured by SAXS, is about 0.7 nm[13,14]. D.s.c. experiments on this sample showed that the PTMO soft segments are crystallizable at low temperature. Soft segment crystallinity indicates that a portion of the soft segment rich phase must be relatively pure or crystallization would not occur. Hard segment crystallinity was also detectable by d.s.c.. Based on these physical property characterization data, it is then suggested that phase mixing in ET-2-39 occurs mainly in some regions of the soft-segment-rich phase. If the hard segments dissolved in the soft segment matrix or mixed at the interface are not considered as a part of the hard segment phase, the hard segment phase volume fraction would be about 0.23 (hard segment volume fraction assuming ideal phase separation × the percentage of hard segments segregated in the hard segment phase, 70%). This estimation is consistent with the HVEM observation of the sample morphology.

Figure 2 shows an HVEM micrograph of a thin section of ET-2-26 stained with RuO_4. The HVEM image, recorded at critical focus, does not reveal any structural information which can be interpreted as microdomains. It is also noticeable that the image contrast is very low in this micrograph. ET-2-26 has only 26 wt% hard segments which due partly to phase mixing, may not be sufficient to provide a large enough fraction of hard segment microdomains to be observed by HVEM. When the hard segment microdomains are very small compared to the sample thickness, it is impossible to resolve the morphology due to smearing effects[6]. We have also examined two polyether polyurethane samples containing polyethylene oxide and polypropylene oxide with about 40% hard segments using the RuO_4 staining technique. No interpretable microstructure was observed from the HVEM micrographs of these two samples because of the presence of a substantial degree of phase mixing.

An HVEM micrograph of a solvent-cast, RuO_4-stained, thin film of ET-2-50 is shown in *Figure 3*. This micrograph shows short, alternating dark and bright stripes which can be interpreted as a lamellar morphology corresponding to the soft and hard segment microdomains, respectively. The phase separation in the thin film of ET-2-50 seems to be rather complete as indicated by the high contrast and well defined microstructure. The lamellar morphology was further confirmed by observing the change of the HVEM image while tilting the specimen. The width of the repeating structure is about 13 nm. The lamellar length varies from 40 to 130 nm with an average value of 55 nm measured from selected areas in the micrograph. It is interesting to observe that the lamellar structure in ET-2-50 is much more tortuous and disordered than that in the polybutadiene polyurethanes. *Figure 4* shows an HVEM micrograph of a RuO_4-stained thin section of an ET-2-50 bulk sample prepared by DMAc solvent casting. The thin section was obtained by cryo-ultramicrotomy. Comparing *Figure 4* to *Figure 3*, the morphology observed in the thin section of solvent cast bulk sample is not as well defined as in that of the

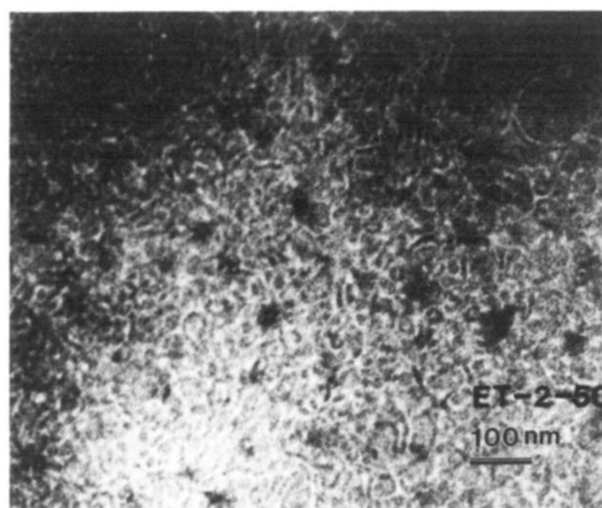

Figure 3 An HVEM micrograph of a DMAc solvent cast thin film of ET-2-50. The film was stained with RuO_4 to enhance contrast and some RuO_4 condensation spots also appear on the sample

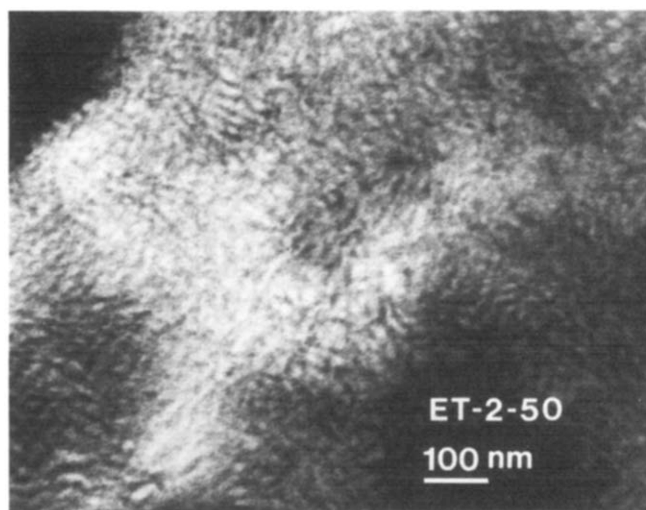

Figure 4 An HVEM micrograph of an RuO_4 stained, microtomed thin section of a bulk sample of ET-2-50 prepared by DMAc solvent casting

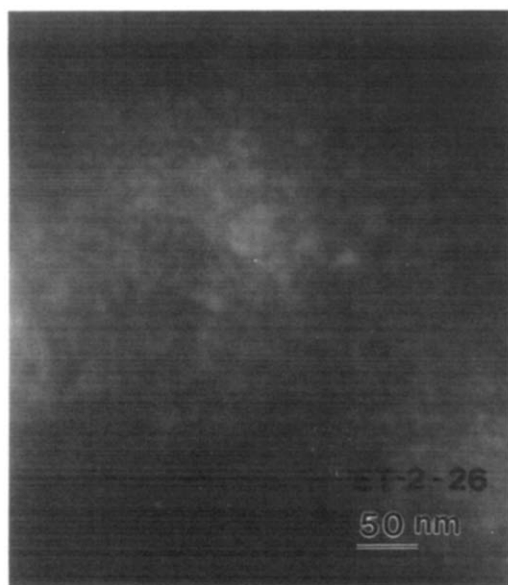

Figure 2 An HVEM micrograph of an RuO_4 stained ET-2-26 film cast from solution

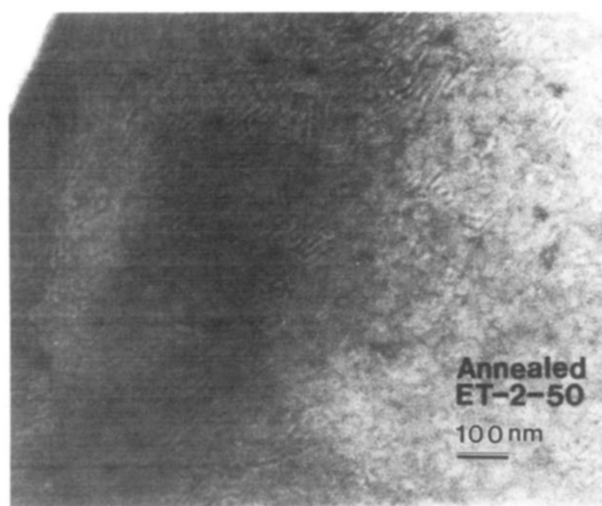

Figure 5 An HVEM micrograph of an RuO_4 stained thin film of solvent cast ET-2-50 annealed at 125°C

thin film. The interlamellar spacing in the sectioned ET-2-50 bulk sample is the same as that in the thin film (about 13 nm). Miller and Cooper[13] have shown that in a solvent cast bulk sample of ET-2-50, the long spacing of electron density variation measured by SAXS is 13.4 nm and about 30% of the hard segments resides outside of the hard-segment phase. Our results are consistent with Miller and Cooper's microdomain spacing calculations.

Figure 5 shows an HVEM micrograph of a solvent cast thin film of polyether polyurethane ET-2-50 annealed at 125°C under nitrogen for 24 h. The thickness of the films is about 20 to 40 nm as measured by profilometry. During annealing, the polyether polyurethane ultrathin film was free-standing on a 1000 mesh, gold TEM grid. No supporting carbon film was used. No change in the film was observed by optical microscopy after the annealing process. The lamellae in ET-2-50 are longer and more ordered after the annealing process as can be seen by comparing *Figure 5* to *Figure 3*. The spacing of the lamellae, however, did not show a noticeable change. The lamellar lengthening process is attributed to further improvement in the phase separation, especially in purifying the hard segment phase by improved hard segment packing. The microphase separation may still be incomplete in the solvent cast thin film because DMAc is a good solvent for both the soft and the hard segments[13]. At the annealing temperature (125°C), the soft segments, the amorphous hard segments, and the unsegregated hard segments have high enough mobility to rearrange themselves into a more ordered structure. Because the annealing temperature (125°C) was much lower than the hard-segment melting temperature (about 200°C), the physical crosslinks of crystalline hard segments can still provide dimensional stability to the thin film. It appears this high level of microdomain rearrangement induced by annealing may be enhanced in the unsupported thin film where the segmental mobility is enhanced by the presence of free surfaces on both sides.

Annealing of a DMAc solvent cast bulk sample of ET-2-50 at 125°C for 24 h did not induce any dramatic change in the sample morphology. A cryo-microtomed thin section of the annealed bulk sample of ET-2-50 was examined by using HVEM and it was found to possess a similar microstructure to the section from the unannealed sample (*Figure 4*). The segmental mobility in a bulk sample is much more restricted by the viscosity of the system even at elevated temperatures. It has been reported previously that annealing of a set of polyether polyurethane bulk samples at elevated temperature did not provide measurable changes in long spacings calculated from their SAXS profiles or in their mechanical properties[15]. The peak scattering intensity was shown to increase with annealing as a result of improved phase separation which increased the electron density difference. The annealing temperature dependent endotherms found in d.s.c. experiments on polyether polyurethanes are probably due to changes within the hard-segment microdomain as proposed by Van Bogart *et al.*[16]. Gibson and Cooper[15] also suggested that the shifting of the high temperature d.s.c. endotherms is related to intradomain ordering in the semicrystalline hard-segment phase as opposed to microdomain rearrangement. The effect of annealing on the morphology of polyether polyurethane samples at higher temperatures is to be investigated in future studies.

Miller and Cooper have extensively studied the correlation between the compression moulding parameters (temperature, pressure, moulding time, and cooling rate) and morphology of the polyether polyurethane ET-2-50 by d.s.c. and SAXS[13,14]. The moulding temperature was found to have a strong influence on morphology and thermal properties because phase mixing, crystallization, and decomposition are all sensitive to temperature. The thermal properties and SAXS results were found to be relatively insensitive to other moulding parameters. They also observed that a DMAc solvent cast sample has a different SAXS profile and d.s.c. curve compared to the moulded samples. They suggested that the morphology in the solvent cast sample is different from that in the moulded specimens. It was concluded that careful control of sample preparation conditions, especially moulding temperature, is necessary for obtaining accurate representation of morphology from SAXS results.

A compression moulded sample of ET-2-50, designated as ET-2-50M, was also examined in this study using HVEM. The sample was moulded at 170°C for 5 min and then quenched with ice-cooled clamps[13,14]. After being stored at room temperature for a week, the moulded sample was cryo-ultramicrotomed to obtain a thin section for HVEM viewing of its morphology. RuO_4 staining was used to enhance contrast. *Figure 6* shows the HVEM micrograph of this sample. The morphology of compression moulded ET-2-50 showed a substantial difference from that observed in the solvent cast thin film (*Figure 3*) and the solvent cast bulk sample (*Figure 4*). Short lamellae or cylinders with low image contrast are characteristic of the microstructure of thin sections of moulded ET-2-50M while solvent cast thin films showed well defined but tortuous lamellae. The difference in the observed morphology can be attributed to a higher level of phase mixing in the compression moulded sample of ET-2-50M compared to the solvent cast thin film. The volume fraction of segregated hard segments is lower in ET-2-50M due to mixing of hard segments in the soft-segment rich phase. Therefore, the material's morphology is similar to those with lower hard-segment content.

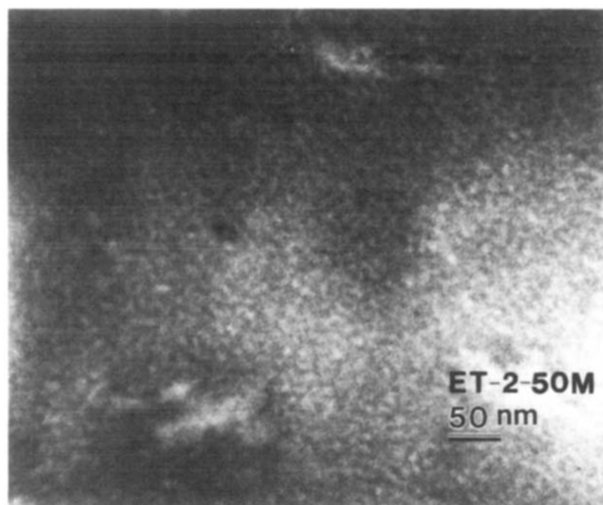

Figure 6 An HVEM micrograph of an RuO_4 stained thin section of compression moulded ET-2-50

SUMMARY

The micromorphology of segmented polyurethanes based on poly(tetramethylene oxide) soft segments can be studied by high-voltage electron microscopy under suitable staining conditions. Microdomain spacings measured from HVEM micrographs agreed with the long spacing calculated from previous SAXS results. Phase mixing in the polyether polyurethane block copolymers reduces image contrast in the HVEM micrographs. No interpretable HVEM image was recorded for ET-2-26 which possesses a low hard segment content and a considerable degree of phase mixing. A short cylinder hard segment microdomain morphology was observed from ET-2-39 and a lamellar microstructure was found to be characteristic of ET-2-50 solvent cast thin films. HVEM micrographs of thin sections microtomed from a solvent cast bulk sample of ET-2-50 also revealed lamellar microdomains of segregated hard segment phase in that material. Upon annealing ET-2-50 at 125°C the lamellae in the block copolymer thin film became longer and more ordered. Lamellae rearrangement in the thin film was attributed to the increased segmental mobility in the ultrathin (20 to 40 nm) films with free surfaces on both sides. Annealing a bulk sample of ET-2-50, however, failed to produce any substantial change in the morphology. Thin sections of compression moulded ET-2-50 were also examined by HVEM to detect possible differences between the morphology of the moulded and the DMAc solvent-cast samples. The thin sections of the moulded sample ET-2-50M revealed a disordered lamellar morphology which suggests a higher level of incomplete phase separation due to the fast cooling rate in the moulding process.

ACKNOWLEDGEMENTS

We gratefully acknowledge excellent technical support from, and helpful discussions with, Dr Grayson L. Scott, Dr Peter H. Cooke and Mr Alan R. Kutchera of the NIH Integrated Microscopy Resource at the University of Wisconsin-Madison. This study was funded in part by the National Science Foundation (DMR-8603839) and by the Office of Naval Research (N00014-83-K0423).

REFERENCES

1 Fridman, I. D. and Thomas, E. L. *Polymer* 1980, **21**, 388
2 Chang, Y. J. P. and Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 455
3 Briber, R. M. and Thomas, E. L. *J. Macromol. Sci.-Phys.* 1983, **B22**, 509
4 Koutsky, J. A., Hein, N. V. and Cooper, S. L. *J. Polym. Sci. Polym. Lett.* 1970, **8**, 353
5 Roche, E. J. and Thomas, E. L. *Polymer* 1981, **22**, 333
6 Handein, D. L., MacKnight, W. J. and Thomas, E. L. *Macromolecules* 1980, **14**, 795
7 Chen-Tsai, C. H. Y., Thomas, E. L., MacKnight, W. J. and Schneider, N. S. *Polymer* 1986, **27**, 659
8 Pawley, J. B. *Ultramicroscopy* 1984, **13**, 387
9 Foks, J. and Michler, G. *J. Appl. Polym. Sci.* 1986, **31**, 1281
10 Serrano, M., Ottino, J. M., Thomas, E. L. and MacKnight, W. J. *Polymer* 1987, **28**, 1667
11 Li, C., Goodman, S. L., Albrecht, R. M. and Cooper, S. L. *Macromolecules* 1988, **21**, 2367
12 Chen, S., Cao, T. and Jin, Y. *Polymer Comm.* 1987, **28**, 314
13 Miller, J. A. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 1065
14 Miller, J. A. *PhD Thesis* Chemical Engineering Department, University of Wisconsin, Madison, WI, 1985
15 Gibson, P. E. and Cooper, S. L. *Bull. Am. Phys. Soc.* 1986, **31**, 612
16 Van Bogart, J. W. C., Bluemke, D. A. and Cooper, S. L. *Polymer* 1981, **22**, 1428