Morphology of crystalline polyurethane hard segment domains and spherulites

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(Received 4 September 1979)

Chemical staining of the unsaturated hard segment portion of a segmented polyurethane based on poly(propylene oxide)/4,4′-diphenyl methane-diisocyanate/butenediol (PPO/MDI/BEDO) permitted observation of the hard segment domains by electron microscopy. The hard segment phase forms (para)-crystalline domains which are fibrillar in nature. The fibrils are arranged radially into spherulite structures. The concentration of the hard segment is greatest at the centre of the largest spherulites suggesting the preferential agglomeration of molecules with the longest hard segment sequences at the beginning of the phase separation process from solution.

INTRODUCTION

Since the initial suggestion by Cooper and Tobolsky[1] in 1966 that polyurethane systems were microphase separated, a number of workers have attempted to visualize directly the domain structure of urethane polymers with transmission electron microscopy. The substantial work on polystyrene/polybutadiene and polystyrene/polyisoprene blends and diblock and triblock copolymer systems has lead to a general understanding of the nature of phase separation in regular amorphous block copolymer systems[2,3]. However, the additional complexities of multiblocks with variable block length as well as possible hard and/or soft segment crystallinity makes the morphological characterization of polyurethane systems a challenge. The results thus far on polyurethanes have been ambiguous. The hard segment domains were first observed as equiaxed grains of 30–500 Å diameter in solvent etched and iodine stained polyether or polyester/MDI/butanediol-based urethanes[4]. A fibrillar structure has been observed in another polyether/MDI/butanediol system. The ordered hard segment phase is thought to be composed of domains of thickness (dimension parallel to chain axis) equal to the hard segment length[5]. Harrell[6] showed that hard segment crystallization could occur for blocks as short as one unit for a piperazine-based urethane. Harrell also reported that increasing the hard segment block length did not appreciably affect the degree of order with the hard segment domains though the melting point of the hard segment rich phase was raised.

Hard segment domains can also arrange into spherulite structures[7,8]. Models for hard rich spherulite structure include both the possibility of radial as well as tangential oriented hard segment domains[7]. Wilkes and coworkers[7,9] characterized Harrell's polymer and found both spherulitic superstructure and an indistinct granular domain structure. Domain size apparently increased with increase in hard segment content as evidenced by sharpening of the WAXS reflections[9].

A significant problem in studies of urethane morphology is obtaining sufficient contrast in electron micrographs to visualize the system. Since even highly phase separated systems will possess regions of similar density, mass thickness contrast will be intrinsically low. The use of diffraction contrast depends on having both reasonably crystalline and radiation resistant structures. Phase contrast imaging is possible but the complex problem of image formation due to phase differences introduced by the microscope system as well as the object makes interpretation of the images difficult, particularly for domain structure at the 100 Å scale and below[10]. Another possible source of contrast is selective electron-beam etching of one of the phases[11]. If present and ignored, this effect could cause problems with proper image interpretation; however, by conducting suitable screening tests on the pure segments (e.g. poly(propylene oxide)/MDI copolymer and MDI/BEDO copolymer) one can determine if different etching does occur during the *TEM* observations. We have previously shown that such etching, if understood, can serve as a convenient means of producing contrast between the phases[11].

The technique of heavy atom staining to increase mass thickness (amplitude) contrast depends on finding a selective stain. Previous investigations employing phosphotungstic acid (PTA) are contradictory with PTA being claimed as both a stain for the polyether soft segment in a polyether–polyester elastomer system[12] and as a stain for the hydrogen bond forming hard segment in a polyester/MDI/ethylene glycol system[2]. Iodine staining has been used[4] but is complicated by the unknown solubility, diffusivity and chemical specificity of iodine in the different phases. The well developed technique of OsO_4 staining by Os addition to double bonds[13,14] seems the most reliable contrast enhancement technique and we have utilized a chain extender containing a double bond to enable selective staining of the hard segment in the present study.

EXPERIMENTAL

The polyurethane system investigated consists of atactic poly(propylene oxide) polyol endcapped with ethylene oxide (PPO, $\bar{M}_n = 2000$) and 4,4′-diphenyl methane diisocyanate (MDI) chain extended with a 1,4-dihydroxy butene-2 (BEDO). The mole ratio was approximately 1/6/5 PPO/MDI/BEDO corresponding to 45% by weight of

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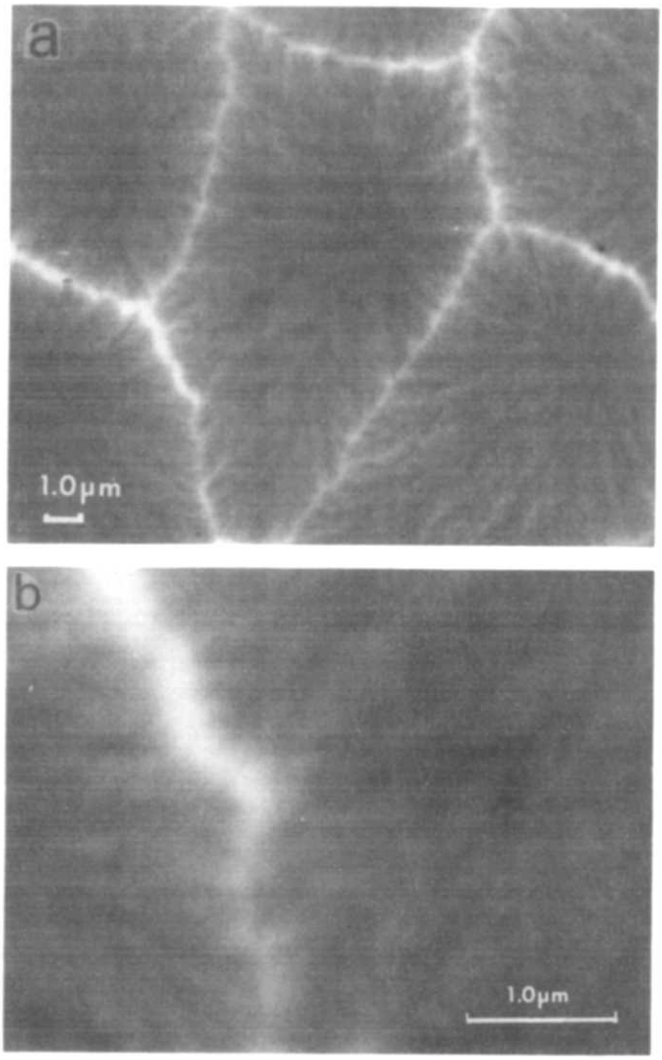

Figure 1 Unstained PPO/MDI/BEDO film (45% hard segment) as it appears after the casting procedure. (a) 5000x, (b) 25 500 x (an anlargement of the lower left portion of the centre spherulite

MDI/BEDO hard segment. The sample was made by a one step batch process with curing at 100°C for 16 h. Details of the polyurethane polymerization are described elsewhere[15].

Thin films were made by solution casting onto glass slides from a 0.5% by weight dimethyl formamide solution followed by solvent evaporation and drying for 3 h in a vacuum oven at 50°C. The films were then exposed to the vapours of a 2% aqueous solution of OsO_4 at room temperature for increments of 20 min. The films were floated off on distilled water and mounted on 400 mesh copper grids, dried at room temperature overnight and examined at 100 keV in a JEOL 100-CX Temscan electron microscope. Electron etching studies of pure copolymers, e.g. PPO/MDI and MDI/BEDO showed significant etching only of the pure soft segment. OsO_4 stained urethane samples were, however, very stable and did not appear to suffer significant mass loss.

RESULTS

By choosing an atactic material for the soft segment, one is limiting the appearance of any crystallinity to the hard segment phase. By using an unsaturated chain extender, the hard segment phase can also be provided with additional electron density.

Figure 1a is a bright field micrograph of an unstained film of PPO/MDI/BEDO showing a volume filling spherulitic superstructure outlined by the thin (bright) spherulite boundaries. At higher magnification (*Figure 1b*) the coarse radiating structure shows some intensity variations most likely due to small thickness variations and local compositional changes but does not show any distinct features on the 100 Å scale.

After an OsO_4 exposure of 60 min (see *Figure 2a*), the film is less electron transparent and the centres of the largest spherulites have darkened considerably. The dark regions extend several microns along the radial direction before diminishing gradually. The radial texture of the spherulites has become much more well defined. An enlargement (see *Figure 2b*) shows the presence of dark fibrils arranged in bundles, branching out in 'palm-leaf' configurations oriented along the radial direction of the spherulites. The small dark particles of about 500 Å average diameter appearing randomly in the films have been shown by X-ray microanalysis in combination with secondary electron imaging to be osmium particles lying on the film surface. The branched fibrils are of the order of 0.5 µm in length and the smallest fibril cross-section is about 60 Å with

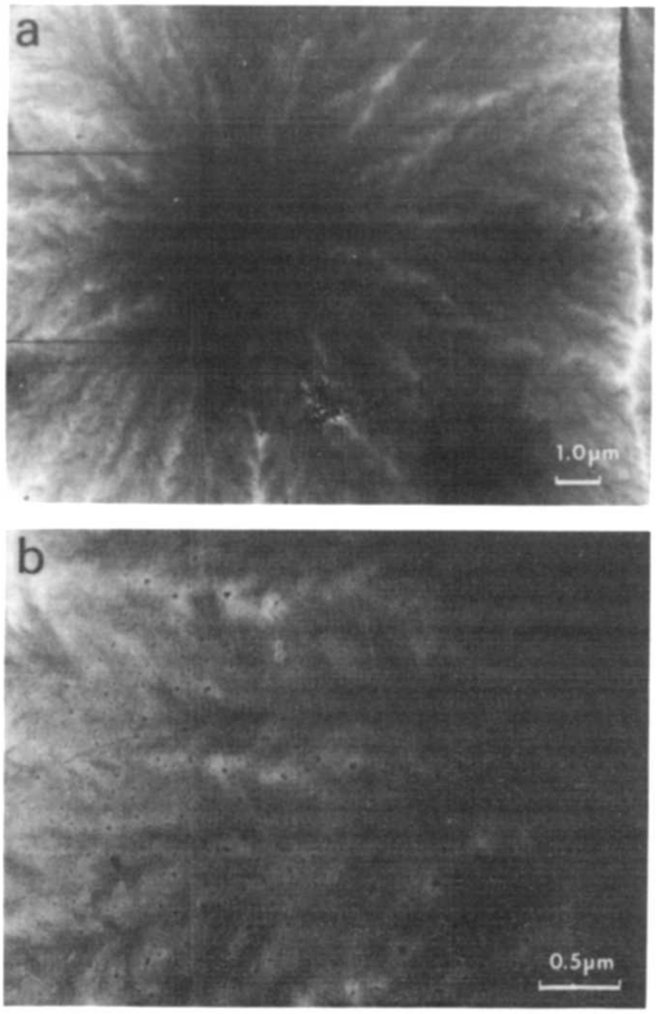

Figure 2 PPO/MDI/BEDO solvent cast film after 60 min of OsO_4 vapour exposure: (a) 7500x, (b) radial fine structure discernable from left central portion of spherulite (25 500x)

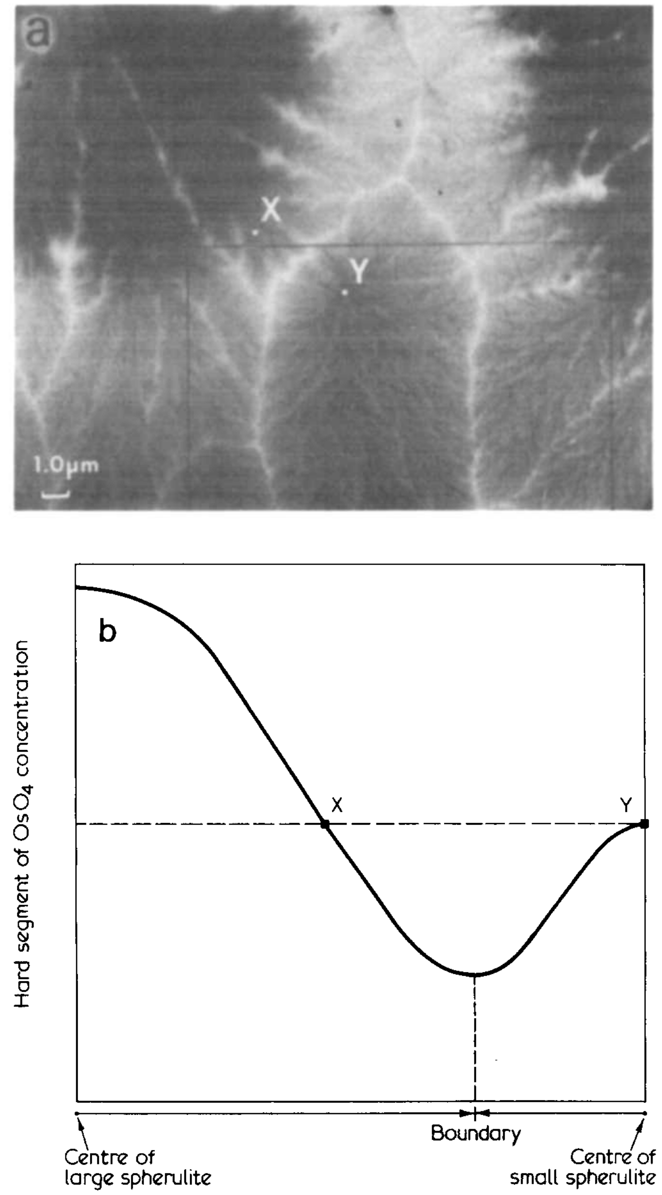

Figure 3 (a) PPO/MDI/BEDO after 80 min of OsO_4 vapour exposure. Note difference in darkening of centres between large and small spherulites. (b) Schematic diagram showing points of equal hard segment concentration in large and small spherulites (points X and Y)

aggregates of fibrils forming bundles of up to 0.5 μm in diameter. The radiating branching fibrils surround regions of lower electron density. The brightest regions are between branches where the electron density is lowest.

It is important to point out that not all of the spherulites display the same extreme darkening at their centre (see *Figure 3a*). There is a difference on the basis of spherulite size, i.e. larger spherulites are always much more heavily stained than smaller spherulites in the same sample. Also the size of the extreme dark centre region increases with increasing staining time (see *Figure 4*).

D.s.c. of the solution cast film indicates a T_m of the hard segment phase of approximately 195°C. The heat of fusion value (3.5 cal/g of hard segment) if compared to that of the MDI/BDO hard segment[16] suggests a low degree of hard segment ordering in the (para)-crystalline fibrils. The present degree of ordering of the butenediol-based hard segment phase is very similar to that of the butanediol-based hard segment phase in films cast from DMF under comparable conditions[8].

DISCUSSION

Film casting from solution is a separation process between a solvent and its solute, carried out at approximately constant temperature. The course of solidification of the film can be best appreciated by referring to *Figure 5*. The sample starts at point A in the single liquid solution region of known composition, and as the solvent slowly evaporates in an open system we approximately follow an isothermal path enriching the system with solute. The evaporation must take place very slowly in order to be close to equilibrium in the condensed phase(s) at any point along the path. At point B we enter the biphasic region where a liquid phase coexists in equilibrium with the first formed solid phase. This solid

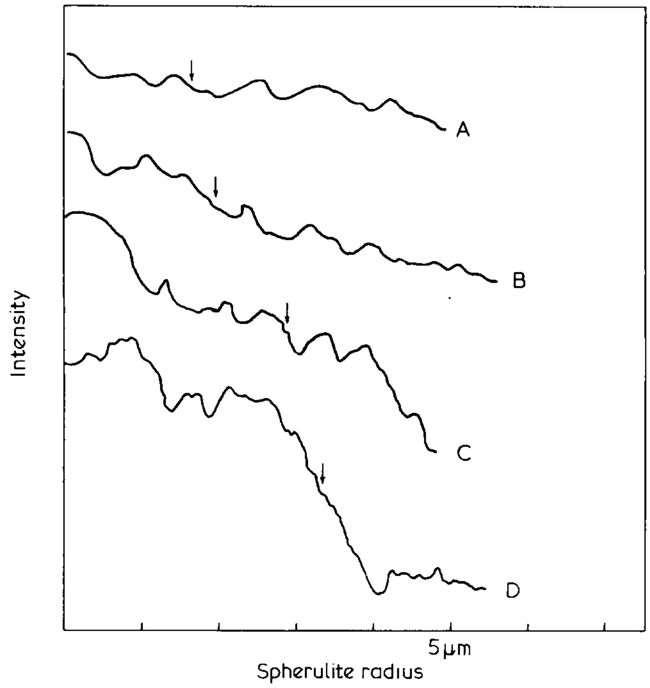

Figure 4 Microdensitometer scans across approximately 10 μm diameter spherulites showing the radial position for 50% intensity decrease as a function of OsO_4 vapour exposure time. Intensities are not normalized

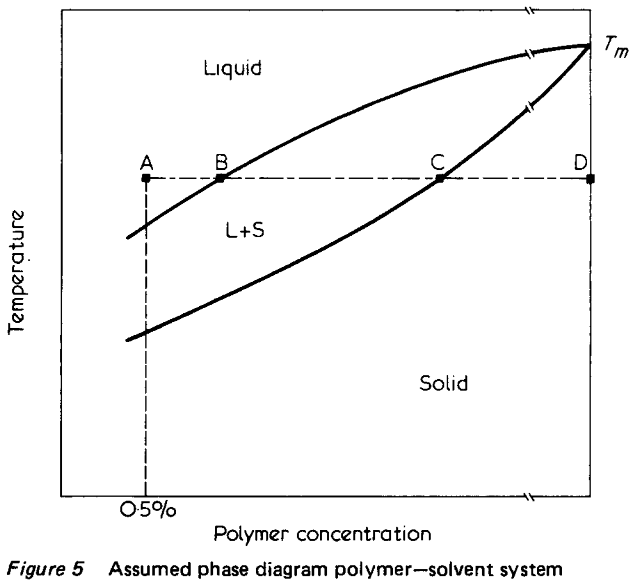

Figure 5 Assumed phase diagram polymer–solvent system

phase consists of those portions of the polyurethane molecules having the highest potential for hydrogen bond formation (i.e. the longer hard segment sequences). The relative amount of each phase as one moves towards point C can of course be calculated by the lever rule. As one transits from B to C, more solute molecules come out of solution on the basis of their ability to crystallize, namely chains possessing predominantly long hard segment sequences, followed by chains with on the average shorter hard segment sequences. From point C and on, the polymer is essentially in a swollen solid phase. With further drying one arrives at the solid polymer film, represented by point D.

This rationale suggests that the centres of the largest spherulites are composed primarily of molecules with long hard segment sequences inasmuch as nucleation is expected to initiate with the most easily precipitated species. The polymer molecules with the fewest and shortest hard segment sequences remain in solution longest and eventually form the peripheral regions of the spherulites. By the same reasoning, the population of stainable double bonds will be highest at the centre of the largest spherulite and decrease with spherulite radius. Since at any time during solvent evaporation the remaining liquid phase can be assumed homogeneous, then the centres of the later nucleating spherulites should have approximately the same hard segment content as the region of an already growing spherulite (e.g. compare points *X* and *Y* in *Figures 3a* and *3b*). At longer staining times the darkening of the central position of the spherulites becomes progressively larger and increasingly darker. The degree of darkening seems far beyond what would be expected by addition only to double bonds and must involve some unknown mechanism for additional osmium uptake in the previously stained regions.

Careful observation of the micrographs yields a detailed morphological picture of this polyurethane that is in good agreement with Schneider's model for crystalline spherulite forming hard segment urethanes[5]. Overall there are three general levels of intensity discernable: (i) the dark branched structures, (ii) uniform areas of an intermediate intensity with no distinct features and (iii) small very light areas. These three structures seem to correspond well to the previously proposed (i) crystalline hard segment fibril domains, (ii) unorganized mixed hard (presumably short sequences) and soft segment phase and (iii) a soft segment rich phase with low hard segment content. Such correspondence is not unexpected since Schneider's polyurethane is essentially the same but with butanediol as chain extender.

The smallest fibrils observed previously were somewhat thicker (200–300 Å diameter) and formed an open network containing material of lower electron density; but, while part of a spherulitic superstructure, the fibrils did not show a pronounced radial orientation[5]. This difference is mainly due to the different solidification conditions used in each study as well as possibly the nature of the different chain extenders employed. Furthermore, solution casting promotes the partitioning of the polyurethane molecules on the basis of hard segment sequence length, resulting in a radial dependence of the hard segment concentration in the spherulites. The well known increase in the melting point[6] and the sharpening of X-ray reflections[9] with volume fraction of hard segment is accepted to imply an increase of domain size with increased hard segment content. Thus a distribution of domain sizes follows quite naturally for a given sample possessing both molecular weight and sequence length distributions.

A further feature of the present work indicates a definite branching tendency of the fibril structures. This can be understood by noting that as hard segment solidification–crystallization proceeds, the incorporation of shorter hard segment units into the growing fibril requires accommodation of the intervening connecting soft segment units which regults in an intrinsic need for fibril branching (see *Figure 6b*). The minimum observable fibril diameter of about 60 Å corresponds to about 3 consecutive hard segment units. This suggests a minimum crystallizable MDI/BEDO hard segment block size of about 3 units. An earlier study on a polyester/MDI/BDO system suggested a critical block size of 6 units based on d.s.c. studies of solution cast films. Other workers[17] have postulated a minimum hard segment block size for phase separation. Fibrils appear to have diameters up to a large fraction of a micron. Such structures are very likely agglomerates of smaller fibrils although the techniques employed cannot distinguish substructure within these bundles. The fibril volume fraction in *Figure 6a* measured using the grid point fraction method is approximately 14%. This supports considerable phase mixing of shorter hard segment sequences in the surrounding matrix which is in agreement with the uniform Os staining of the matrix.

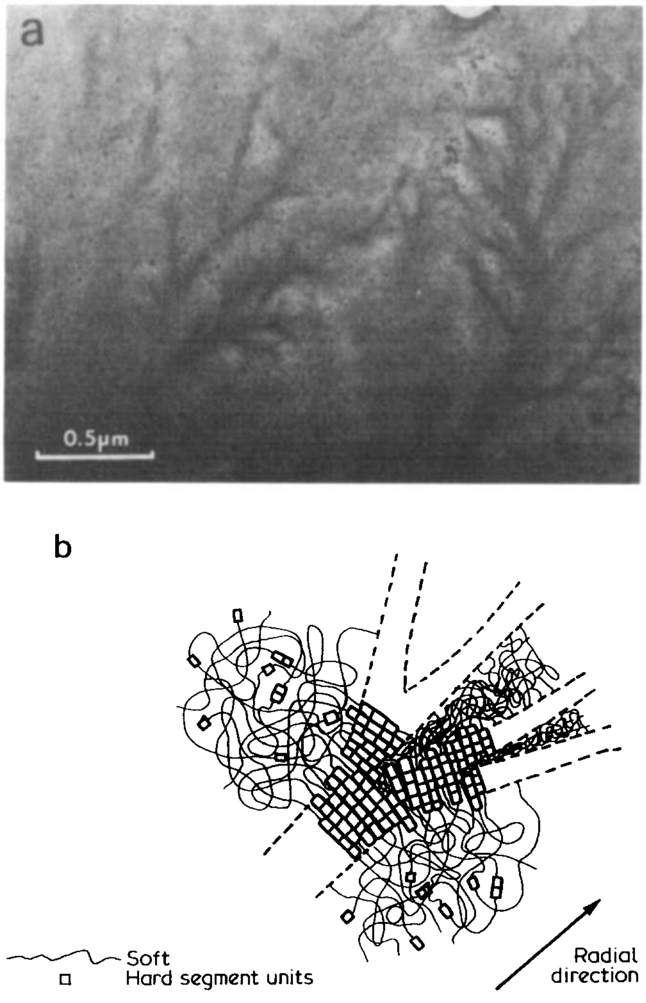

Figure 6 (a) High magnification of 80 min OsO_4 stained film showing fine fibrillar texture. Volume fraction of fibrils approximately 14%. (b) Proposed structure of hard segment domains. Branching occurs to allow accomodation of soft segment units. Approximate 10:1 ratio of soft segment to hard segment length is drawn

CONCLUSION

The preferential heavy atom tagging of the hard segment in a PPO/MDI/BEDO polyurethane has permitted visualization of the phase separated microstructure. Solvent cast films consist of volume filling spherulites with fibrillar hard segment domains. The matrix surrounding the fibrils is further comprised of a mixed phase containing significant but unorganized hard segment and a second predominantly soft segment phase. Because the solution casting process is rather slow the spherulites develop a radial variation of hard segment content. Slow spherulite growth enables the hard segment sequences to precipitate sequentially on the basis of their length which leads to fibril branching during growth in order to accommodate the connecting soft segment units.

ACKNOWLEDGEMENTS

We are grateful to Dr. R. J. Zdrahala from the Chemicals and Plastics Division of Union Carbide Corporation for the synthesis of the special polyurethane used in this study, and to Robin Rufner from the Department of Food Science of the University of Massachusetts for valuable suggestions and discussion. A grant in aid from Union Carbide Corporation for support of IDF is gratefully acknowledged.

REFERENCES

1 Cooper, S. L. and Tobolsky, A. V. *J. Appl. Polym. Sci.* 1966, **10**, 1837
2 Aggarwal, S. L. *Polymer* 1976, **17**, 938
3 Beecher, J. F., Marker, L., Bradford, R. D. and Aggarwal, S. L. *J. Polym. Sci.* (C) 1969, **26**, 117
4 Koutsky, J. S., Hein, N. V. and Cooper, S. L. *J. Polym. Sci. (B)* 1970, **8**, 353
5 Schneider, N. S., Desper, C. R., Illinger, J. L., King, A. O. and Barr, D. *J. Macromol. Sci. (B)* 1975, **11**, 527
6 Harrell, L. L. Jr. *Macromolecules* 1969, **2**, 607
7 Samuels, S. L. and Wilkes, G. L. *Polymer Lett.* 1971, **9**, 761
8 Chang, A. L. and Thomas, E. L. *Adv. Ser. Chem.* 1979, **176**, 31
9 Samuels, S. L. and Wilkes, G. L. *J. Polym. Sci. Symp. (D)* 1973, **43**, 149
10 Thomas, E. L. and Roche, E. J. *Polymer* 1979, **20**, 1413
11 Thomas, E. L. and Talmon, Y. *Polymer* 1978, **19**, 225
12 Buck, H. W., Cella, R. J., Gladding, E. K. and Wolfe, J. R. *J. Polym. Sci. (D)* 1974, **40**, 37
13 Kato, K. *Polym. Eng. Sci.* 1967, **7**, 38
14 Kato, K. *J. Electron Micros (Japan)* 1965, **14**, 220
15 Seefried, C. G., Jr., Koleske, J. V. and Critchfield, F. E. *J. Appl. Polym. Sci.* 1975, **19**, 2493
16 MacKnight, W. J., Yang, M. and Kajiyama, T., *Polym. Prepr.* 1968, 1, **9**, 860
17 Frensdorff, H. K. *Macromolecules* 1971, **4**, 369