polymer papers

Double lamellae of low-molecular-mass fractions of poly(ethylene oxide) crystallized from the melt

Stephen Z. D. Cheng*, H. S. Bu† and Bernhard Wunderlich‡
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590, USA

(Received 20 July 1987; revised 25 September 1987; accepted 30 September 1987)

A 'double-lamella' morphology has been observed during a study of molecular segregation and nucleation of low-molecular-mass fractions of poly(ethylene oxide) (PEO) from the melt. It is only observed in cases of crystals with an odd number of folds per molecule. The formation of the double lamellae is thought to be based on association of the OH end-groups of the PEO chains. Ordered hydrogen bonding on facing folded crystals is being suggested as an explanation for the observation.

(Keywords: chain folding; crystal growth; hydrogen-bonding lamella; low molecular mass; morphology; poly(ethylene oxide); single crystal; double lamellae)

INTRODUCTION

Poly(ethylene oxide) (PEO) is one of the most extensively studied crystalline polymers. Its thermodynamic and kinetic data for fractions and binary mixtures have been well established[1-10]. Kovacs *et al.* have presented a systematic report on the morphology of low-molecular-mass fractions observed by optical microscopy (OM) and transmission electron microscopy (TEM)[1-5]. The recent development of a new etching method[11,12] has allowed us to study the morphology of PEO in bulk samples, and therefore molecular segregation from the melt can be observed by TEM for the first time. The molecular nucleation approach has been applied to PEO nucleation and crystal growth[13].

A quantized increase of lamellar thickness for low-molecular-mass fractions of PEO with temperature has been reported[1-5,13,14]. This indicates (1) that adjacent re-entry folding must be retained in these crystals, and (2) that all OH end-groups of chains are rejected onto the fold surfaces, and are free to form hydrogen bonds. It is generally assumed that these H bonds distribute randomly on the two fold surfaces and have an equal effect on the surface free energy of both[1,6,7].

Some years ago, a double lamella was briefly reported by Price *et al.* for one molecular mass of PEO at several temperatures[15]. However, little explanation was given because of the lack of detailed experimental information on low-molecular-mass crystals of PEO. In this paper, we would like to report on this morphology of low-molecular-mass fractions of PEO crystallized from the melt. The double lamella has been observed by TEM when the crystals are composed of odd-numbered folded chains. They apparently grow almost simultaneously. A proposal of H bonding on facing folded chain crystal surfaces will be made.

MATERIALS AND EXPERIMENTS

All materials used in this research have been described in detail before[2-5]. The low-molecular-mass fractions of PEO were purchased from Polyscience Inc. and Pressure Chemical Co. The polydispersities of the fractions are smaller than 1.1. In this study four fractions were used: $MW = 3500$, 7000, 9230 and 11 000. The extended chain crystals are thermodynamically stable, and one may observe them using differential scanning calorimetry (d.s.c.) at any heating rate. The integral m-folded chain crystals, however, are metastable or even unstable since they can always be annealed to $(m-1)$-folded crystals depending on temperature or heating rate. For the fraction of $MW = 3500$, the lamellar thickness (L) of extended chain crystals is 22.1 nm. The once-folded chain crystals can crystallize at sufficiently high supercooling, and show a lamellar thickness of 11.1 nm. They are metastable when a heating rate of 5 K min^{-1} is used. For the fraction of $MW = 7000$, we find $L = 44.2$ nm for extended chain crystals (stable) and 22.1 nm for once-folded chain crystals (metastable). The twice-folded chain crystals with $L = 14.8$ nm are unstable and reorganize after initial growth at the same heating rate. For the $MW = 9230$ fraction, $L = 58.3$ nm (stable), 29.2 nm (metastable), 19.4 nm (metastable) and 14.6 nm (unstable) for extended chain, once-folded, twice-folded and triply folded chain crystals at the same heating rate, respectively. Finally, the fraction of $MW = 11\,000$ has lamellar thickness $L = 71.1$ nm (stable) for extended chain crystals, 35.6 nm (metastable), 23.7 nm (metastable), 17.8 nm (metastable) and 14.2 nm (unstable) for once-, twice-, triply and quadruply folded chain crystals[8].

---

* Present address: Institute and Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

† Visiting Professor from Fudan University, Shanghai, China

‡ Present address: Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996-1600, USA

0032-3861/88/040579–05$03.00

The low-molecular-mass fractions of PEO bulk samples were crystallized from the melt in a temperature-controlled Tamson water bath. The bulk sample size was 10 x 10 x 1.5 mm. The samples were molten at 373.2 K and held for 15 min to destroy all prior crystal nuclei. Then they were cooled to selected crystallization temperatures at which crystals with the selected fold number were formed. For example, at $T_c = 331.2$ K the $MW = 3500$ fraction crystallizes as an extended chain crystal. A once-folded chain crystal is observed at $T_c = 331.2$ K for $MW = 7000$. For $MW = 9230$, a twice-folded chain crystal is formed at 330.2 K. Finally, a triply folded chain crystal can be found if the fraction of $MW = 11\,000$ is crystallized at $T_c = 331.2$ K[1,6]. After complete crystallization, the samples were quickly cooled to room temperature. Temperatures of the water bath were controlled to an accuracy of ±0.1 K. A nitrogen atmosphere was maintained during the crystallization.

A standard, one-stage replication process by shadowing the samples with heavy metal (Au/Pd, 0.4/0.6) and backing with carbon was employed. The polymer was then washed out from the replica with water. The replicas were picked up with TEM grids in acetone. The replicas were examined in the TEM mode of a Hitachi HS-7S electron microscope with 50 kV acceleration voltage. The resulting micrographs thus have negative relief.

When the newly developed etching method with C_2H_5OCa was applied before replication[11,12], the internal crystalline textures could be observed. There was no difference in the observation to be found before and after etching. Thus, the same texture prevails throughout the samples. The micrographs that we present here are of the crystalline textures observed on the free surfaces.

RESULTS

Figure 1 shows the typical crystalline texture of extended chain crystals for $MW = 3500$ crystallized at 331.2 K. The texture of all four analysed samples was of the same uniformity on the surface and throughout the samples. The lamellar crystals have a thickness of about 23 nm. They stack closely, and the crystalline *c*-axis is largely perpendicular to the surface of the samples. It seems also that, except for the initial nucleation, every lamellar crystal grows independently.

For the once-folded chain crystals of $MW = 7000$, crystallized at 331.2 K, one can see a different texture as shown in *Figure 2*. Two lamellae are coupled and form apparently one growth unit. A thickness of 46 nm has been estimated from shadow length for such a unit, or about 23 nm for each single lamella, which is expected for a once-folded chain crystal. We call this microstructure 'doubly lamellar'. Five different samples were prepared for $MW = 7000$ at 331.2 K, and the double lamellae were observed without exception. Surprisingly, the double lamellae persist also during branching of the lamella, as shown close to the centre of *Figure 2*. Sometimes, one can see thicker lamellar crystals with a thickness of 46 nm for which the doubly lamellar structure is difficult to recognize, as shown in *Figure 3*. However, a careful analysis tells us that they also consist of two lamellae.

Turning now to molecules that are twice-folded, the texture is again made up of mostly single lamellae. *Figure 4* shows the crystalline texture of $MW = 9230$, crystallized at 331.7 K, where a twice-folded chain crystal forms. The texture is similar to that of the extended chain crystals shown in *Figure 1*. Individual lamellae crystallize independently with lamellar thickness of about 20 nm (four samples were examined). Occasionally, doubly or multiply lamellar structures are also found.

Double lamellae are, nevertheless, observed again in the case of triply-folded chain crystals for $MW = 11\,000$ and shown in *Figure 5*. The lamellar thickness was found

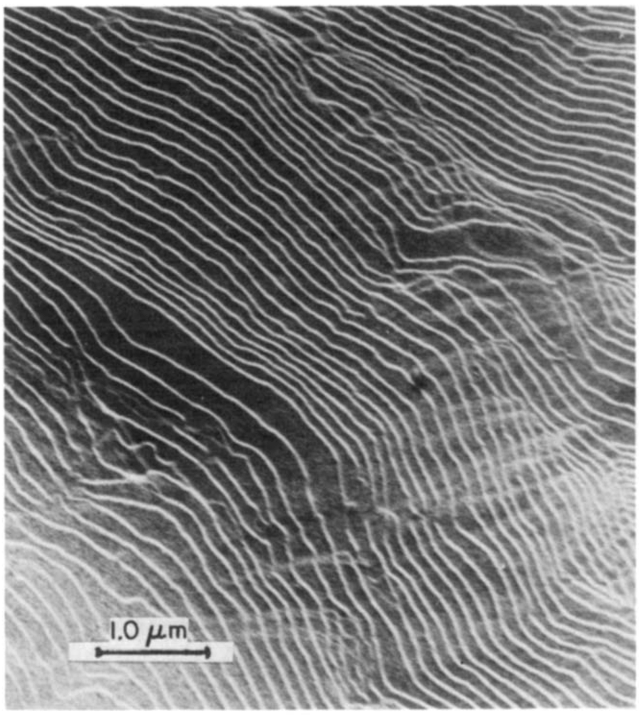

Figure 1 Lamellar microstructure of a $MW = 3500$ PEO fraction crystallized from the melt. The crystallization temperature is 331.2 K

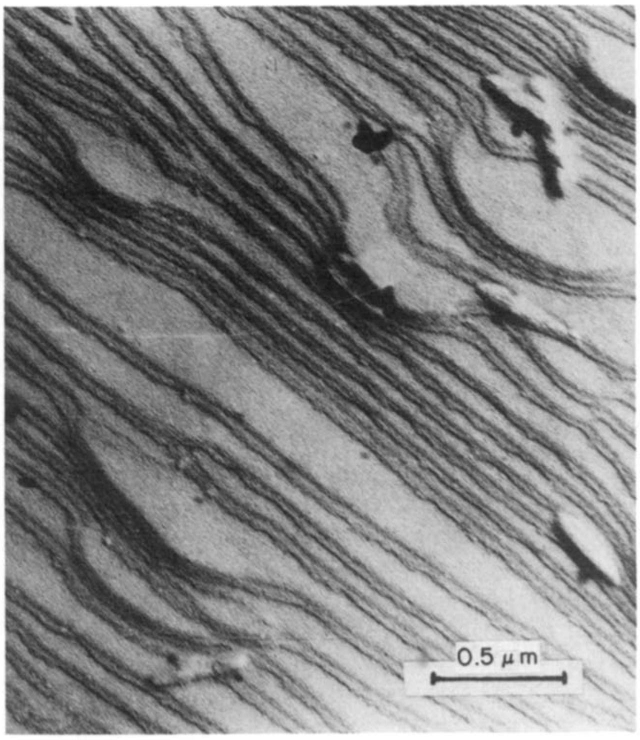

Figure 2 Double lamellae of $MW = 7000$ PEO fraction crystallized from the melt. The crystallization temperature is 331.2 K. A branching of such lamellar crystals can also be seen in the centre of the figure

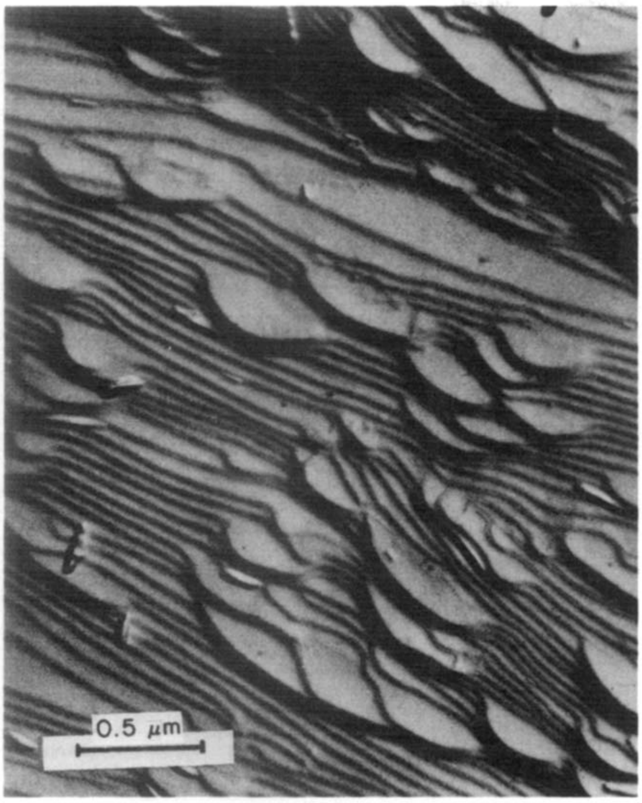

Figure 3 Double lamellae as in *Figure 2*. Note the frequently thicker lamellar crystals double the thickness of the two lamellae shown in *Figure 2*

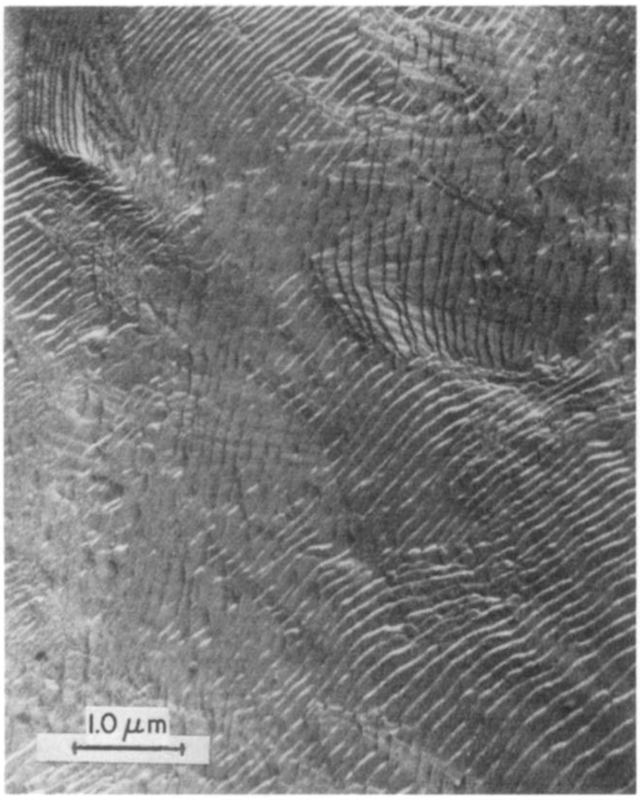

Figure 4 Lamellar microstructure of $MW = 9230$ PEO fraction crystallized from the melt. The crystallization temperature is 331.7 K

to be about 18 nm for each individual lamella in the double lamellae, or 36 nm for the double unit (in total three different preparations were checked). The doubly lamellar structure is, however, less uniform than those observed in the once-folded chain crystals shown in *Figures 2* and *3*. Sometimes, other multiple lamellae are also seen.

DISCUSSION

The quantized increase of lamellar thickness for low-molecular-mass PEO crystals with temperature is well known[1-5,13,14]. One direct deduction from this folding is that all OH end-groups of PEO chains are rejected onto the two fold surfaces. The end-groups may form intra- and interlamellar H bonds. According to the model suggested by Kovacs *et al.*[1-5], the chain ends are randomly distributed on those two surfaces. Extended chain crystals must then have the highest H-bonding density since there is no folding. Approximately only half this H-bonding density may be found in the case of once-folded chain crystals, etc. H bonding has a negative contribution to the fold surface free energy. Buckley and Kovacs suggested[6,7], based on the Flory and Vrij model[16] of closely stacked lamellar crystals with chain-end pairing, a simplified calculation of the fold surface free energy. The average surface free energy per stem on both sides of the lamella for m-folded chain crystals is:

$$\sigma_e(m) = [\sigma_{e,e}(m) + m\sigma_{e,f}]/(1+m) \qquad (1)$$

where $\sigma_{e,e}(m)$ is the surface free energy of the two chain ends of m-folded molecules, and $\sigma_{e,f}$ is the fold surface free energy. The parameters for equation (1) are $\sigma_{e,f} = 2.88\ \mathrm{kJ\ mol^{-1}}$, $\sigma_{e,e}(m \geqslant 1) = 4.49\ \mathrm{kJ\ mol^{-1}}$ and $\sigma_{e,e}(0) = 3.28\ \mathrm{kJ\ mol^{-1}}$ (refs. 6 and 7). The difference $\sigma_{e,e}(m \geqslant 1) - \sigma_{e,e}(0)$ characterizes the H-bonding efficiency. Based on equation (1), one can find that $\sigma_e(m)$ increases on going from $m = 0$ to $m = 1$, and then gradually decreases towards $\sigma_{e,f}$ as m increases further[6,7].

According to the experimental observations, a general rule for the appearance of the double lamellae suggests

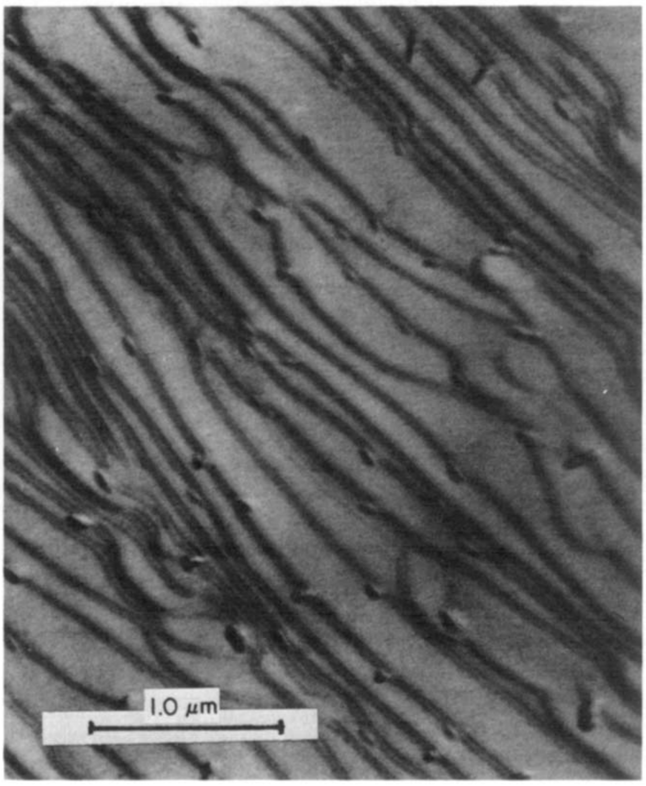

Figure 5 Double lamellae of $MW = 11\,000$ PEO fraction crystallized from the melt. The crystallization temperature is 331.2 K

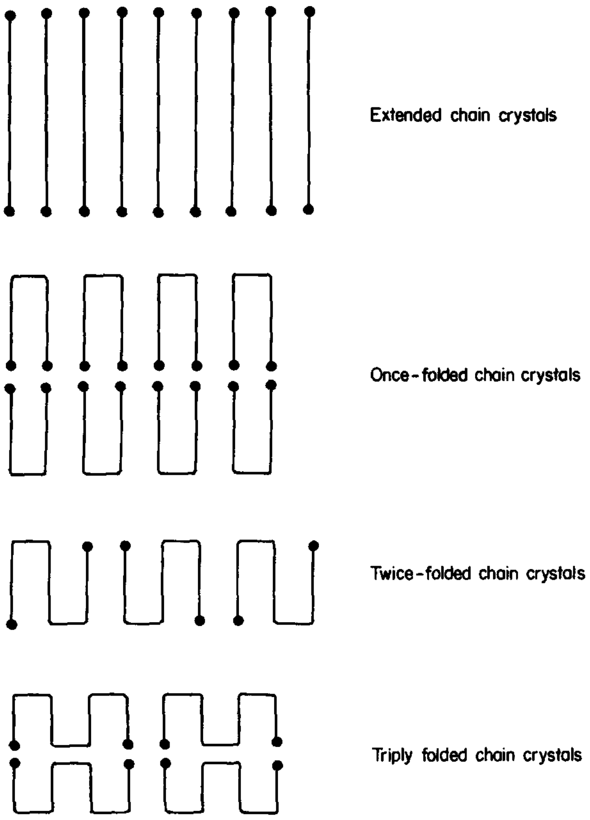

Figure 6 A schematic drawing of H bonding on crystal surfaces for integral folding

itself: double lamellae appear in cases of odd numbers of chain folds. An obvious deduction can be made from this observation: the PEO chains try to maximize OH contacts in bulk samples as shown in *Figure 6*. For an odd number of folds in the bulk samples, equation (1) can no longer hold since there are now two types of fold surfaces: one with almost only folds, and another with almost only ends. The average surface free energy of once-folded chain crystals can thus be calculated by $[\sigma_{e,f} + \sigma_{e,e}(0)]/2$, and is 3.08 kJ mol^{-1}, instead of 3.68 kJ mol^{-1} for the statistical placement of chain ends. The Kovacs model is only applicable for even numbers of folds and also for all folding in the case of quick crystallization or growth of single lamellar crystals[1-5].

Other supporting experimental evidence comes from d.s.c.[6-8] and small-angle X-ray scattering[14]. First, once-folded chain crystals below $MW = 5000$ are more stable than similar folded-length crystals of higher molecular mass (i.e. molecules with larger numbers of folds on the surface)[7,8]. Secondly, the zero-entropy-production melting temperature of once-folded chain crystals for $MW = 6000$, $T_m(1)$, which is measured by d.s.c., displays a value 0.6 K higher in the bulk samples than that observed from the zero-growth-rate criterion in the single lamellar crystals[3,7].

However, at present we understand very little about the principles of crystal growth of the double lamellae. It seems necessary to have a special arrangement of the folded chains in the crystals (see *Figure 6*) in order for most of the chain ends to concentrate on facing folded chain crystal surfaces. Two different sequences for the growth of double lamellae may be expected. First, crystal growth could occur by deposition of pairing chains (ring-like) with opposite single folds, i.e. it is necessary to have a permanent association of H bonds between two chain ends in the melt, and two lamellae grow at the same time. Or secondly, one lamella could grow a few layers beyond another, and the latter one would follow closely because of the high concentration of H bonds on the fold surface, therefore giving a decrease of surface free energy. Even though an infra-red study has been reported showing that almost all chain ends of the low-molecular-mass fractions of PEO are associated by H bonds in both the melt and in the crystalline state[17], we believe that those associations are quite different in the two states. In the melt the associations may be exchangeable among the ends, even between ends and C–O–C bonds of a chain. On the other hand, in the crystals they are permanent. The twice-folded chain crystals could not form in the low-molecular-mass fractions of PEO if permanent associations existed in the melt, since at least one of the two H-bond associations between two chains would have to be broken during crystal growth. We thus prefer the second sequence predicted for the growth of double lamellae. Furthermore, the crystal growth rate of the double lamellae must be somewhat different from that of a single lamellar crystal. Some time ago, Kovacs *et al.* correctly pointed out such a difference[1]: 'the growth of double or multi-layer crystals will be faster than that of single lamella, provided that the concentration of OH groups in the matching area is high enough to contribute significantly to σ_e' (see figure 15 in ref. 1). Nevertheless, there has not been any systematic report on the kinetics.

Finally, it has been well known that multilayers in polymer crystals can only grow through screw dislocation, which leads to growth spirals with their axes along the chain direction[18]. Price *et al.*[15] have reported such spiral growth in doubly lamellar crystals of PEO. The screw dislocation can be thought of as being generated by a slip of one part of the crystal relative to the rest. Its dislocation line vector marks the line of termination of the slip. The Burgers vector, which measures the size of the dislocation, should have in this case an approximate magnitude equal to the double-lamellar thickness because of double-lamellar branching during crystallization. Experimental observation in our work has proved such a statement. Indeed, the double lamellae are still retained during the branching (see *Figure 2*). In this case the double lamellae grown earlier gradually split into two single lamellae possibly due to internal stress within the crystals. Therefore, re-entrant faces may form during this process, as shown be Geil and Reneker[19]. Another two layers can thus grow on the re-entrant faces as soon as the faces are thick enough to accommodate them, and form two sets of new doubly lamellar crystals. This observation itself indicates that two lamellae grow in close proximity, but independently.

CONCLUSIONS

Double lamellae have been observed for the low-molecular-mass fractions of PEO crystallized from the melt. It appears only in those cases of odd-numbered fold molecules. Consequently, formation of the double lamellae is attributed to a high concentration of H bonds on facing folded chain surfaces. A proposal of H-bonding distribution on the folded chain crystal surfaces for different numbers of folds has been made. A sequence of the growth and the mechanism of branching for the double lamellae are predicted. However, much more study is necessary in order to understand fully the principle of formation and growth of doubly lamellar crystals.

ACKNOWLEDGEMENT

This work was supported by the National Science Foundation, Polymer Program, Grant No. DMR 83-17097.

REFERENCES

1 Kovacs, A. J. and Gonthier, A. *Kolloid Z. Z. Polym.* 1972, **250**, 530

2 Kovacs, A. J., Gonthier, A. and Straupe, C. *J. Polym. Sci., Polym. Symp.* 1975, **50**, 283

3 Kovacs, A. J., Straupe, C. and Gonthier, A. *J. Polym. Sci., Polym. Symp.* 1977, **59**, 31

4 Kovacs, A. J. and Straupe, C. *Faraday Disc. Chem. Soc.* 1979, **68**, 225

5 Kovacs, A. J. and Straupe, C. *J. Cryst. Growth* 1980, **48**, 210

6 Buckley, C. P. and Kovacs, A. J. *Prog. Colloid Polym. Sci.* 1975, **58**, 44

7 Buckley, C. P. and Kovacs, A. J. *Kolloid Z. Z. Polym.* 1986, **254**, 695

8 Cheng, S. Z. D. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 577

9 Cheng, S. Z. D. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 595

10 Grebowicz, J., Suzuki, H. and Wunderlich, B. *Polymer* 1985, **26**, 581; *Makromol. Chem.* 1985, **186**, 1109

11 Cheng, S. Z. D., Bu, H. S. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* to be published

12 Bu, H. S., Cheng, S. Z. D. and Wunderlich, B. *Polym. Bull.* 1987, **17**, 567

13 Wunderlich, B. and Cheng, S. Z. D. *Macromolecules* to be published

14 Spegt, P. A. *Makromol. Chem.* 1970, **139**, 139; Arlie, J. P., Spegt, P. A. and Skoulions, A. E. *Makromol. Chem.* 1966, **99**, 170; 1967, **104**, 212

15 Barnes, W. J. and Price, F. P. *Polymer* 1964, **5**, 283

16 Flory, P. J. and Vrij, A. *J. Am. Chem. Soc.* 1963, **85**, 2548

17 Shimada, T., Okui, N. and Kawai, T. *Makromol. Chem.* 1980, **181**, 2643

18 Wunderlich, B. 'Macromolecular Physics', Vol. I, 'Crystal Structure, Morphology, Defects', Academic Press, New York, 1973

19 Geil, P. H. and Reneker, D. H. *J. Polym. Sci.* 1961, **51**, 569