Molecular association complex of urea with polyethylene: 2. The new preparation methods and morphological study

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(Received 16 July 1979)

New systems for preparing urea–polyethylene complex have been discovered: (a) solid urea–polyethylene solution in xylene with a small amount of aniline; (b) solid urea with seeds–polyethylene solution in xylene. Scanning electron microscopy showed that the complex consisted of lamellae of the order of 1000 Å in size. Polyethylene molecules perpendicular to the lamellae exist as extended chains in the hexagonal urea tunnels, much as paraffin molecules in the urea–paraffin complex. Extended chain crystals similar to those crystallized under high pressure were obtained by elimination of the skeletal urea lattices of the complex by methanol. This morphology reflects the conformation of the guest polyethylene molecules.

INTRODUCTION

Urea forms a crystalline complex with linear hydrocarbons[1,2] such as paraffins and their derivatives. Crystallization proceeds with the formation of hexagonal urea lattices[3] in which guest molecules are enclosed by a zig-zag conformation. Branched or bulky hydrocarbons[4] are rejected during crystallization because of the steric constraints of the hexagonal urea tunnel. Separation of linear hydrocarbons has been achieved on an industrial scale by this method. Attempts to obtain stereoregular polymers by channel polymerization have also been carried out[5,6].

We have previously prepared the complex by the 'substitution' method[8], obtaining needle-like crystals with large lamellar structures. In addition we have discovered new preparation systems: (a) solid urea–polyethylene solution in xylene with a small amount of aniline, based on the preparation methods for urea–paraffin complexes[9]; and (b) solid urea with seeds–polyethylene solution in xylene. An investigation into crystal type and the conformations of the enclosed molecules has been carried out together with an investigation of the morphology of polyethylene crystals obtained by decomposing the complex.

EXPERIMENTAL

Polyethyelene

Commercial linear polyethylene was used to prepare the complexes. The viscosity-average molecular weight of the sample was 59 000, determined in tetralin by Tung's equation[10], using an Ubbelohode viscometer at 130°C.

Preparation of the complexes

(a) Solid urea–polyethylene solution in xylene with a small amount of aniline. 5 g of polyethylene was dissolved in 50 ml of xylene in a flask. The temperature of the solution was controlled at 122°C. 3 g of urea powder with particle size less than 145 mesh was added to the solution. A small amount of aniline, varying from 0 to 4% as a percentage of xylene present by volume, was added dropwise to the solution and the flask was sealed under a nitrogen atmosphere. The system was allowed to crystallize under still conditions. After 72 h the remaining polyethylene solute was removed with a large amount of xylene and the solid products were isolated by filtration and dried under vacuum.

These preparations were preceded by crystallization of the complex on the surface of a single crystal of urea (~1 mm) carried out at 116°C for 48 h with 10 ml of xylene, 1 g of polyethylene and 1% of aniline against xylene. This complex was used for scanning electron microscopy.

(b) Solid urea with seeds–polyethylene solution in xylene with a small amount of aniline. Complexes prepared by (a) milled to fine powder of less than 400 mesh, were used as seeds. A mixture in the ratio 1 part powdered seeds to 100 parts powdered urea was prepared and used as a starting material for the preparation. The crystallization conditions and the procedures were the same as those in (a).

Polyethylene crystals from the complexes

Polyethylene crystals were obtained by decomposing the complexes with methanol at 60°C for 1 h; these were used for d.s.c. thermal analysis, molecular weight measurements and morphological observation.

D.s.c. thermal analysis

A Perkin–Elmer differential scanning calorimeter (DSC-1) was used for thermal analysis of the complexes and the polyethylene crystals obtained from them. The temperature scale was calibrated using indium and urea at the same heating rate, 5°C min^{-1}.

X-ray analysis

An X-ray diffractometer with Ni-filtered CuKα radiation was used to determine the cell constants of the urea–n-hexadecane and urea–polyethylene complexes. The former complex was prepared by the usual method[13]. A powder mixture in the ratio of 1 part of sodium chloride: 9 parts of the complex by wt was used. Sodium chloride was selected as an internal standard for diffraction angle. The diffraction angles for the complex were corrected using the three peaks for sodium chloride [(200), (220) and (400)] which were isolated from the peaks for the complex. Cell constants were determined by the least squares method. Measurement conditions were as follows: scanning rate, 1/8° min^{-1}; slit widths, 1°, 1° and 0.15 mm for divergence, scattering and receiving, respectively; radius of the diffractometer, 185 mm; time constant 0.1 s, which is much smaller than the time width[11]; temperatures, 13.5 ± 1°C for urea–paraffin complex and 17.0 ± 1°C for urea–polyethylene complex, respectively.

Morphological observation

The complexes were shadowed with carbon and gold on a rotary stage and the morphologies were studied by scanning electron microscopy.

Fine structure for the complexes and the polyethylene crystals obtained from them were observed by transmission electron microscopy, using the following carbon replica method.

Polyethylene crystals (powder aggregates) were wrapped in alluminium foil and fractured by hammering at liquid nitrogen temperature. In order to estimate the effect of pressure on morphology, samples were pressed under 2500 atm pressure in silicone oil medium for 1 h at room temperature. They were then fractured as above. We did not attempt to fracture the complexes. A powder sample was moulded as a small disc of about ~1 mm thickness in a piston cylinder so as not to crush the surface structures by pressure. The disc was shadowed by Pt–Pd metal and carbon progressively evaporated onto the surface. In order to eliminate sample cohering to the carbon film, methanol and xylene were used for the complex but only xylene for the polyethylene crystal.

RESULTS AND DISCUSSION

Preparation of the complexes

Homogeneous solutions of urea and polyethylene could not be obtained using any solvent; this was due to the large difference in the solubilities of the components. We previously obtained urea–polyethylene complexes using the heterogeneous preparation system[8,12], urea–paraffin complex/polyethylene solution in xylene.

Aniline and other solvents[9] act as activators in the heterogeneous crystallization process. Here, aniline was used as one of the additives to the preparation system. The availability of seeds of the complex was also confirmed.

The crystallization of the complex on a single crystal of urea (~1 mm) from (a) was confirmed by visual observation of the surface, which at first was transparent, but gradually became cloudy. However, in spite of the use of the same single crystal, there were some cases in which crystallization was not observed at all. Calderbank *et al.*[15] reported that in urea/n-octane/solvent systems, urea particle sizes less than 150 mesh reacted with n-octane rapidly but 35 mesh urea did not react appreciably. In the case of finely powdered

urea crystallization was always observed (see below). Urea particle size is an important factor in the crystallization of urea–n-alkane complexes. In the following experiments, we used powdered urea (particle size < 145 mesh).

Table 1 gives yields of the complex in the solid product. Thermograms of the product showed two endothermic peaks. One at 133°C resulted from tetragonal urea which did not form a complex with polyethylene. The other resulted from a urea–polyethylene complex, which exhibited a melting peak at 149°C, higher than for the constituent urea and polyethylene. Other monomer–polymer complexes[17] also showed higher melting points than those of the constituents. We define *yield* as wt % urea transformed into the complex divided by the total urea in the product. Values were calculated by the procedure given in refs 13 and 14.

When aniline was absent in (a) crystallization was not observed. Addition of a small amount of aniline made the yields considerable, indicating that aniline has the function of accelerating at least the primary nucleation. Though yields increased with concentration of aniline, we did not attempt crystallization at a concentration higher than 4%, since polyethylene might have precipitated.

Addition of 1% seeds against powdered urea [(b)] resulted in high yields. Since the seeds are fine powder complexes with particle sizes < 400 mesh, they provide suitable sites for the secondary nucleation. Results shown in *Table 1* indicate that nucleation can proceed even when aniline is absent. Urea molecules in solid urea must be transferred to the nucleation sites of the complex. This is possible by sublimation because the vapour pressure of tetragonal urea[16] is expected to be appreciable at the crystallization temperature.

Morphology of the complexes

Scanning electron micrographs of urea–polyethylene complex grown on the surface of a large urea single crystal by (a) are shown in *Figure 1*. The smooth surface at the top of *Figure 1a* is the (110) cleavage surface of tetragonal urea exhibited by fracture after crystallization; the rough surfaces of bowl-shaped aggregates which surround the urea surfaces correspond to the complex phase, which appeared cloudy by visual observation. Crystallization proceeds by converting solid urea into complexes. It is expected that the overall crystallization rate will depend on the urea particle size. *Figure 1b* shows that the complex phase consists of hexagonal prism-like crystals of the order of 10 μm. The end surfaces of the lamellae are shown in *Figure 1c* to be of the order of 1000 Å. These develop laterally and stack along the c-axis with copious screw dislocations.

The scanning electron micrograph of the complex prepared from (a) with 0.5% aniline are shown in *Figure 2*. A large and roughly hexagonal prism was frequently observed with a central concavity around which many complex crystals show spherical growth.

Table 1 Yields of urea–polyethylene complex

Aniline (%)	Yield (%)	
	(a) seeds = 0%	(b) seeds = 1%
0.0	0	98
0.5	12	92
1.0	57	95
2.0	76	95
4.0	72	91

The scanning electron micrograph of the complex prepared from (b) [urea powder with 1% seeds—polyethylene solution in xylene] is given in *Figure 3*. The same development as shown in *Figure 1* is apparent.

The basic structural unit is thus a lamellar crystal, though the shape of the complex is individually variable, depending on the preparation conditions. Flexible polyethylene molecules generally crystallize with a lamellar thickness of the order of 1000 Å; condensation of urea molecules occurs with the formation of a rigid, hydrogen-bonded network. The lamellar crystal arises from the association of 'rigid' urea and 'flexible' polyethylene.

Complexes prepared by method (b) in the absence of aniline were used in successive studies.

The transmission electron micrograph of a carbon replica of the (100) surface of the complex is shown in *Figure 4*.
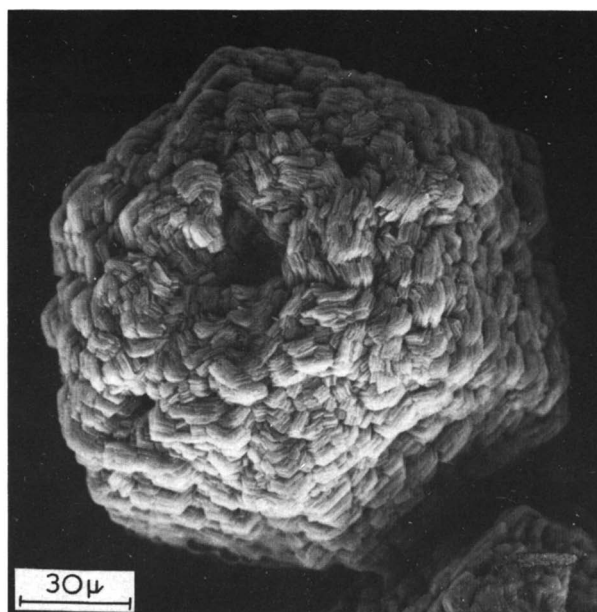

Figure 2 Scanning electron micrograph of urea—polyethylene complex prepared from system (a)

Figure 1 Scanning electron micrographs of urea—polyethylene complex grown on the surface of a single crystal of tetragonal urea: (a) total view; (b) complex phase; (c) end view of the lamellae
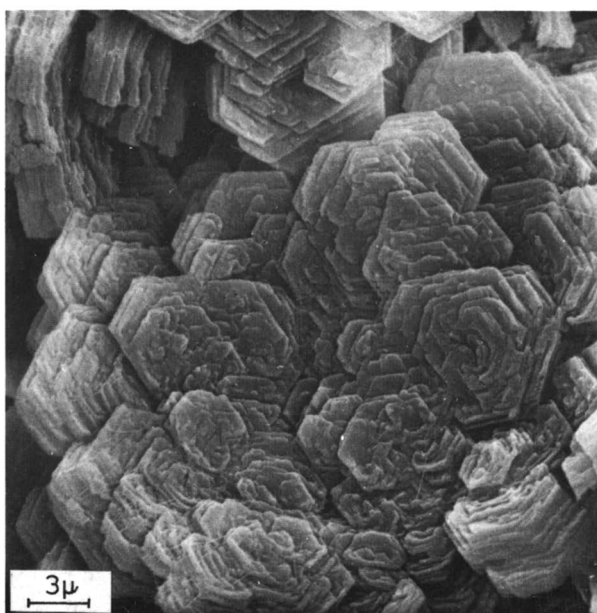

Figure 3 Scanning electron micrograph of urea—polyethylene complex prepared from system (6)
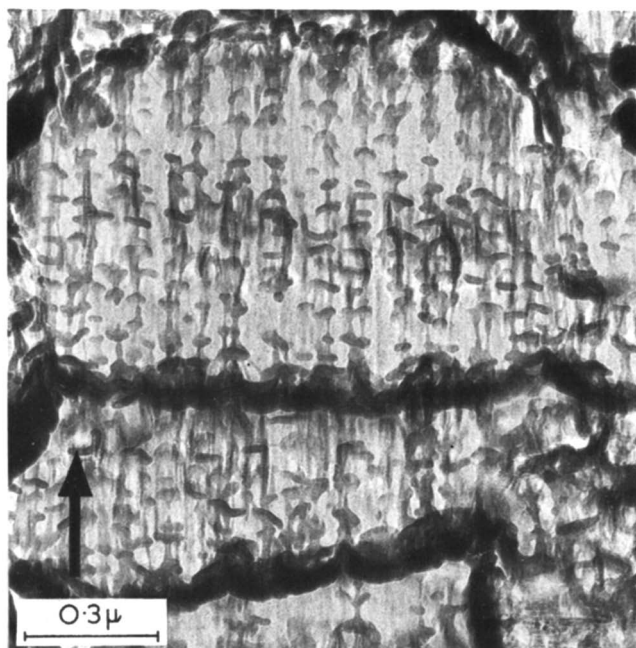
Figure 4 Transmission electron micrograph of a replica of urea—polyethylene complex. Arrow indicates *c*-axis

The arrow corresponds to *c*-axis of the complex. Distinct shish-kebab structures can be seen on the surface. Pennings *et al.*[18,19] proposed that the shish-kebab structure obtained by solution stirring consisted of an extended-chain core (shish) with folded-chain crystals deposited upon it (kebab). We postulate that the shish-kebab structures observed on the complex surface are formed by intermolecular condensation of the guest polyethylene molecules originally enclosed in the urea hexagonal lattices in an extended chain form. This occurs by sublimation of the host urea molecules which surround the guests when the complex is heated in hot xylene with concurrent elimination of an excess of solute polyethylene. Generation of the shish-kebab structure from the complex suggests the presence of the extended-chains within the complex.

Conformation of the guest molecules

Smith[3] indicated that the paraffin molecules in a hexagonal tunnel take a *trans* zig-zag conformation and rotate freely or distribute randomly around *c*-axis. If the guest molecules adopted a distorted conformation different from the *trans* form, the *a*-axis would expand because of its bulky conformation. Estimation of unit cell dimensions will provide indirect but significant information about the conformation of the guest molecules.

The hexagonal unit cell constants of urea—n-hexadecane complex[3,20,21] and urea—polyethylene complex are given in *Table 2*. The dimensions of both complexes coincide with few discrepancies. This indicates that there is not a large difference in conformation between polyethylenes and paraffins in each complex. More detailed X-ray analysis on the guests will be presented in near future.

Morphology of polyethylene crystals

Polyethylene crystals were readily obtained by decomposition of the complexes with methanol, producing powder particles, between μm and mm in size, reflecting the original size of the complex. The polyethylene obtained from the

complex sample was polydisperse, having M_v = 62 000 compared with an original M_v of 59 000. This shows that some of low fractions were rejected during the crystallization because of the thermal instability of the complexes with short chains.

Figure 5 shows transmission electron micrographs of a replica of a fracture surface from polyethylene crystals.

The growth surfaces of the complex are six equal (100) surfaces. Polyethylene molecules longer than the lamellar thickness must fold back and forth along the (001) end surface. The fracture surfaces shown in *Figure 5a* might appear by cleavage along the fold plane, because the fracture occurs in a relatively regular manner and the angle between the surfaces appears to be identical to the interfacial angle of the fold plane, 120°. The band structures in *Figure 5a* originate from the lamellar structures in the complex, and their widths are similar to those of the complex. *Figure 5b* shows an enlargement of a section of *5a*; we find that the band structures consist of extended-chain crystals.

Electron micrographs of a replica of the fracture surface of polyethylene crystals pressed in silicon oil under 2500 atm for 1 h at room temperature are shown in *Figure 6*. Distinct extended-chain crystals, similar to those formed at elevated pressure[22,24] are apparent; these are composed of microfibrils more densely and regularly than before pressing. The obscure extended-like structures shown in *Figure 5* result from the loose lateral packing of fibrils with many voids[8].

The polyethylene crystals from the complex are characterized by instantaneous intermolecular condensation of the guest molecules. Morphologies similar to those of the complexes are produced. The melting points before and after pressure treatment exhibited the same value, 137°C, a few degrees lower than specimens crystallized under high pressure[23]. The condensation process is thus expected to introduce defects and disorders, not released by pressure treatment; these occur within the condensed phase by rotational distortions around the *c*-axis and translational displacements along the long axis. Introduction of defects into the crystal phase by chain ends cannot be avoided, because the chain ends of the guest molecules in the urea lattices probably distribute randomly within the crystal phase of the complex, in contrast to those in polyethylene single crystals formed from dilute solution. In these single crystals, the chain ends are mostly rejected[25] from the crystal phase during crystallization.

CONCLUSION

Urea—polyethylene complexes have been crystallized from new heterogeneous preparation systems. The complex not only exhibits the same X-ray crystal structure as that of the urea—paraffin complex, but also shows interesting morphological features. The basic structural unit of the complex is a lamellar crystal of the order of 1000 Å in thickness. Poly-

Table 2 Unit cell constants of urea complex

Guest molecule	Cell constants (Å)		Reference
	a_0	c_0	
n-Hexadecane	8.22	11.01	this paper
	8.227	11.005	Chatani (20)
	8.230	11.005	Smith (3)
Polyethylene	8.22	11.02	this paper

Figure 6 Transmission electron micrograph of a replica of the fracture surface of polyethylene crystals pressed under 2500 atm at room temperature. Arrow indicates c-axis
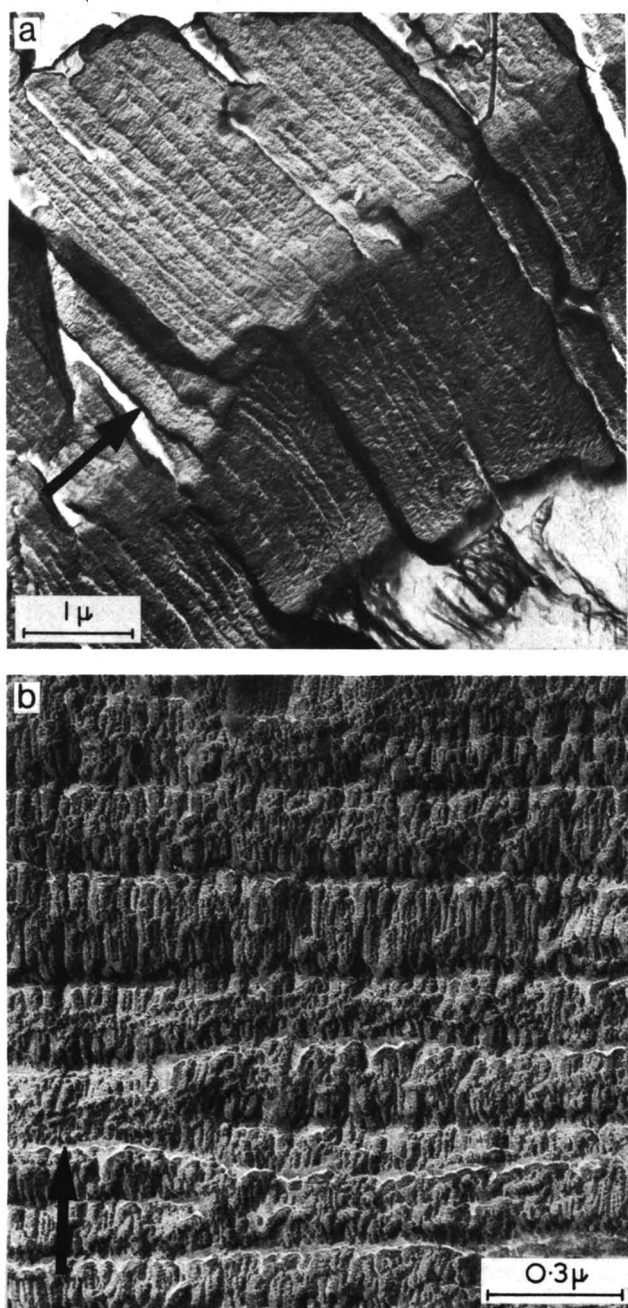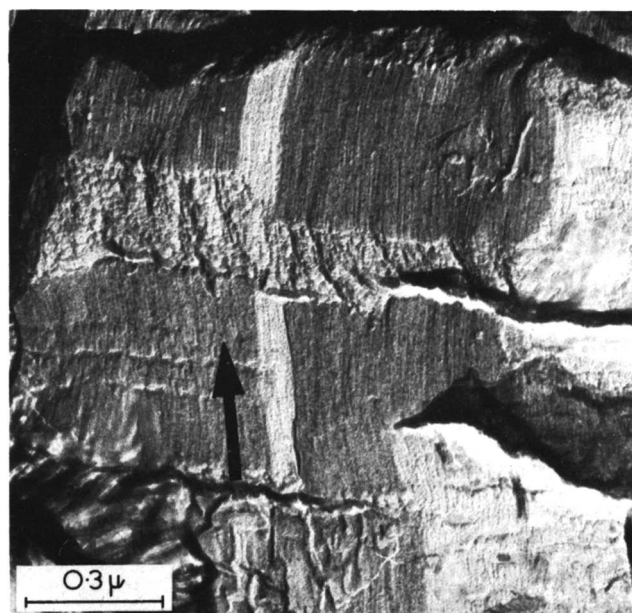

Figure 5 Transmission electron micrographs of a replica of the fracture surface of polyethylene crystals obtained from the complex: (a) stacking of band structures; (b) extended-chain crystals. Arrow indicates c-axis

ethylene molecules lie normal to the lamellar surface and assume an extended form in the hexagonal urea tunnels.

Crystallization of flexible polymers leads to folded-chain structures but under high pressure and solution flow conditions extended-chain structures are obtained. Molecular conformation in the condensed phase is thus controlled by a crystallization field determining the kinetic process. Preparation systems for urea–polyethylene complexation enable flexible polyethylene molecules to extend.

ACKNOWLEDGEMENTS

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