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3.B Progress in Ablation Layer Fabrication

An ablatively driven inertial fusion experiment requires a precise, layered target consisting of concentric spherical shells. Incident laser radiation is absorbed at the critical density surface of the outermost layer called the ablation layer. Thermal conduction then carries the absorbed energy inward from the critical density surface and heats adjacent layers of material which expand radially outward. To conserve the momentum associated with this expansion, the material comprising the inner layers of the target implodes. To achieve uniform implosions and prevent hydrodynamic instability, the ablation layer must be uniform in thickness and density, and its surface irregularity must be minimized.

The ablation layer consists of low Z materials, most commonly polymeric hydrocarbons. Layers of this type have been deposited on shells in a variety of ways. One method employed at LLE involves the vapor phase pyrolysis of di-para-xylylene. In this process the di-para-xylylene molecule is sublimated and, upon heating to 600° C in vacuum, pyrolyzes into two monomers. The monomers deposit onto a room temperature substrate, instantly polymerizing into poly-para-xylylene, or parylene.

This deposition process is unique in that it produces an ablation layer free of pinholes that conforms well to the target surface. The rate of layer deposition is relatively fast. The disadvantages of this technique are 1) the method is material specific and works only for di-para-xylylene and its derivatives, and 2) the resultant crystalline texture of parylene introduces small-scale density fluctuations in the coating and also promotes a coarse surface finish. A coating density variation of 5 percent and a surface roughness of 1 μm work against uniform implosions of laser fusion targets, but they are characteristic of the inherent crystalline texture of pure parylene films, which are approximately 60 percent by volume crystalline.

Transforming this polymer material to an amorphous structure will cause the resulting film to be smoother, and the density fluctuations to be dramatically diminished. Because crystallization occurs simultaneously with polymerization, retardation of crystallization can be accomplished by increasing the complexity and bulky nature of the intermediate monomer stage. In fact, it has been shown that chlorine substituted monomers result in more amorphous parylene films than those obtained from unmodified di-para-xylylene.[1] At LLE, we have been modifying the structure of the di-para-xylylene starting material so that less crystalline parylene films may be obtained.

In order to limit the composition of the ablation layer to hydrocarbons, the modification of di-para-xylylene was done with alkyl groups only. As reported earlier,[2] alkyl substituted di-para-xylylenes were produced via a Freidel-Crafts electrophilic substitution using aluminum chloride as the Lewis acid.[3] (2,2) paracyclophane (di-para-xylylene) was reacted with alkyl halide in the presence of aluminum chloride and the catalyst was neutralized by hydrolysis. The resulting alkylated (2,2) paracyclophane was purified by recrystallization. With the above procedure we have prepared ethyl, isopropyl, and normal butyl (2,2) paracyclophanes whose structures have been verified by infrared and NMR spectroscopy. Since no improvement in coating surface finish is accomplished from the use of longer alkyl pendant groups and because the yield and purity of the product decreases with longer chain length, we have selected ethyl di-para-xylylene as the starting dimer of choice for our work.

Alkylation of di-para-xylylene introduces significant changes in the properties and structure of the resulting polymers. Crystallinity, melting temperature (T_m), and glass transition temperature (T_g) of the pure polymer decrease when modified. These changes are tabulated in Table 2. X-ray diffraction studies[4] indicate that alkyl modification does not alter the monoclinic unit cell structure. Unit cell dimensions of several alkyl-substituted and a chloro-substituted poly-para-xylylenes are compiled in Table 3. As this table shows, the monoclinic cell β angle is unchanged.

Polymer	T_m, °C	T_g, °C	Crystallinity %
PPX	442	180	59
Et-PPX	148	115	32
iP-PPX	64	–	–

T458

Table 2
Physical properties changes to parylene when alkylated. The addition of ethyl or isopropyl groups causes the melting and glass transition temperatures of parylene to decline. The crystallinity of the modified polymer is also reduced.

	Monoclinic Lattice			
Polymer	a(Å)	b(Å)	c*(Å)	β(degrees)
PPX	5.9	10.6	6.6	135
Et-PPX	5.9	13.4	6.5	135
iP-PPX	5.9	14.0	6.5	135

*the c-axis lies along the chain direction

T459

Table 3
Unit cell dimensions of alkylated parylenes. Only the cell length along the b-axis is affected by alkyl modification. β is the angle formed by the a- and c-axes in the monoclinic lattice.

The lengths of the a-axis and c-axis remain constant but the length of the b-axis increases with the size of the pendant group. Since the c-axis lies along the chain direction and is parallel to the layer surface, the alkylated monomer is believed to form a polymer with the alkyl pendant group aligned perpendicularly to the layer surface.

X-ray diffraction experiments show ethyl parylene to consist of finely dispersed crystallites. The diminished crystallinity achieved with our alkyl modification serves a dual purpose. The surface roughness arising from crystalline texture is greatly diminished. Figure 17 shows that the ablation layer surface smoothness is better than 1000 Å. In addition, density fluctuations within the layer are minimized.

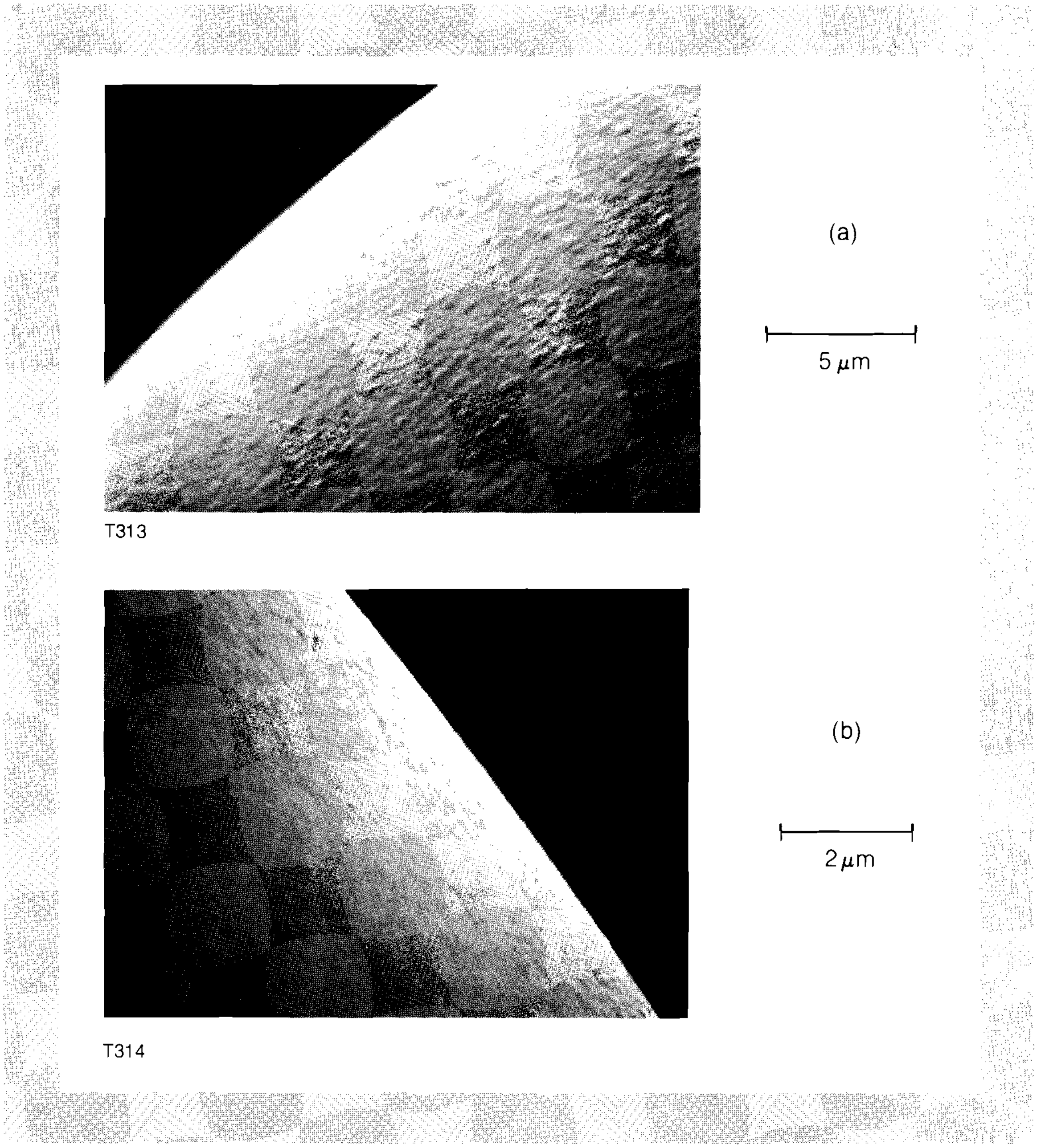
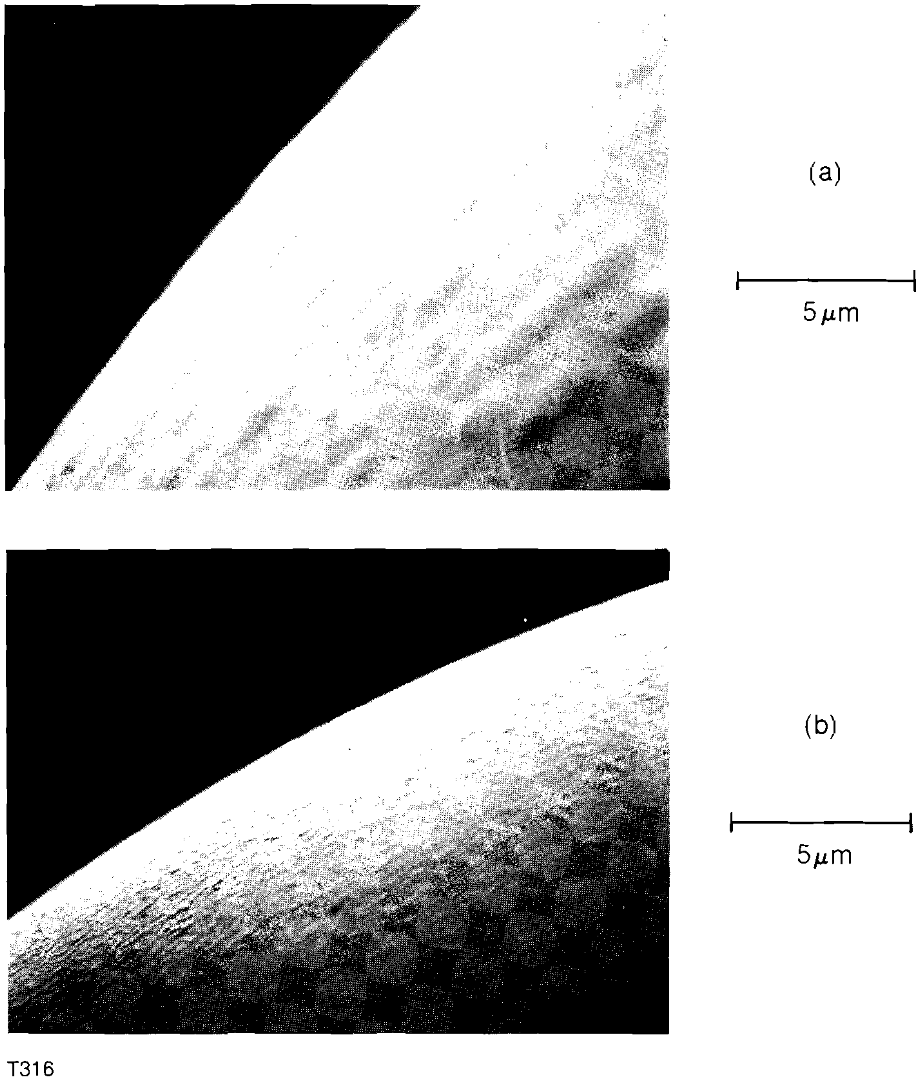


Fig. 17
Surface smoothing by alkyl modification of di-para-xylylene. The surface finish of polymer films obtained by the deposition of alkylated di-para-xylylene improves significantly due to reduced crystallinity of the polymer.
- *a) surface topology of poly-paraxylylene*
- *b) surface topology of ethyl poly-para-xylylene*

An ancillary advantage to using ethyl di-para-xylylene arises from the ability to anneal ethyl parylene because of its reduced value of T_g. The 70 percent volume fraction of ethyl parylene, which exists in a glassy state, can be made to flow by heating the coated target above T_g. Dimensional stability of the coating is retained during the annealing process because of the cross-linking provided by the dispersed microcrystalline phase. Melting of the crystal phase does not occur provided that the annealing temperatures are kept below T_m.

Geometrical surface defects can be reduced with the proper thermal annealing cycle of ethyl substituted parylene. The efficacy of annealing for the removal of cone defects[5] is shown in Fig. 18. Cone defects are frequently observed in ablation layers and originate from minute defects

Fig. 18
Annealing of ethyl parylene films. Surface tension smooths away cone defects when thermal annealing of ethyl parylene films is performed. The layer's residual microcrystallinity preserves dimensional stability during the anneal.
a) as coated ethyl parylene film showing cone defects.
b) surface after annealing at 120 degrees C for 20 hours.



on the target surface during coating. The cone defects in Fig. 18a have a lateral size of several microns. After annealing the polymer at 120 degrees C for 20 hours, these defects disappear as shown in Fig. 18b. Other defects not originally present in Fig. 18a can be seen to have formed in Fig. 18b. Of much smaller size, these new defects form during the annealing cycle and are expected to be minimized through optimization of annealing parameters.

In summary, modification of the dimer di-para-xylylene via alkylation has resulted in the deposition of ethyl parylene ablation layer coatings on fusion targets with improved surface finish (1000 **Å**) and more uniform bulk density. This accomplishment is a direct consequence of reducing the polymer crystallinity from 60 percent to 30 percent. The modified polymer allows us to reduce, by thermal annealing, cone defects present on our ablation layer surfaces.

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