Formation of a Porous, Patternable, Electrically Conducting Carbon Network by the Ultraviolet Laser Irradiation of the Polyimide PMDA-ODA (Kapton)

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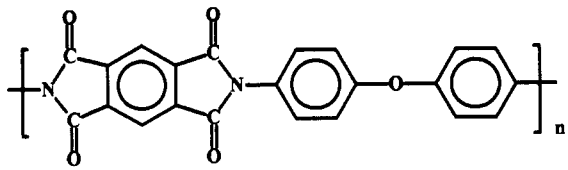
It has been known since 1965[1] that the pyrolysis of 1, which is formed by the condensation of pyromellitic dianhydride(PMDA) and *p,p'*-oxydianiline (ODA, bis(4-aminophenyl) ether)) gives rise to electrically conducting



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polymers. Two studies[2,3] on the nature of this conducting material failed to establish either the nature of this conductivity or the chemical structure that leads to it. Radiation from a continuous-wave, visible laser[4] or an excimer laser[5,6] has also been used to transform the irradiated areas of the surface to an electrically conducting material. Analytical data on the transformed material (Table 1) showed[5] that the carbon content of the product had increased from 69.1 to 91.8%. Both the oxygen and nitrogen content had diminished considerably relative to 1. The hydrogen content was found to be zero. The use of excimer laser pulses had the drawback that the process was slow and that any attempt to speed up the irradiation by the use of intensities greater than the threshold for ablation resulted in the etching of the surface rather than mere modification.

In the present work a scanning cw beam of ultraviolet (275–380 nm) laser radiation at intensities (10–1000 kW/cm^2) below the threshold for ablation were used to write patterns (typical write speed = 40 cm/s) on the surface of films of 1. Although the process proceeds satisfactorily in an air atmosphere, experiments were also conducted in a vacuum system in order to isolate and volumetrically measure the volatile products. The process is accompanied by the loss of principally CO (60.3% of gas products), CO_2 (18.8%), HCN (14.6%), C_2H_2 (11.4%) and trace amounts of methane, ammonia, ethylene, and water. The transformed product, which is black, has a composition (Table 1) similar to that reported for the material that was obtained by excimer laser irradiation but different from that reported for the pyrolysis product. At a scan speed of <10 cm/s, the black material separated as filaments (Figure 1a) from the underlying 1 that had not been transformed. On extracting these filaments with either methanol or methylene chloride, a yellow oil of low volatility was washed away. The solid residue gave a consistent analysis (Table 1) of C 95.21%, H 0.25%, and essentially 0% of nitrogen. If the balance is taken to be oxygen, this analysis corresponds to the atomic composition of C 93.7, H 2.9%, and O 3.4%. The specific conductivity of the black filaments was found to be 20–25 S/cm. This should be taken as a minimum value because the large fraction of void space in these samples which is evident in Figure 1b makes any volumetric measurement to be an underestimate of the actual value.

Table 1. Combustion Analysis on the Solid Product from the Pyrolysis and Photolysis of PMDA-ODA

sample history	C%	H%	N%	O[a]	ref
PMDA-ODA (theory)	69.11	2.64	7.33	20.93	
pyrolysis, 597 °C	84.17	2.69	7.14	5.99	8
pyrolysis, 700 °C (argon)	89	1	4	6	3
photolysis, (excimer)	91.80	0	2.8	5.4	5
photolysis in air, as obtd	92.09	0.55	1.69	5.67	*b*
photolysis in helium or in vacuo + solvent extraction	95.21[c]	0.25[d]	0.00[e]	4.54	*b*

[a] By difference. [b] This work. [c] ±0.41. [d] ±0.44. [e] ±1.65.

Scanning electron microphotographs (Figure 1b–d) of the conducting black polymer show that it is extremely open in structure as confirmed by its density of <0.1 g/cm^3. The SEM photographs at high magnification show not only the foamlike nature of the material but also that the walls are as thin as 50 nm. The intrinsic specific conductivity may exceed the value for carbon black composites and approach the values for graphitic sheets which are made from the pyrolysis of ladder polymers. The formation of such a highly conducting, patternable, porous carbon network from 1 which is *not* a ladder polymer by a high-speed process suggests many novel applications. The mechanistic implication of the formation of the black polymer in UV laser ablation and photokinetic etching has already been pointed out.[7]

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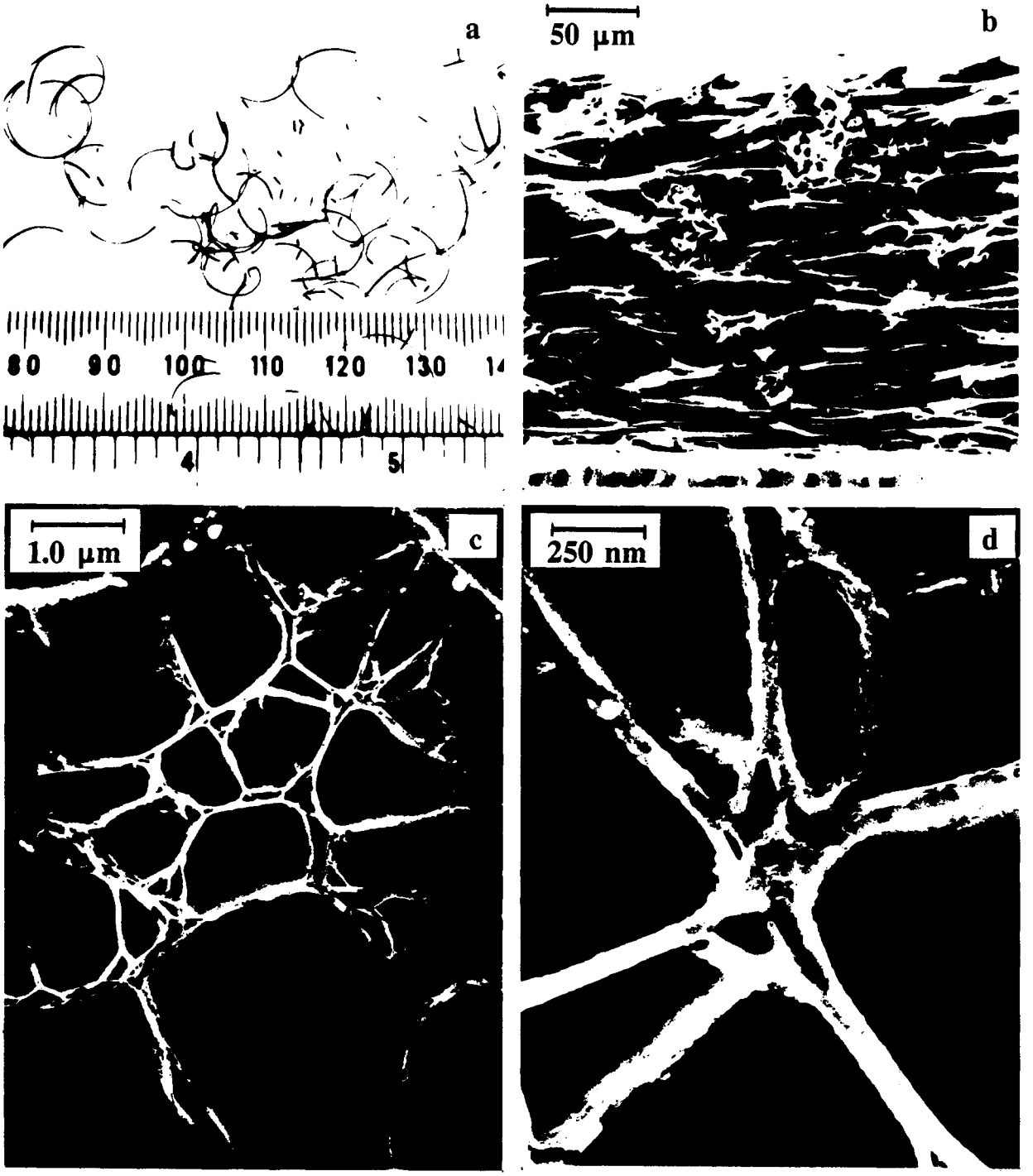

Figure 1. Microphotographs of the product of the UV laser irradiation of PMDA-ODA. (a) Filaments of black polymeric product at low magnification. (b) SEM photograph of a filament. (c) SEM photograph of a PMDA-ODA surface after irradiation (low magnification). (d) Same as c at high magnification.

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