

cannot be considered in isolation. In contrast, the individual steps of overall production must be adapted to one another. Thus the powder properties determine the suitability of the powder for a specific molding technique. That means that the developer of high-performance ceramics must be given the opportunity, as early as possible, to scale up his work in order to be able to incorporate the processing steps into the materials development with the help of parallel (and particularly nondestructive) testing methods.

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## Communications

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### Spatially Selective Conducting Patterns in Transparent Films Derived from Ladder Type Polymers\*\*

By Igal Belaish, Dan Davidov\*, Hany Selig, Malcolm R. McLean, and Larry Dalton

Conducting patterns can be created in the insulating pristine ladder type polymer films BBL and BBB (see Fig. 1) by spatially selective heating using laser annealing. The

conducting regions consist of cross-linked, stable, ladder polymers. Subsequent fluorination leads to conducting patterns embedded in a completely transparent film. These features may lead to a variety of possible applications.

In the last decades there has been significant progress in the synthesis, processing, and characterization of rigid rod polymers.<sup>[1]</sup> A few examples of such polymers are shown in Figure 1. These polymers have exceptional properties such as high tensile strength and modulus.<sup>[2, 3]</sup> They are stable at

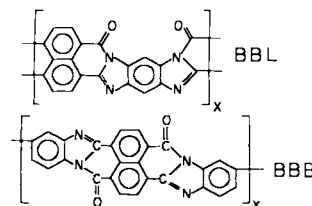


Fig. 1. Examples of ladder type polymers.

elevated temperatures (which may exceed 600 °C) and may be processed into fibers or highly packed films with excellent planar arrangements.<sup>[2]</sup> The conductivity of these rigid rod polymers can be controlled by thermal pyrolysis.<sup>[4]</sup>

Particularly, BBB polymer undergoes a phase transformation at a temperature  $T_p$  of 680 °C to a new ladder type polymer with high intrinsic conductivity.<sup>[4]</sup> Exposure of

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pristine BBB (and BBL) to fluorine leads to a colorless, transparent material, while the heat treated polymers ( $T_p > 700^\circ\text{C}$ ) are hardly affected by fluorination.

The synthesis and processing of BBB and BBL has been described previously.<sup>[1]</sup> In this work we have used free standing films as well as films on glass substrates, both having thicknesses of about 20  $\mu\text{m}$ . These films exhibit excellent planar arrangement of the polymer chains as shown by the large anisotropic resistivity  $\rho_{\perp}/\rho_{\parallel} \cong 1000$ . Here  $\rho_{\perp}$  and  $\rho_{\parallel}$  are the resistivities perpendicular and parallel to the film, respectively. Films of BBB are shiny brown and exhibit a room temperature in-plane conductivity  $\sigma_{\text{RT}}$  of  $10^{-9}$  S/cm and an optical energy gap of approximately 1.8 eV.<sup>[5, 6]</sup>

Heat treatment of ladder type polymers changes the conductivity dramatically. Figure 2a shows the in-plane room temperature conductivity,  $\sigma_{\text{RT}}$ , for BBB subsequent to heat treatment at a temperature  $T_p$  ( $200^\circ \leq T_p \leq 1000^\circ\text{C}$ ) for several minutes in a vacuum oven. As clearly seen, the room temperature conductivity changes by 10 orders of magnitude and reaches a value of 30 S/cm for  $T_p = 950^\circ\text{C}$ . Even higher in-plane conductivities were achieved for polymers with better in-plane ordering. This change in conductivity is associated with a  $\sim 30\%$  weight loss<sup>[7]</sup> and color changes. The highly conducting films are silvery-gray and stable in air.

A most dramatic change in conductivity (Fig. 2a) occurs for a pyrolysis temperature near  $T_p \cong 680^\circ\text{C}$ . Indeed, a plot

of  $d(\log \sigma_{\text{RT}})/dT_p$  vs.  $T_p$  (Fig. 2b) shows the clear maximum at  $T_p = 680^\circ\text{C}$ . We take this maximum as evidence for a transformation to a cross-linked network. Other evidence for such a phase transformation is provided by ESR studies<sup>[4]</sup> which indicate a clear maximum in the spin-density for  $T_p \cong 680^\circ\text{C}$ . Photoluminescence measurements also suggest that the high temperature conducting, condensed aromatic structure is a different ladder polymer with a smaller band gap (1.4 eV).<sup>[8]</sup>

Pristine BBB and BBL were exposed to about 400 torr  $\text{F}_2$  at room temperature. After exposure for several hours the brown shiny polymers became transparent and colorless. Optical absorption studies indicate that the energy gap is larger than 3.2 eV in the fluorinated material.<sup>[8]</sup> Infrared spectra of the product show strong absorptions in the C-F stretching region as well as absorptions in the 2900–3000  $\text{cm}^{-1}$  range indicating the presence of C-H bonds. Weight uptake measurements (Table 1) using a Sartorius

Table 1. Weight uptake of pristine BBB and BBL.

material	initial weight (mg)	weight increase (mg)	F/BBL (BBB)
BBL	6.40	6.0	$16.4 \pm 0.5$
	6.92	6.1	$15.5 \pm 0.5$
	3.80	3.4	$15.7 \pm 0.5$
BBB	12.26	13.5	$23.6 \pm 0.5$
	12.40	12.7	$22.0 \pm 0.5$
	7.49	7.0	$20.1 \pm 0.5$

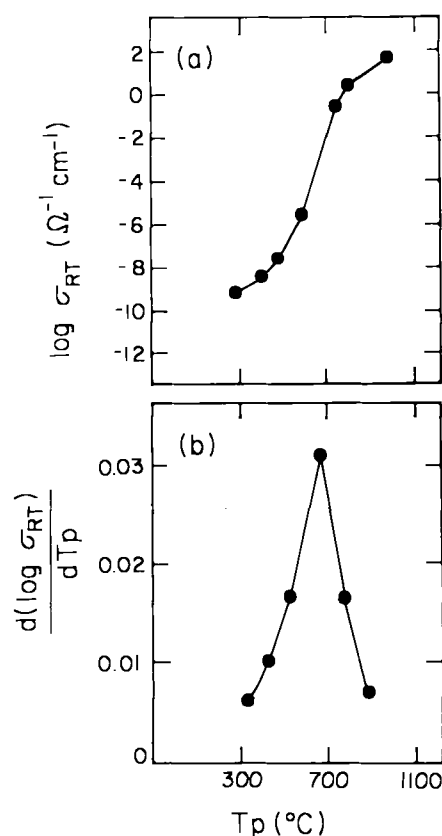


Fig. 2. a) The room temperature conductivity (but after annealing at  $T_p$ ) vs. pyrolysis temperature  $T_p$ . b) A plot of  $d(\log \sigma_{\text{RT}})/dT_p$ . Note maximum at  $T_p = 680^\circ\text{C}$ .

Magnetic Suspension Balance indicate that BBL and BBB take up about 16 and 22 fluorine atoms per monomer unit, respectively. This is exactly the number of aromatic carbon atoms per monomer unit (see Fig. 1) for BBL and BBB, respectively, suggesting formation of C-F bonds and partial or full conversion of the conjugated system to a saturated one. Exposure to air leads to a yellow transparent film after several days. The fluorinated materials are soluble in water, giving a yellow solution. Heat treated polymers ( $T_p < 600^\circ\text{C}$ ) also become transparent upon fluorination. However, *conducting polymers, heat treated at  $T_p > 700^\circ\text{C}$  are almost unaffected by exposure to fluorine and retain their high conductivity and absorbance after exposure for several days.* Exposure to higher fluorine pressure for longer periods converts the silvery-brown conducting polymers into a more bluish, rather than a transparent material. This shows that polymers heated above  $700^\circ\text{C}$  exhibit different structures. In a few cases we found that fluorination of films which had been heat treated at around  $T_p = 680^\circ\text{C}$ , may lead to transparent films with enhanced conductivities relative to pristine BBL and BBB.

The properties described above can be used to form spatially selective conductive patterns in a completely transparent film. This is achieved by shining laser light ( $\text{Ar}^\oplus$ , 2 watt/ $\text{cm}^2$ ) through a metal mask or a slit onto the BBB insulating

film on a glass substrate for several seconds. Figure 3a shows a series of embedded "conducting lines" of approximately 0.5 mm thickness in insulating BBB films treated in this way. The conductivity of these lines is approximately 50 S/cm. The conductivity of the shiny-brown polymer background remains unaffected by the laser heating. Using this masking technique, we can produce conducting lines approximately 10  $\mu\text{m}$  in width (width is determined by the slit, laser focusing and exposure time). The pattern shown in Fig. 3a is stable in air and upon subsequent heating to 200 °C. We assume that laser annealing affects the polymer mainly through heating, so the "conducting lines" are composed of cross-linked polymers with the properties described above. Upon exposure to fluorine, the "conducting lines" remain unaffected, but the remaining pristine BBB becomes completely transparent and colorless. Figure 3b pictures this new structure consisting of "conducting lines" in a transparent material. This structure is stable in a humidity-free environment.

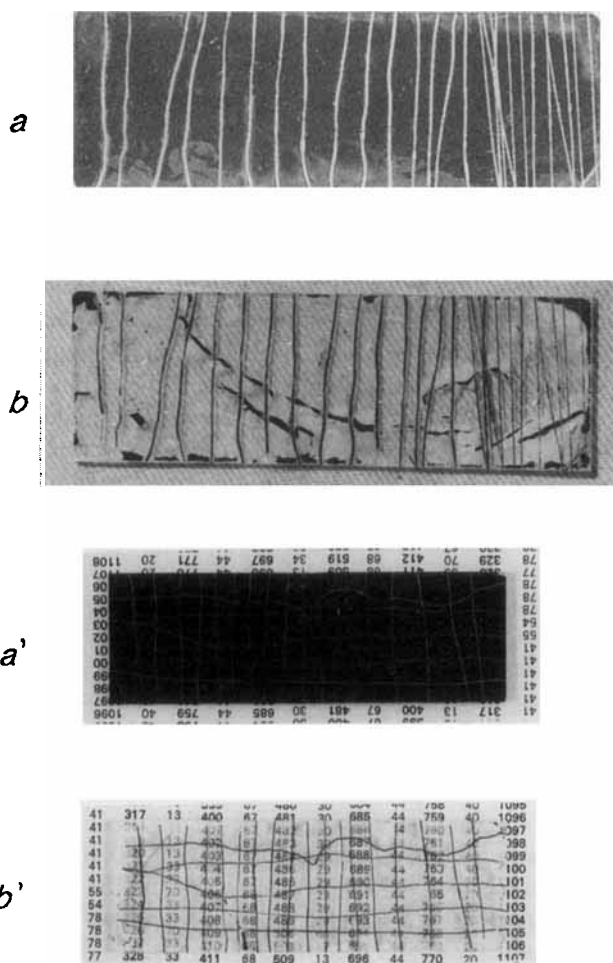


Fig. 3. a) "Conducting Lines" produced by the laser annealing technique in BBB polymer. The conducting lines are shiny-silver and reflect light and thus appear more bright in photo. a') Fine conducting lines produced by laser annealing of BBB. b) After fluorination: The "conducting lines" in a transparent film. b') Same as a', but after fluorination. (Numbers in background shown to emphasize degree of transparency).

We have now preliminary evidence that the heating and fluorination process affects other rigid-rod polymers as well. The transparent films so produced are optically anisotropic and less affected by humidity. The fluorination of polyacetylene was published recently<sup>[9]</sup> but in this case the fluorinated material is white rather than transparent.

The possibility to produce highly aligned transparent films with anisotropic optical properties and particularly the generation of spatially selective conductive patterns in insulating aligned transparent polymers opens new routes for applications in fields such as lithography, microelectronics, optics and molecular electronics. For instance, "writing" using selective laser heating and eliminating the rest of the film by fluorination and washing (using water or other solvents) might be important in both lithography and microelectronics. The fabrication of very fine grids composed of fine alternate stripes of conducting and transparent polymers with anisotropic optical properties is another interesting possibility. Optical disks should be considered as well. Generally speaking, the possibility to fabricate miniature conducting microstructures with novel electronic properties is now more realistic.

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### Highly Conjugated, Substituted Polyacetylenes via the Ring-Opening Metathesis Polymerization of Substituted Cyclooctatetraenes\*\*

By Christopher B. Gorman, Eric J. Ginsburg, Seth R. Marder, and Robert H. Grubbs\*

Soluble, highly conjugated polymers such as substituted polythiophenes, poly(*p*-phenylene vinylenes),<sup>[1]</sup> and most

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