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# Percolation of Conducting Polymers on a Gel

Recently, Fizazi et al.[1] studied percolation of conducting polymers in a polymer gel. They reported evidence of conducting paths at extremely small volume fractions of conducting polymer—orders of magnitude below that required for percolation of the soluble conducting polymer alone. In this letter, we propose an explanation for this phenomenon based upon two-dimensional continuum percolation of conducting polymers on the surface of the preexisting network of gel.

In the experiment by Fizazi et al.,[1] the conducting gel of high molecular weight polyethylene and the conjugated polymer poly(3-octylthiophene) was prepared by thermoreversible gelation from semidilute solutions in decalin and subsequent doping with iodine. The morphology and structure of gels produced by quenching semidilute solution of high molecular weight polyethylene in decalin were reported by Smith et al.[2] They showed evidence that the polyethylene network is composed of interconnected fibrillar and lamellar crystals.

Since the conducting polymer adsorbs onto the mechanically connected gel network after the crystallization of the polyethylene, the formation of conducting paths occurs on the surfaces of such fibrillar and lamellar crystals, which we assume themselves constitute fully percolating pathways in the system for the adsorbed polymer. Therefore, this percolation problem becomes two dimensional.

The continuum percolation threshold in two dimensions is inversely proportional to the excluded area.[3] The conducting polymer adsorbed onto the crystals may form rod or pancake morphologies.[4] The excluded area for those structures is $l^2$, where $l$ corresponds to the length of the rod or the gyration radius of the pancake. The area fraction for percolation, $\phi_c$, is expressed with a coefficient of order unity, $\alpha$, as

$$\phi_c = \alpha s / l^2 \qquad (1)$$

where $s$ denotes the actual surface area occupied by the conducting polymer: For a rod, $s \cong al$; for a pancake, $s \cong l^2$, where $a$ denotes a monomer size of the conducting polymer.

The volume of the conducting polymer at the threshold is expressed with the surface area of the gel-constituting structural elements, $A$, as

$$\nu_c \cong A \frac{\alpha s}{l^2} a \qquad (2)$$

The volume of the polyethylene gel network is expressed in terms of $d$, which denotes the diameter of the fibrillar crystals or the thickness of the lamellar crystals:

$$V = Ad \qquad (3)$$

Thus the volume ratio between conducting polymer and gel at the threshold is

$$\rho_c = \upsilon_c / V \qquad (4)$$

The critical volume fraction of conducting polymer for percolation in the gel is expressed in terms of the volume fraction of the gel, $\Phi_0$, as

$$\Phi_c = \rho_c \Phi_0 \qquad (5)$$

$$= \frac{a^2}{dl} \alpha \Phi_0, \quad \text{for a rod} \qquad (6)$$

$$= \frac{a}{d} \alpha \Phi_0, \quad \text{for a pancake} \qquad (7)$$

According to the studies by Smith et al.,[2] $d$ is approximately 100 Å. The molecular weight of poly(3-octylthiophene) and the volume fraction of the polyethylene gel used by Fizazi et al.[1] are $M_w \approx 89\,000$ and $\Phi_0 = 2 \times 10^{-2}$, respectively. Hence, we deduce $a \approx 3$ Å and $l \approx 1000$ Å for a rod and $l \approx 100$ Å for a pancake. Thus, we obtain $\Phi_c \approx 2 \times 10^{-6}\, \alpha$ for a rod and $\Phi_c \approx 6 \times 10^{-4} \alpha$ for a pancake. The reduced percolation threshold is due to the adsorption of the conducting polymer on the surfaces of the gel. For rod morphology, there is an additional lowering of the threshold due to the small threshold for one-dimensional objects. In principle, the rod and pancake morphologies of the conducting polymer could be differentiated by a neutron-scattering experiment with labeled molecules. The optical properties of the conducting polymer may also depend on the morphology.

This simple argument is consistent with the observation of Fizazi et al.[1] that there was no indication of a percolation threshold in their experiment even at the extremely small volume fraction (less than $5 \times 10^{-4}$) of the conducting polymers.

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## References and Notes

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