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The applicability of a percolation model to photoconductivity in guest–host thermotropic nematic liquid crystal systems

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Photoconductivity is investigated for a thermotropic nematic low molar mass liquid crystal which has been doped with carbazole, a known photoconductor. The dopant is oriented by a guest–host mechanism and is studied as a function of concentration. Threshold levels of photoconductivity occur at levels three orders of magnitude below that predicted from simple percolation theory. Some possible explanations for this as well as its implications are proposed.

I. INTRODUCTION

Since the idea was proposed some ten years ago that random walk efficiency on a percolating cluster increases drastically with increasing occupied site concentration, the percolation model has enjoyed considerable success as a unifying description of transport properties for multicomponent and multiphase materials.[1] This interest has motivated the publication of several comprehensive reviews.[2–4] The essence of the model[5,6] is that for small concentrations of guest impurities, macroscopic diffusion will not be possible since the guests will behave as isolated entities or independent clusters. When the fraction of active sites p exceeds some critical percolation threshold p_c there is a finite probability P_∞ that an infinite cluster appears. Only if a percolating network exists, i.e., $p > p_c$ will the lattice have a nonzero bulk electrical conductivity. Above the threshold the weight of the infinite cluster $P_\infty(p)$ increases with the power β:

$$P_\infty(p)\,\alpha(p-p_c)^\beta\,, \tag{1}$$

where β is predicted to be 0.45 and p_c to be ~ 0.2 by numerical simulation on three-dimensional systems.

The electrical conductivity Ω^{-1} above the threshold varies as

$$\Omega^{-1} = \Omega_0^{-1}(p-p_c)^t\,, \tag{2}$$

where p is now the fraction of conducting lattice sites. This is an example of dynamic percolation. The value of t is 1.7–2.0, which remembering that $p \ll 1$, means that the conductance increases much more slowly than the weight of the infinite cluster. This is due to the presence of dangling ends in the network as well as contorted paths which the current must follow.

The reasonableness of such a model has been verified in two dimensions using transmission electron microscopy on thin vapor deposited gold films and comparing the visual formation of the infinite cluster with the onset of electrical conductivity as a function of p.[7]

The percolation model has been used successfully, e.g., in describing the electrical conductivity of thermoplastics doped with insoluble dendritic crystals of one-dimensional organic conductors,[8] the photoconductivity of dissolved chromophores in polycarbonate,[9] the conductivity of mixtures of discrete conductive and insulating particles,[10] and the conductivity of ionomer membranes.[11]

Similarly, Kopelman has applied the model in a series of papers to describe exciton migration dynamics in mixed crystal guest–host systems. Phenomena of interest are the diffusion, followed by the trapping[12–17] and annihilation[18–20] of singlet and triplet excitons as modeled through the fluorescence and phosphorescence emission intensities.

II. RESULTS

Based on the above it was decided to recast recent results emanating from this laboratory exploring the photoconductive properties of thermotropic liquid crystals in terms of a percolation model.[21,22] These liquid crystals were doped with varying amounts of carbazole, a known photoconductor. The nematic state of the liquid crystalline phase enables the dissolved carbazole dopant to be favorably aligned with respect to orientation by a guest–host mechanism in a mono-domain uniaxial array. The liquid crystals employed in this investigation were NP-1132 and RO-TN-651 courteously supplied by Merck and Hoffmann–La Roche, respectively, and were chosen because of their nominal transparency at 335 nm where the carbazole was pumped. This system showed markedly enhanced levels of photoconductivity at low carbazole concentrations, and surprisingly, even some photoconductivity in the undoped state where the absorption is minimal, but apparently nonzero. These results were interpreted in terms of the favorable influence of long range orientational order of the carbazole dopant on the electrical conduction.

Since the dopant in the nematic phase is otherwise randomly distributed with respect to position and the morphology of the aligning matrix can be carefully controlled, it appears that this represents an interesting system on which to investigate the applicability of a percolation model to an anisotropic material. While the carbazole guest dopant will be subject to positional and angular fluctuations associated with the dissolved nature of the guest–host system, it will otherwise be free of traps inherent in many polymers due to structural impurities, e.g., imperfect tacticity, head-to-tail disorder, and conformational multiplicity.

In applying percolation theory to model the photoconductivity of this type of system, we make the implicit assumption that the magnitude of the steady state photoconductivity Ω^{-1} follows Eq. (2). The dependence of the photoconductivity on the carbazole concentration c, expressed in molarity M, in RO-TN-651 is shown by the upper

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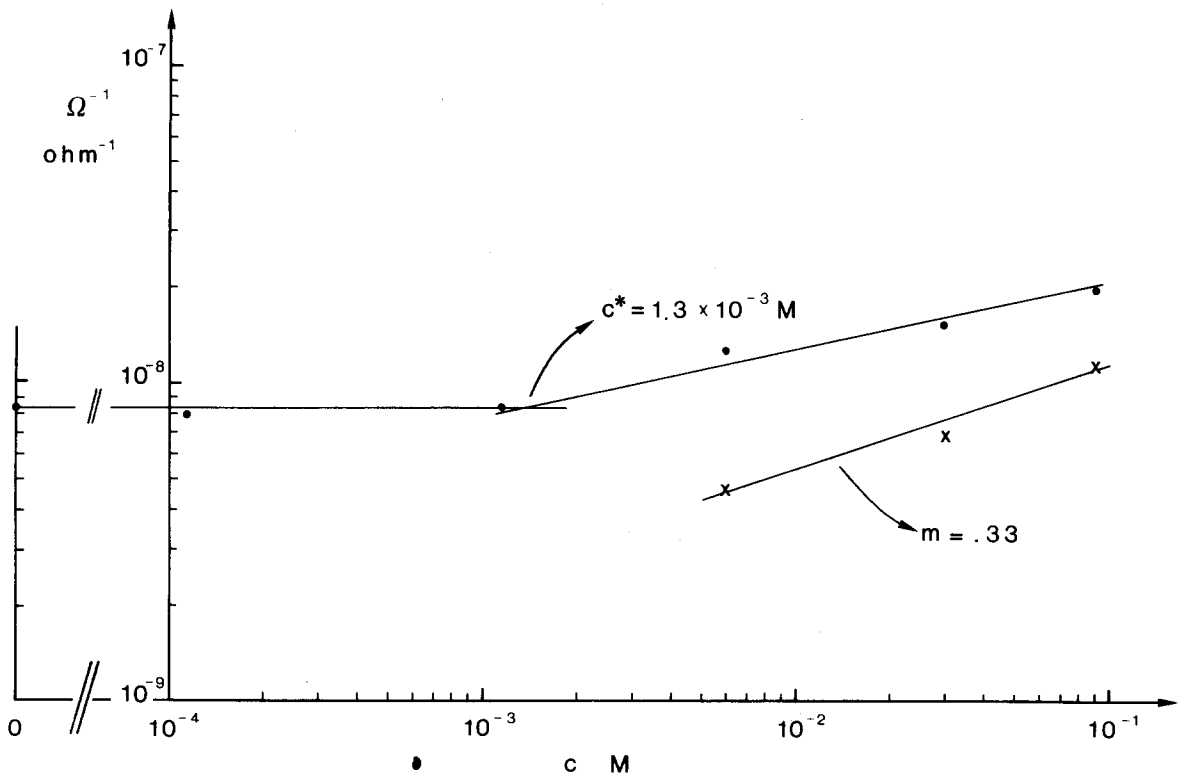

FIG. 1. There is no dependence of photoconductivity on carbazole concentration for RO-TN-651 for a cell of thickness 23 μm subjected to a 10 V electric field. See the text for further clarification. (•) represent raw conductivity data as measured as a function of concentration C, given in molarity M. C^* is the threshold concentration as given by the intersection of the two lines. (×) represent raw data above the threshold value C^*, from which the horizontal line for $C < C^*$ has been subtracted. m is the experimentally determined slope of this new line defined by (×).

curve of Fig. 1. In accordance with the expectations of a percolation model a critical threshold concentration C^* exists below which there is no concentration dependence, and is given at the intersection of the two straight lines. This value expressed in molarity of carbazole is determined to be 1.3×10^{-3} M or ~0.02% w/v. The lower curve in the figure is the concentration dependence of the photoconductivity from which the value of the photoconductivity in the low concentration limit has been subtracted. It was not possible to obtain data at higher concentrations due to limited guest solubility. The regression line drawn with a correlation coefficient of 0.978 has a slope m equal to 0.33.

In order to evaluate this data in terms of a percolation model it is necessary to convert the units for the threshold concentration from molarity to fraction of occupied lattice sites. By assuming the molar volume of carbazole and liquid crystal to be comparable, p is given approximately by the volume fraction of carbazole in the system, giving

$$p_c \cong \frac{C^* \cdot \mathrm{MW}}{1000\rho} \cong 2.2 \times 10^{-4}, \tag{3}$$

where MW is the molecular weight (g/mol) and ρ is the density (g/ml).

III. DISCUSSION

A comparison of these results with theory indicates that this system is much more efficient with respect to the effectiveness of guest molecule activity than would be predicted, i.e., p_c is fully three orders of magnitude smaller and the measured critical exponent is a factor of 5 less than that anticipated. While Ottavi *et al.*,[10] Bässler,[9] and Wódzki *et al.*[11] have found good agreement with theory, Kryszewski *et al.*[8] found a critical concentration of 0.2%, i.e., much smaller than predicted and only a factor of 10 greater than that found here. Their system involved the study of percolation currents transported through hetero-phase charge transfer "metallic" crystals of TTT (tetra-this-tetracene)-TCNQ in polycarbonate matrices. There was difficulty in rationalizing this behavior in terms of the dendritic morphology, implying distributional correlation to make the formation of the infinite cluster more probable than would be expected from statistical mixing.

An explanation for the increased chromophore efficiency in promoting photocurrents in thermotropic liquid crystals is lacking at this writing and additional experiments need to be performed. The following speculations are put forth, however:

(i) The "effective" chromophore concentration can be greater than the actual due to the contribution of diffusion in the low viscosity liquid crystal. This is analogous to the diffusional contribution observed in fluorescence quenching processes.[23]

(ii) The orientational correlations in the nematic phase facilitate the photoconduction process, e.g., by a contribution from exciton migration prior to the dissociation to form the charge carrier.[24] Förster energy transfer is angularly dependent on $\cos^2 \theta$ for the implicated transition moments and will accordingly be facilitated in nematic systems with their

large order parameters. Exciton migration could thus occur by a long range percolation process in which isolated clusters could be effectively joined. Critical distances for energy migration of this type are of the order of 50–100 Å, i.e., ~25–50 lattice sites, and the dependence on distance for Förster hopping, r^{-6}, would conserve the threshold-like feature of the concentration dependence. Long range percolation effects have been noted for triplet exciton migration in mixed crystals[25] and have been the object of modeling studies.[26,27] These studies show that the apparent percolation threshold p_c is strongly dependent on the interaction range. Charge carrier mobility might also be expected to be increased by the nonzero order parameter[28] making it desirable to perform time-of-flight experiments on this kind of system.

(iii) There are distributional correlations making the formation of the infinite cluster more probable than would be expected from statistical mixing.

IV. IMPLICATIONS

It would appear to be of fundamental importance for biological systems, with their high degree of organization, that photoconductivity in ordered systems exceeds the effectivity predicted by percolation theory.[12,29–31] Included in this consideration are related areas such as Langmuir–Blodgett films, membrane mimetic chemistry,[32] and molecular electronic devices.[33] The expected advantages of using anisotropic materials with well defined morphologies for device applications has been expounded upon.[34–36]

V. CONCLUSION

The concentration dependence of the photoconductivity for nematic thermotropic phases doped with photoconductive chromophores greatly exceeds the efficiency predicted by simple percolation theory.

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