Percolation on a Self-Assembled Network: Decoration of Polyethylene Gels with Conducting Polymer

A. Fizazi, J. Moulton, K. Pakbaz, S. D. D. V. Rughooputh, Paul Smith, and A. J. Heeger

Institute for Polymers and Organic Solids, University of California at Santa Barbara,
Santa Barbara, California 93103

Conducting gels of ultrahigh-molecular-weight polyethylene (PE) and the soluble conjugated polymer poly(3-octylthiophene), P3OT, were prepared by thermoreversible gelation from semidilute solutions in decalin, and subsequent doping with iodine. We report the results of frequency-dependent complex conductivity measurements (from 1 kHz to 1 GHz) on these gels. Although the volume fraction of P3OT in the gel ranged from less than 5×10^{-4} to about 3×10^{-2}, we found evidence of connected conducting paths with no indication of a percolation threshold. The results are discussed in terms of adsorption of the P3OT onto the preformed PE gel network which organizes the P3OT into connected paths.

The study of connected pathways through percolation theory has provided important insight into the condensed-matter physics and materials science of composite systems. Two particular examples are the following: (1) application of percolation theory to the mechanical properties of gels made up from interacting macromolecules dissolved in a solvent; and (2) application of percolation theory to the electrical conductivity of composites made up of conducting material in an insulating medium. In the first case, the system behaves as a complex fluid at polymer volume fractions below the critical percolation threshold. However, at volume fractions sufficiently high that the interacting macromolecules form an infinite connected pathway, a gel is formed in which the connected polymer network becomes rigid and exhibits a finite shear modulus. In the second case, the system behaves as an insulator at volume fractions of the conductor below the critical percolation threshold. However, at volume fractions sufficiently high that the conducting regions form an infinite connected pathway, uninterrupted electronic transport can occur, and the composite exhibits a finite electrical conductivity.

By using soluble conducting polymers, both shear rigidity and electrical conductivity can, in principle, be realized simultaneously with the formation of conducting gels. It is of interest, however, to consider percolation of a conducting polymer on the preexisting network of a polymer gel. Since the conjugated polymer may adsorb onto the mechanically connected gel network, the formation of conducting paths may be guided by (or assembled by) the preexisting network. In this way, one can envision obtaining conducting gels at volume fractions of a conducting polymer far below that required for percolation (gelation and conductivity) of a soluble conducting polymer alone.

In this paper, we present initial studies of conducting gels made by decorating the connected paths of a gel of ultrahigh-molecular-weight polyethylene [~1%-3% ultrahigh-molecular-weight polyethylene (UHMW PE)

in decalin] with a conducting polymer. We report the results of frequency-dependent complex conductivity measurements on these gels over the frequency range from 1 kHz to 1 GHz. Although the volume fraction (f) of P3OT, poly(3-octylthiophene), in the gel ranged from below 5×10^{-4} to about 3×10^{-2}, we found evidence of connected conducting pathways even at $f = 5 \times 10^{-4}$, with no indication of a percolation threshold. The conductivity is constant at low frequencies, crossing over to the well-known ω^s power law characteristic of transport in disordered systems.

The gels were prepared by first dissolving the desired amount of the soluble conjugated polymer[1] P3OT, along with an antioxidant (IRGANOX 1010), into decahydronaphthalene (decalin), which resulted in a yellow solution. The P3OT was provided by Dr. J.-E. Osterholm of Neste, Finland; the molecular weight was determined by gel permeation chromatography to be $M_w \approx 89\,000$ with a polydispersity index $M_w/M_n \approx 3.3$. To prepare the UHMW PE gels,[2] the temperature of the solution was raised to $\approx 105\,°C$, at which point a proper amount (e.g., 2% by weight) of powdered, ultrahigh-molecular-weight polyethylene (Hostalen GUR 415; $M_w \approx 4 \times 10^6$) was added. While stirring continuously, the temperature was raised further until the mixture became viscous ($\approx 117\,°C$). The stirring was then stopped, and the temperature of the solution was raised to $150\,°C$. The solution was left standing at this temperature for 2 h to allow optimal dissolution of the PE. The polyblend solution was subsequently left to cool to room temperature to form a red gel. All of the above procedures were conducted under an atmosphere of dry nitrogen. The gels were doped by exposure to iodine vapor; doping was accomplished by simply placing the gel in a closed container with iodine under a nitrogen atmosphere at room temperature.

Figure 1 shows a log-log plot of the conductivity as a function of frequency $\omega/2\pi$ for several PE-P3OT gels (each with 2 wt% UHMW PE) containing different
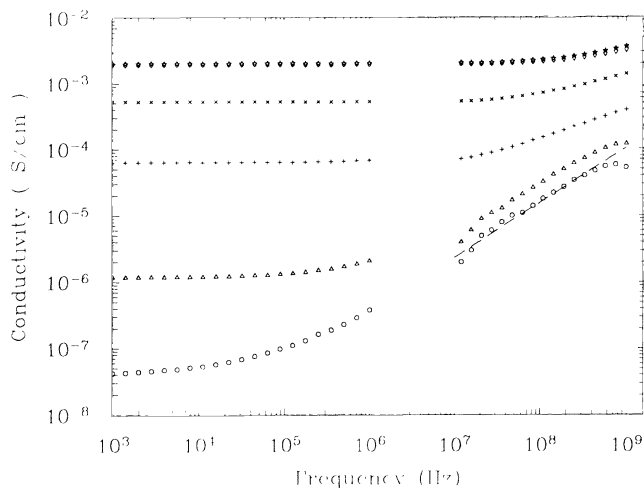
FIG. 1. A log-log plot of the conductivity of the gel as a function of frequency, for several PE-P3OT gels (each with 2 wt% PE) containing different volume fractions f of P3OT: $f=5\times10^{-4}$ (o), $f=1.1\times10^{-3}$ ($\triangle$), $f=5\times10^{-3}$ (+), $f=1.3\times10^{-2}$ ($\times$), $f=2\times10^{-2}$ ($\star$), and $f=3\times10^{-2}$ ($\diamond$).
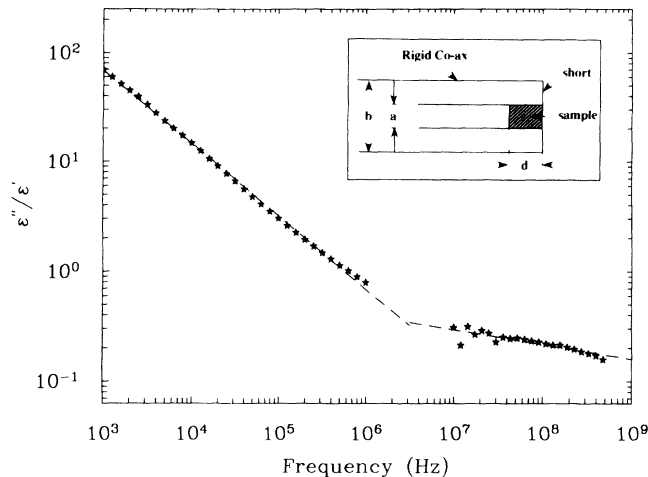

FIG. 2. The ratio $\sigma/\omega\epsilon'$ as a function of frequency for the gel with $f=1.1\times10^{-3}$. Inset: A sketch of the rigid coaxial line used for the measurements; the sample was inserted between the inner conductor and a terminating short.

volume fractions of P3OT. The complex impedance measurements were performed using a Hewlett-Packard 4192A impedance analyzer in the frequency range from 1 kHz to 1 MHz, and a Hewlett-Packard (HP) 4191A impedance analyzer for frequencies from 10 MHz to 1 GHz. The reflection method was used, with the sample inserted between the inner conductor and a terminating short in a rigid coaxial line (excited in a TEM mode) as sketched in the inset to Fig. 2 ($a=3.04$ mm, $b=7.0$ mm, and $d=1.15$ mm).

The impedance of the equivalent lumped circuit can be represented as a complex sample capacitance (C_0) in parallel with the fringe capacitance (C_F) of the line,[3]

$$C=C_0+C_F=\pi a^2\epsilon_0\epsilon/4d+2a\epsilon_0\ln(b-a)/2d , \qquad (1)$$

where ϵ is the complex permittivity of the sample ($\epsilon=\epsilon'-i\epsilon''$), and ϵ'' is proportional to the conductivity, $\epsilon''=\sigma/\omega\epsilon_0$. The value of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are calculated from the measured amplitude and phase. The instruments are calibrated with an open circuit, a short, and a matched load in place of the sample. For low-temperature measurements, the sample cell was cooled using a cold finger with the temperature controlled by nitrogen gas. Data acquistion and storage were automatic and carried out using an HP PC305 linked to the impedance analyzers.

Figure 1 shows that for all volume fractions of conducting polymer, the conductivity is essentially constant at low frequencies. Beyond a crossover frequency ω_c, σ increases monotonically with a power-law dependence,

$$\sigma=c_1\omega^s , \qquad (2)$$

where c_1 is a constant. At the lowest concentrations,

$s\approx0.8$, typical of an amorphous conductor;[4] the dashed line in Fig. 1 has a slope of 0.8. Because of the large frequency-independent contribution and the high cross-over frequency, it is difficult to obtain the limiting slope at higher concentrations; however, after subtracting the frequency-independent contribution, the data are consistent with s being only weakly dependent on f. The $\sigma(\omega)$ results were reproducible; different samples, doped independently by exposure to iodine, and then cut for ac-impedance measurements gave results that agreed within 15%.

Since a power law with $0<s<1$ is the only function invariant under the Kramers-Kronig transformation,[5] Eq. (2) implies that the real and imaginary parts of the complex dielectric function should have the same frequency dependence, and that the ratio ϵ''/ϵ' ($=\sigma/\omega\epsilon_0\epsilon'$) should be constant. In Fig. 2, we plot ϵ''/ϵ' as a function of frequency for the gel with $f=1.1\times10^{-3}$. In the high-frequency regime above ω_c, ϵ''/ϵ' is nearly constant ($\sim\omega^{-0.1}$). At low frequencies, where both σ and ϵ' approach constant values, ϵ''/ϵ' decreases approximately as $\omega^{-0.7}$ (if σ and ϵ' were precisely constant, the low-frequency dependence would be $\sim\omega^{-1}$).

The percolative aspect of the conducting network[6] is shown in Fig. 3 where we plot the conductivity as a function of the volume fraction of conducting polymer for two frequencies, 1 kHz and 1 GHz. The 1-kHz data characterize the low-frequency regime (below ω_c) in which the transport is independent of length scale; the 1-GHz data are in the power-law regime (above ω_c) in which the conductivity is strongly sensitive to length scale. Although no specific percolation threshold was observed, for volume fractions of P3OT less than $f\cong2.5\times10^{-4}$ the 1-kHz conductivity was too small to measure with the shorted-coax configuration. The con-
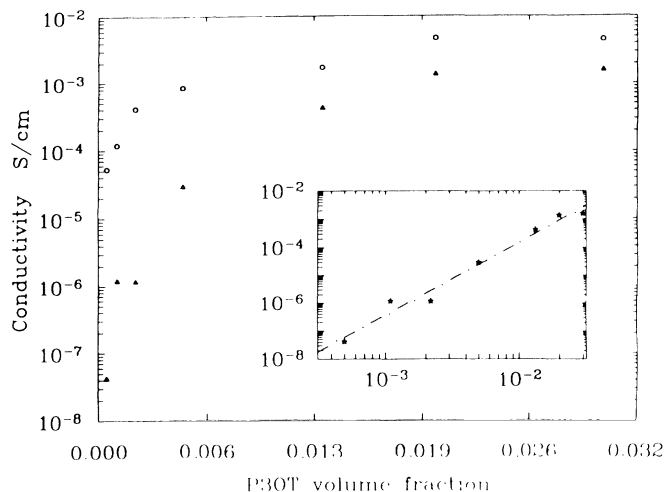
FIG. 3. The conductivity as a function of the volume fraction of conducting polymer for two frequencies, 1 kHz and 1 GHz. Inset: A log-log plot of the conductivity (at 1 kHz) vs volume fraction of P3OT.

ductivity increases by several orders of magnitude for f in the range $5 \times 10^{-4} < f < 3 \times 10^{-2}$. For f greater than approximately 2×10^{-2}, the conductivity of the network saturates toward values in the range $\sigma \sim 10^{-3}$–10^{-2} S/cm.

The inset to Fig. 3 is a log-log plot of the 1-kHz conductivity versus volume fraction of P3OT. The results indicate that over a relatively wide range of concentrations, the conductivity follows a simple power law previously observed for polyaniline–poly-p(phenylene terephthalamide) systems,[7]

$$\sigma = c_2 f^\alpha , \qquad (3)$$

where c_2 is a constant and $\alpha \approx 2.6$. The dashed curve in Fig. 2 shows the power-law fit to the 1-kHz data with $\alpha \approx 2.6$.

Percolation theory[6] predicts that at concentrations sufficiently dilute so that there are no connected paths, the conductivity is zero. As f is increased above the percolation threshold (f_p), the conductivity becomes finite and increases as the connectivity (i.e., the number of conducting paths) increases. In contrast, the data presented in Fig. 3 show no indication of a well-defined percolation threshold. By attempting to fit the data by the form $\sigma = c_2 (f - f_p)^\alpha$, we conclude that $f_p < 2.5 \times 10^{-4}$ P3OT. By contrast, classical percolation theory[6] for a three-dimensional network of conducting globular aggregates in an insulating matrix predicts a percolation threshold at a volume fraction $f_p \approx 0.16$, in agreement with results obtained for composites of poly(3-alkylthiophene) in polystyrene[8] and for other conducting polymer composites.[9]

The exponent α has been calculated within percolation theory.[10] Assuming an idealized fractal structure near the percolation threshold, one can estimate $\alpha \approx 1.87$

for a three-dimensional system and 1.33 for a two-dimensional system. The experimental value $(\alpha \approx 2.6)$ is somewhat higher.

Two other observations help clarify the nature of the P3OT-UHMW PE gels. First, the conjugated polymer is not expelled from the gel when stored in a larger volume of decalin, even for the lowest concentrations of P3OT. Since decalin is a good solvent for P3OT, this result is important and implies that the conjugated chains are either adsorbed onto or entangled within the PE network. Second, we have observed that the color of the P3OT-UHMW PE solution changes gradually from yellow to red as the temperature is lowered and gelation occurs. A color change from yellow (the color of P3OT in solution) to red (the color of solid crystalline films) is well known[11] for poly(3-alkylthiophenes). Reversible, disorder-induced thermochromism (red-to-yellow color change) has also been observed even in solid films;[12] in this case, it appears that the disorder is due to side-chain melting.[13] Thus, the red color of the gel suggests the adsorption of relatively well-ordered P3OT chains onto the PE network, since more complex entanglement of the conjugated polymer would lead to sufficient disorder to cause the P3OT to retain a yellow color. An extensive study of the spectroscopy of the P3OT-UHMW PE gels will provide more detailed information on the electronic structure of the conducting polymer during gel formation and in the gel.

Measurements of the conductivity were carried out on doped P3OT *solutions* at concentrations up to 5×10^{-3}. Since the P3OT solutions would be expected to gel when the concentration exceeds that required for chain overlap,[14] $f = 5 \times 10^{-3}$ must be below the overlap concentration. Although the conductivity of the *solutions* was below our limit of detectability, the corresponding PE-P3OT gels *do* conduct, even at a concentration 1 order of magnitude lower. This implies that the very small threshold for the onset of conductivity in the PE-P3OT gels results from decoration of the PE network by the P3OT chains leading to the percolative behavior of the conductivity.

Preliminary measurements of the temperature dependence of the electrical conductivity of the P3OT-UHMW PE gels have been carried out. The gel becomes a frozen glass at temperatures well below the melting point of pure decaline, $-43\,^\circ$C. Since the conductivity remains high in the frozen glass, and since there is no discontinuity in $\sigma(T)$ when the gel freezes, the measured conductivity must be of electronic (rather than ionic) origin. This is consistent with the fact that the conductivity of the doped solutions was below our limit of detectability. Details on the temperature dependence will be published elsewhere.

In summary, we have used ac-impedance measurements (1 kHz to 1 GHz) to study the percolation of a conducting polymer on the preexisting network of a polymer gel. Since the P3OT adsorbs onto the mechanically

connected gel network, the formation of conducting paths is organized by the preexisting network. The σ vs ω data are typical of an amorphous conductor: constant at low frequencies and crossing over to a power-law dependence, $\sigma \sim \omega^s$, with $s \approx 0.8$ at high frequencies. Over a relatively wide range of concentrations, the conductivity follows a simple power law $\sigma \sim f^\alpha$, where $\alpha \approx 2.6$, demonstrating connected conducting paths with no indication of a percolation threshold even at fractional volumes of conducting polymer as low as 5×10^{-4}. For f greater than approximately 2×10^{-2}, the conductivity of the network saturates to values in the range $\sigma \sim 10^{-3} - 10^{-2}$ S/cm.

The relatively highly conducting gels described in this Letter constitute a novel state of matter with an unusual combination of properties. The use of a preexisting gel network to guide the formation of conducting paths at volume fractions which are orders of magnitude below that needed for bulk percolation may be a useful method for achieving conducting composites with a small volume fraction of conducting polymer.[7]

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