

# Articles

## Conductivity Percolation in Polyiodide/Polymer Complexes

Maria Forsyth, Duward F. Shriver,\* Mark A. Ratner, Donald C. DeGroot, and Carl R. Kannewurf

Northwestern University, Departments of Chemistry, Electrical Engineering and Computer Science and Materials Research Center, Evanston, Illinois 60208

Received September 18, 1992. Revised Manuscript Received June 8, 1993

Variable-temperature four-probe conductivity measurements and Raman spectroscopy were investigated for iodine in poly(propylene oxide) (PPO) and  $\text{NaI}_3$  in PPO. The Raman spectra indicate the presence of both triiodide and polyiodide species in samples of  $\text{I}_2$ -doped PPO. The conductivity of these PPO/ $\text{I}_2$  samples increased with increasing  $\text{I}_2$  concentration and reached a plateau at approximately 12 vol % iodine. Raman spectra at 20 °C indicate that, at concentrations less than 23 vol %  $\text{I}_3^-$ , the dominant species is the triiodide. Polymer salt complexes with varying amounts of  $\text{I}_3^-$  appear to display a conductivity threshold near  $T_g$ , at 0.2 vol fraction of triiodide.

### Introduction

Polymer electrolytes generally involve an alkali-metal salt dissolved in a polyether-based polymer.<sup>1</sup> These materials are ionically conducting and application of a dc potential will result in ion polarization, and hence the current will decay to zero. The addition of  $\text{I}_2$  to these polymer-salt complexes can increase the conductivity by several orders of magnitude.<sup>2-4</sup> In contrast with simple polymer-salt complexes application of a dc potential from blocking electrodes across the  $\text{I}_2$ -containing material results in a *nonzero* current that does not decrease with time. These systems behave as electronic conductors. The possible mechanism of conduction has been presented elsewhere<sup>3</sup> and is discussed briefly below. Similarly,  $\text{I}_2$  in polar solvents such as the pure polyethers produces significant conductivities in otherwise insulating materials.<sup>3</sup> Electronic conduction has also been observed upon addition of iodine to unsaturated polymers such as poly(ethylenepyrrrolediyl) and *cis*-poly(isoprene).<sup>5</sup> In such systems, iodine oxidizes the polymer backbone resulting in cationic species. These are apparently responsible for the observed electronic conductivity rather than the polyiodide formation.

Raman spectroscopy indicates that on addition of  $\text{I}_2$  to a polymer-metal iodide complex or indeed even to a pure polymer, two vibrations are observed at approximately 110 and 170  $\text{cm}^{-1}$ . These have been assigned to  $\text{I}_3^-$  symmetric stretching and polyiodide (i.e.,  $\text{I}_5^-$ ,  $\text{I}_7^-$ , etc.) species, respectively, with the ratio of these two peaks being dependent on the  $\text{I}_2$  concentration.<sup>3</sup>

It has been suggested that the steady-state current observed on application of a dc field results from polyiodide species that may have significant electron or hole mobility or undergo an I/I transfer along the polyiodide chains.<sup>3</sup> The latter mechanism seems more favorable because crystalline polyiodide complexes, in which some of the I atoms are pinned by complex formation, are observed to be insulating.<sup>3</sup> In addition, recent variable-temperature Raman experiments suggest that iodide species are locally mobile even at 16 K as indicated by the change in the ratio of peak intensities for  $\text{I}_3^-$  relative to polyiodides as a function of temperature.<sup>6</sup>

If conductivity occurs along the polyiodide chains, then percolation phenomena are expected, which would be manifested by a rapid rise in conductivity around a critical concentration of the conducting species (the percolation threshold). Percolation theory has been applied extensively in composite systems consisting of a conducting phase dispersed in an insulating phase.<sup>7-9</sup> Examples include carbon black in an insulating polymer,<sup>6</sup> metal particles, or fibers in an insulating matrix,<sup>8</sup> and electronically conducting polythiophene in an insulating polymer gel.<sup>9</sup> In our systems, the conducting "particles", which need to form a connected conducting network within the insulating matrix, are considered to be  $\text{I}_3^-$ ,  $\text{I}_n^-$ , or  $\text{I}_2$  species.

A basic concept of percolation theory is that, at a sufficiently low fraction of the conducting phase, a connected pathway ceases to exist so the conductivity becomes extremely small. This conductivity threshold is observed experimentally and it is found to depend on

(1) Armand, M. A. In *Polymer Electrolyte Reviews*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987; Vol. 1.

(2) Lerner, M.; Lyons, L. J.; Tonge, J. S.; Shriver, D. F. *Chem. Mater.* 1989, 1, 601.

(3) zur Loye, H. C.; Heyen, B. J.; Marcy, H. O.; DeGroot, D. C.; Kannewurf, C. R.; Shriver, D. F. *Chem. Mater.* 1990, 2, 603.

(4) Hardy, L. C.; Shriver, D. F. *J. Am. Chem. Soc.* 1986, 108, 2887.

(5) (a) Jiang, Z.; Sen, A. *Macromolecules* 1992, 25, 880. (b) Chollis, A. L.; Thakur, M. J. *J. Chem. Phys.* 1989, 91, 7912.

(6) Forsyth, M.; zur Loye, H. C.; Lerner, M.; Tipton, A.; DeGroot, D. C.; Kannewurf, C. R.; Ratner, M. A.; Shriver, D. F. *MRS Proc.* 1991, 210, 215.

(7) Ezquera, T. A.; Kulesza, M.; Santa Cruz, C.; Balta-Calleja, F. J. *Adv. Mater.* 1990, 2, 597.

(8) Chen, I.-G.; Johnson, W. B. *J. Mater. Sci.* 1991, 26, 1565.

(9) (a) Fizazi, A.; Moulton, J.; Pakbaz, K.; Rughooputh, S. D. D. V.; Smith, P.; Heeger, A. J. *Phys. Rev. Lett.* 1990, 64, 2180. (b) Suzuki, Y. S.; Heeger, A. J.; Pincus, P. *Macromolecules* 1990, 23, 4730.

Table I. Glass Transition Temperatures in the System  $\text{PPO}_n\text{NaI}_3$

complex	$T_g$ (K)	complex	$T_g$ (K)
$\text{PPO}_7\text{NaI}_3$	289	$\text{PPO}_{14}\text{NaI}_3$	247
$\text{PPO}_8\text{NaI}_3$	285	$\text{PPO}_{16}\text{NaI}_3$	236
$\text{PPO}_{12}\text{NaI}_3$	263		

particle shape and dimension.<sup>8-13</sup> Theoretical modeling of percolation behavior also shows the dependence of the threshold concentration on aspect ratio (ratio of particle area to volume). In general the more contact sites available per particle the lower the threshold. Thus long thin wires have a very low percolation threshold as compared to spherical particles.<sup>8,12</sup>

In elastic and fluid systems where particles have a higher mobility, a dynamic (stirred) percolation threshold may be seen as a result of the transient formation of a conducting pathway at any particular instant.<sup>14</sup> When the insulating host is below its glass transition temperature ( $T_g$ ), motion of a conducting second phase should be minimal so a permanent conducting pathway would be necessary to achieve an enhanced conductivity. An exception to this can occur in systems where tunneling occurs,<sup>7</sup> resulting in an ill-defined threshold.

The system studied here differs from the classical percolation systems in that only one phase is present, as judged by a single  $T_g$  transition and X-ray diffraction. These materials consist of an electrically insulating polymer containing dissolved iodine or sodium polyiodide. The conductivity of these systems was determined over a temperature regime above  $T_g$ , where the polymer segments are in rapid motion, to a static region below  $T_g$  of the matrix polymer.

### Experimental Section

Polymer-salt complexes were prepared by dissolution of NaI (Aldrich) and PPO (Arco,  $M_n = 54\,000$  g/mol) in THF followed by the removal of the solvent under vacuum. The complexes were then exposed to high vacuum to remove the last traces of solvent and subsequently stored in a dry  $\text{N}_2$  atmosphere. The polyiodide samples were prepared by exposing the polymer-salt complex (or pure polymer) to the appropriate weighed amount of  $\text{I}_2$  under an inert atmosphere at 60 °C. In cases where the sample  $T_g$  was high, the temperature was briefly increased to 80 °C to ensure complete mixing of the polymer and iodine. Densities of the samples were obtained by weighing samples of accurately known volume. The maximum uncertainty in these measurements is 5%.

Samples were characterized via Raman spectroscopy using a Spex double monochromator with an Argon laser at 488 nm. Differential scanning calorimetry (Perkin-Elmer DSC2) was employed to determine the glass transition temperatures. The heating rate was 10 °C/min, and the value of  $T_g$  was determined from the onset of the glass transition. Conductivity measurements using a four-probe configuration<sup>15</sup> were performed as a function of temperature. The samples were loaded into a Teflon holder under an inert atmosphere and an electrical strip consisting

of four gold-coated electrodes was immersed in the holder. The sample was then sealed using Torr Seal epoxy cement and the measurements were performed under vacuum. The sample was cooled to 80 K over approximately 1 h, and measurements were made as a function of temperature as the sample was heated to 320 K over an 18-h period.

### Results

Conductivity was obtained for two systems. The first system,  $(\text{PPO})_n\text{I}_2$ , consists of pure polymer with increasing iodine loading from 0 to 35 wt % ( $n$  refers to the number of moles of ether repeat units per mole of iodine in this case). The second system consisted of  $\text{I}_2$ , NaI, and polymer and the composition was adjusted to achieve  $(\text{PPO})_n\text{NaI}_3$ . Glass transition temperatures in the latter system are given in Table I. The increase in  $T_g$  with increasing concentration of  $\text{NaI}_3$  reflects the effect of virtual cross-linking of PPO chains by the ions.<sup>16</sup> The addition of further  $\text{I}_2$  to obtain  $\text{PPO}_n\text{NaI}_x$  has been shown to decrease  $T_g$ .<sup>3</sup> This dependence of glass transition temperature on iodine concentration suggests an intimate mixing of ions, polyiodide, and polyether at the microscopic level whereas in the pure polyether/iodine systems, a lack of any change in  $T_g$  is reminiscent, but not proof of phase separated polymer blend systems.<sup>17</sup> The interaction between conductive species and the polymer matrix can influence the value of the percolation threshold.<sup>18</sup>

$(\text{PPO})_n\text{I}_2$ . High conductivities are observed upon addition of  $\text{I}_2$  to polymers such as PPO and MEEP and also to organic liquids such as diethyl sulfide.<sup>2,3,19</sup> In addition, the Raman spectra of these systems (Figure 1) always display peaks at 110 and 170  $\text{cm}^{-1}$ , indicative of the formation of the triiodide, polyiodide, or polyiodine species. Conductivity data as a function of temperature are presented in Figure 2. The glass transition temperature,  $T_g$ , of the samples in this series is, within experimental error, independent of iodine concentration, 205 K ( $\pm 2$  K), thus a direct comparison of conductivities at any given temperature is appropriate. Figure 3 presents the conductivity as a function of  $\text{I}_2$  volume fraction along several isotherms.

$(\text{PPO})_n\text{NaI}_3$ . Raman spectra shown in Figure 4, indicate that both  $\text{I}_3^-$  and longer chain polyiodide species are present. The intensity of the 170- $\text{cm}^{-1}$  peak relative to the symmetric triiodide stretch at 110  $\text{cm}^{-1}$  increases with increasing salt to polymer ratio. (Note that in the formula  $\text{PPO}_n\text{NaI}_3$ , there are  $n$  etheric oxygens/mol of salt so that the higher the value of  $n$  the lower the salt concentration.)

Figure 5 presents the conductivity as a function of reduced temperature in this series. At the lowest nominal  $\text{NaI}_3$  concentration, the lowest temperature at which the conductivity was observed is  $T/T_g = 1.05$ . The general trend in the conductivity curves shows a smooth decrease to  $T = T_g$ , followed by an inflection at this temperature and a continual conductivity decrease with a change in the slope of the curve, which suggests a change in the conduction mechanism. In systems below the percolation threshold, it is possible that the conductivity at  $T_g$  drops

(10) (a) *Metal-Filled Polymers—Properties and Applications*; Bhatnagary, S. K., Ed.; Marcel Dekker: New York, 1986; (b) Delmonte, J. In *Metal/Polymer Composites*; Van Nostrand Reinhold: New York, 1990; Chapter 4.

(11) Bridge, B. J. *Mater. Sci. Lett.* 1988, 7, 663.

(12) (a) Balberg, I.; Binenbaum, N. *Phys. Rev. B* 1983, 28, 3799. (b) Balberg, I.; Binenbaum, N.; Wagner, N. *Phys. Rev. Lett.* 1984, 52, 1465.

(13) (a) Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985. (b) Stauffer, D. *Phys. Rep.* 1979, 54, 1.

(14) (a) Grest, G. C.; Webman, I.; Safran, S. A.; Bug, A. L. R. *Phys. Rev. A* 1986, 33, 2842. (b) Bug, A. L. R.; Gefen, Y. *Phys. Rev. A* 1987, 35, 1301.

(15) Lyding, J. W.; Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. Instrum. Meas.* 1988, 37, 76.

(16) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH Publishers: New York, 1991; p 245.

(17) Utracki, L. A. *Polymer Alloys and Blends*; Hanser Verlag: Munich, 1989.

(18) Wessling, B. *Synth. Met.* 1991, 45, 119-149.

(19) Stegemann, H.; Schittke, A.; Fuellbier, H. *Electrochim. Acta* 1990, 35, 355.

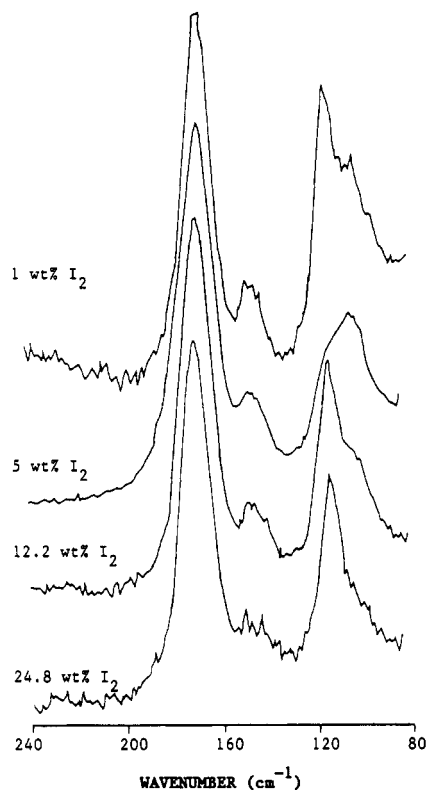


Figure 1. Resonance Raman spectra of  $(\text{PPO})_n\text{I}_2$  at 294 K, as a function of  $\text{I}_2$  concentration in PPO.

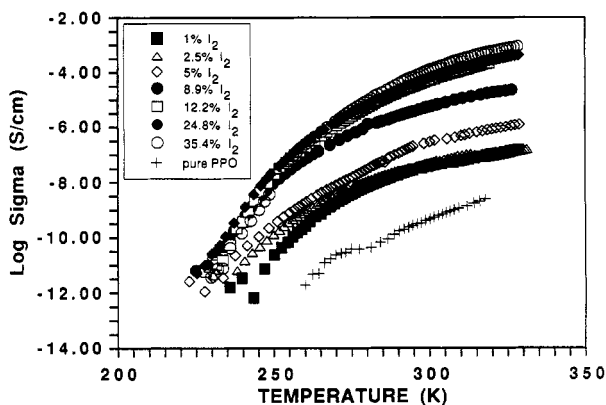


Figure 2. Four probe conductivity data,  $\log \sigma$  versus temperature, for  $(\text{PPO})_n\text{I}_2$  at varying  $\text{I}_2$  concentrations.

much more rapidly as the viscosity increases. Near  $T_g$  the conductivity approaches the limit of our instrumentation. An upper conductivity limit at  $T_g$  can be extracted from the data by fitting the available high-temperature data and then extrapolating to the glass transition temperature. This method was used to estimate the conductivity of  $\text{PPO}_{14}\text{NaI}_3$  at  $T_g$ . This short extrapolation is indicated by the dashed line in Figure 5.

### Discussion

Simulations of percolation models in random systems have shown that there is a power law dependence of conductivity on volume fraction  $p$  of the conducting phase.<sup>16-18</sup>

$$\sigma \propto |p - p_c|^t$$

This power law dependence has also been found to hold in experimental systems, although the values of the

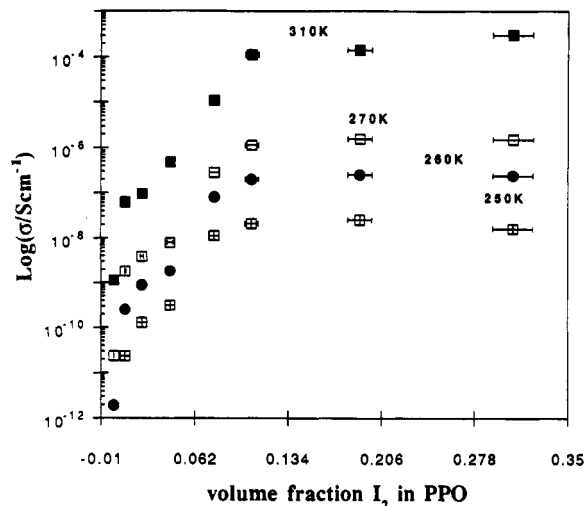


Figure 3. Conductivity isotherms as a function of volume fraction of  $\text{I}_2$  in PPO.

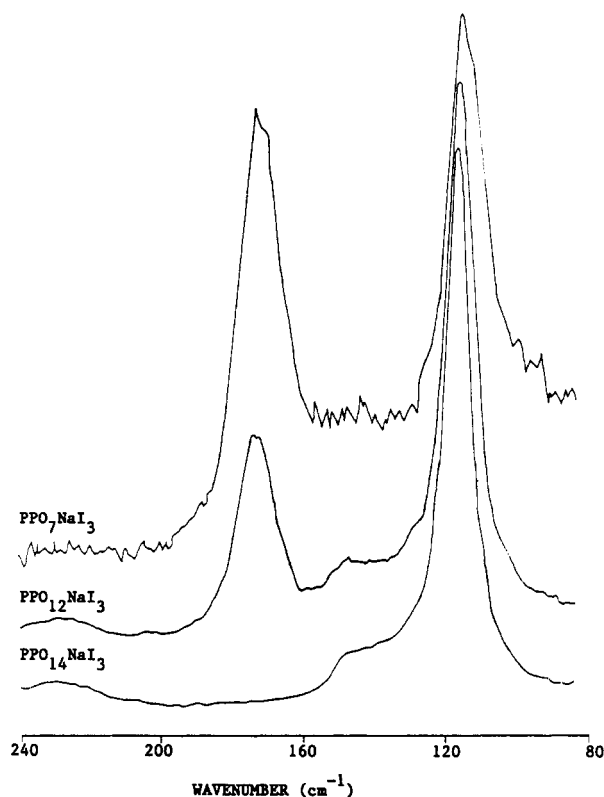
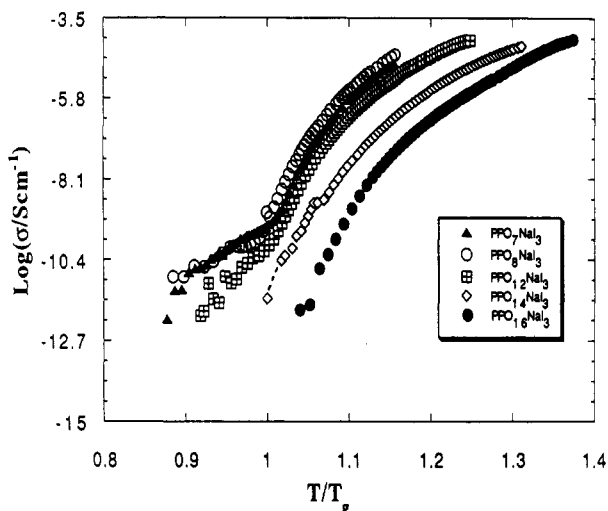
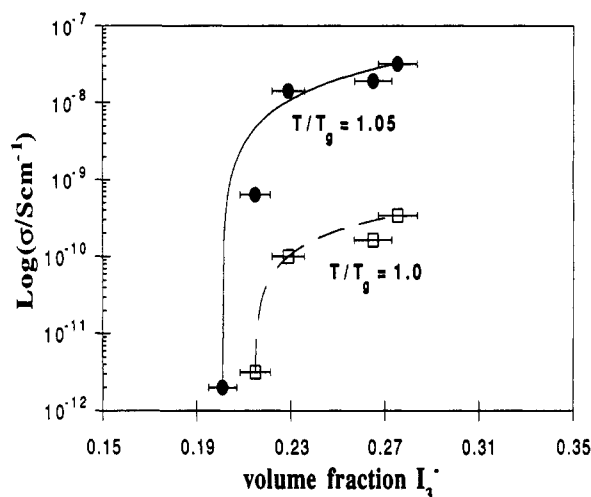


Figure 4. Resonance Raman spectra of  $\text{PPO}_7\text{NaI}_3$ ,  $\text{PPO}_{12}\text{NaI}_3$ , and  $\text{PPO}_{14}\text{NaI}_3$  at 294 K.

threshold,  $p_c$ , and critical exponent,  $t$ , may vary from the simulated model and from system to system since in real systems particles are rarely perfect randomly distributed spheres.<sup>7,8</sup> The numerical calculations of Scher and Zallen<sup>20</sup> suggest a threshold of 0.15 for a system of perfectly random spheres. A critical exponent between 1.6 and 1.8 have been found for three-dimensional systems.<sup>21-23</sup> The effect of particle shape and size on the percolation threshold and the power law behavior is discussed by Chen and Johnson.<sup>8</sup> Their experimental results for a nickel powder dispersed in polypropylene indicate a threshold volume fraction of 0.28 for nodular particles and 0.08 for filamentary-shaped nickel particles. In the case of an Ag-



**Figure 5.** Four probe conductivity data,  $\log \sigma$  versus reduced temperature ( $T/T_g$ ), in the  $\text{PPO}_n\text{NaI}_3$  system. Points of inflection occur at  $T_g$  ( $T/T_g = 1$ ). The dashed line indicates extrapolations of the conductivity data to  $T_g$ , in  $\text{PPO}_{14}\text{NaI}_3$ .



**Figure 6.** Conductivity isotherms as a function of  $\text{I}_3^-$  concentration in the system  $\text{PPO}_n\text{NaI}_3$  at  $T/T_g = 1$  and  $T/T_g = 1.05$ . The lines represent the best fit to the power law expression  $\sigma = \sigma_0(P - P_c)^t$ .

KCl system, the threshold was found at 0.21.<sup>8</sup>

**$\text{PPO}_n\text{NaI}_3$ .** For this system the data were fit to the function  $\sigma = \sigma_0|p - p_c|^t$  by an iterative process in which  $\sigma_0$ ,  $p_c$ , and  $t$  were varied until a fit within 1% was achieved. This system fits the power law behavior, as is seen in Figure 6, with  $p_c = 0.2$  and  $t = 1.15 (\pm 0.33)$  at  $T/T_g = 1.05$ . For a value of  $T/T_g = 1$ , the threshold increases slightly to 0.21. The value of the exponent is considerably lower than those in the literature, however, our system is likely to be more homogeneous than the metal-filled polymer systems previously discussed. The value of the percolation threshold found here is suggestive of spherical rather than fibril particles.

In the  $\text{PPO}_n\text{NaI}_3$  systems, the Raman spectra indicate that polyiodide species are no longer present near the percolation threshold. For example in  $\text{PPO}_{14}\text{NaI}_3$  and  $\text{PPO}_{16}\text{NaI}_3$  only the triiodide species is evident in the

Raman spectra. This supports the idea that, above the threshold concentration, polyiodide species are formed from the intimate contact of triiodide units and this results in an enhanced conductivity.

**$\text{PPO}_n\text{I}_2$ .** This system is more complex in that the identity of the conducting species is unclear. The most likely explanation to account for the high conductivities observed in these systems which nominally do not contain any ionic species, is that traces of  $\text{I}_3^-$  are formed either by oxidation of trace impurities in the polymer or by disproportionation of  $\text{I}_2$  following coordination to an etheric oxygen,<sup>24</sup> and that this  $\text{I}_3^-$  coordinates to long-chain polyiodine groups along which conduction can occur, as discussed previously. The isotherms show that the conductivity is almost independent of  $\text{I}_2$  concentration at levels greater than 12 vol % iodine. At concentrations lower than this, the conductivity drops by several orders of magnitude.

The lowest measurable conductivity in our system was ca.  $10^{-12}$  S/cm. In the  $\text{PPO}_n\text{I}_2$  samples this is reached well before the glass transition temperature. Since the temperatures are above  $T_g$ , the polymer segments are in rapid localized motion so even at the lowest concentrations, dynamic percolation could take place such that close approach between polyiodide ions occurs on a rapid timescale. The probability of forming such links between polyiodide chains is low at the lowest concentrations and therefore so is the conductivity. With increasing  $\text{I}_2$  concentration there is an increased probability of forming a connected pathway and thus an increase in the conductivity is observed. At concentrations above 12 vol %  $\text{I}_2$ , the system may be above its static percolation limit so the addition of molecular iodine does not substantially affect conductivity.

A power law expression, such as that used in many conventional systems exhibiting percolation behavior, could not be fit to the data for this system, and thus a threshold cannot be clearly defined. This behavior has been previously observed in carbon/polyethylene systems where the conductivity does not decrease sharply.<sup>7</sup> In that case, it was postulated that tunneling occurs below the threshold (at 0.27 volume fraction). Electronic tunneling is certainly one possibility in the polyiodide systems, but a more likely explanation is that the polymer segmental motion, which occurs above  $T_g$ , may lead to dynamic percolation of charge, by creating fluctuating contact between the conducting moieties. Dynamic percolation has been implicated in microemulsion systems and modified power law expressions have been predicted.<sup>14</sup> A sharp threshold is not observed in such systems.

In the system  $\text{PPO}_n\text{NaI}_3$ , it is apparent from the Raman spectra that only triiodide species are present for  $n = 14$  or more. When the polyiodide concentration (indicated by Raman spectroscopy) is low, the conductivity is found to be low. A power law dependence of conductivity on volume fraction was found in this system with a percolation threshold at 0.2.

In the case of  $\text{PPO}_n\text{I}_2$ , a sharp conductivity threshold is not observed, and this is attributed to the fact that we cannot measure conductivities in the vicinity and below  $T_g$ .

(21) Grannan, D. M.; Garland, J. C.; Tanner, D. B. *Phys. Rev. Lett.* 1981, 46, 375.

(22) Straley, J. P. *Phys. Rev. B* 1977, 15, 5733.

(23) Kirkpatrick, S. *Phys. Rev. Lett.* 1971, 27, 1722.

(24) Although this latter process is known to occur in more basic media such as pyridine, it has not been possible to isolate a compound containing an  $\text{I}^+$  coordinated to an oxygen.

In summary, the polyiodide systems appear to exhibit static percolation thresholds around their glass transition temperatures. These systems are subject to greater complexity than previous percolation studies on mixtures of discrete phases where the nature of the conducting phase does not change with temperature. In the present case, the equilibrium formation of polyiodide species with dynamic percolation phenomena appear to control the conductivity in the vicinity of the percolation threshold.

**Acknowledgment.** This work was supported by the DOE Basic energy science program, Grant DE-FG02-85ER45220. M.F. gratefully acknowledges a Fulbright Postdoctoral Fellowship. We would like to thank Stephen Druger and A. Nitzan for many insightful discussions. All measurements were performed in the facilities of the Northwestern Materials Research Center, which is supported by the NSF through Grant DMR 8821571. We would like to thank Mr. Jon Schneider and Mr. Tim Hogan for their assistance in the conductivity measurements.