Effect of polymer cross linking on the electrical properties of ethylenevinylacetate poly(3-octylthiophene) polymer blends

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A study of the transport properties of a polymer blend consisting of poly(3-octylthiophene) (POT) and ethylenevinylacetate doped with $FeCl_3$ reveals a change in conductivity mechanism when the material is cross linked by electron irradiation. In heavily irradiated samples and in samples with a high POT content the temperature and the electric field dependences of the dc conductivity are in good agreement with the model of thermal-fluctuation-induced tunneling between metallic particles embedded in a dielectric matrix. In unirradiated samples with a low POT content, however, the data fit best the model of charging-energy-limited tunneling of a granular polymeric metal. These transport properties indicate an increase in the average size of the conducting particles as the polymer blend is cross linked.

INTRODUCTION

Polymer blends consisting of poly(3-alkylthiophenes) and matrix polymers have proved to be successful in combining the crucial properties of conducting polymers: high conductivity, stability, and processability.[1] A percolation threshold obtainable with a conductive polymer content of 5–10 wt. % is an important feature thinking of production costs. The melt processed films of a blend of ethylenevinylacetate and poly(3-octylthiophene) (EVAPOT) studied in this work can be doped, e.g., with iodine in gas phase or in nitromethane solutions of $FeCl_3$. The room-temperature conductivity can thus be varied between 10^{-10} S/cm and 1 S/cm by adjusting the doping level and the amount of POT in EVA. The upper limit of conductivity can be pushed further upwards if the polymer chains are oriented, i.e., by drawing of the film.[2,3]

The academic interest in pure poly(3-alkylthiophenes) arises from the bipolaronic conductivity of the material.[4] Our previous work on the electrical properties of EVAPOT polymer blend showed that there is a phase segregation into metallic and insulating regions in the highly doped material.[5] Here the conductivity is governed by the junctions between the conducting particles embedded in the insulating matrix. Thereby the electric properties of these polymer blends have more similarity to composite materials, i.e., polymers containing carbon particles or metal grains than to inherently conducting polymers. By being able to control the dispersion and the size of the conducting poly(3-alkylthiophene) particles more homogeneous blends with improved stability and strength can be developed.

The reason for the present study on cross linking originates from an attempt to improve the stability of doped EVAPOT above room temperature, where conformational defects[6] and increased diffusion of dopants[7] cause a decrease in conductivity level.

EXPERIMENT

EVAPOT films used in this study were prepared as described elsewhere.[1] POT was polymerized by direct oxidation of 3-octylthiophene by $FeCl_3$. It had a molecular weight of $\bar{M}_w = 81\,000$ and $\bar{M}_n = 21\,400$. It also contained considerable amounts of impurities (0.1% of Cl and 0.07% of Fe) after polymerization. POT was blended with EVA in the molten state and hot-pressed to films with a thickness of 100 μm. The blends were then doped with $FeCl_3$ in a dry nitromethane solution, washed in dry nitromethane, and dried in vacuum for several hours before electron irradiation. POT content was 30% or 10% by weight [to be notated $(EVA)_{70}(POT)_{30}$ and $(EVA)_{90}(POT)_{10}$] which is sufficient for room-temperature conductivity values of 10^{-3}–10^{-1} S/cm.

Polymer cross linking (XL) by electron irradiation was performed by an Electrocurtain CB 150 lab unit. The incident energy was 175 keV and the films were irradiated on both sides so that a homogeneous dose was obtained. $(EVA)_{90}(POT)_{10}$ samples with five different degrees of cross linking were studied: 0%, 10%, 30%, 60%, and 90%. We shall use the notation XL followed by the percentage in naming the samples (e.g., $(EVA)_{90}(POT)_{10}$ XL 10%). The relationship between the dose and the degree of cross linking (Fig. 1) was determined by applying the ASTM D2765 test on the irradiation of pure EVA (acetate content 18%) which is much more easily cross linked than POT. However, POT was cross linked, too. This was observed when pieces of unirradiated and heavily irradiated (500 kGy) samples of pure POT were inserted in chloroform. The unirradiated sample was easily dissolved but the irradiated one remained insoluble even when the solvent was heated and placed in an ultrasonic bath.

dc conductivity was measured by a four-point-method in a cryostat where the temperature could be varied from

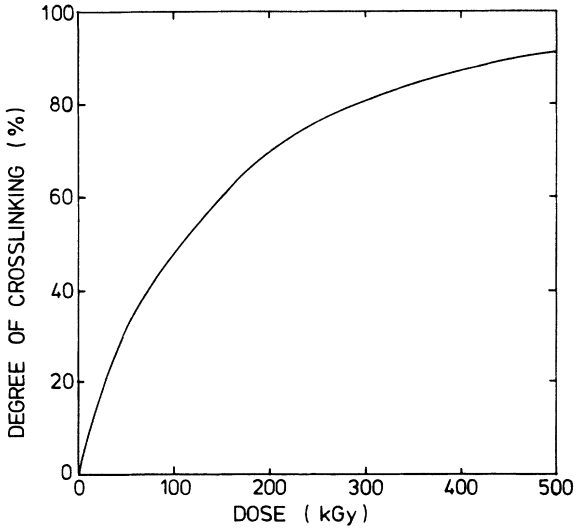

FIG. 1. The degree of cross linking of EVA as a function of the irradiation dose.

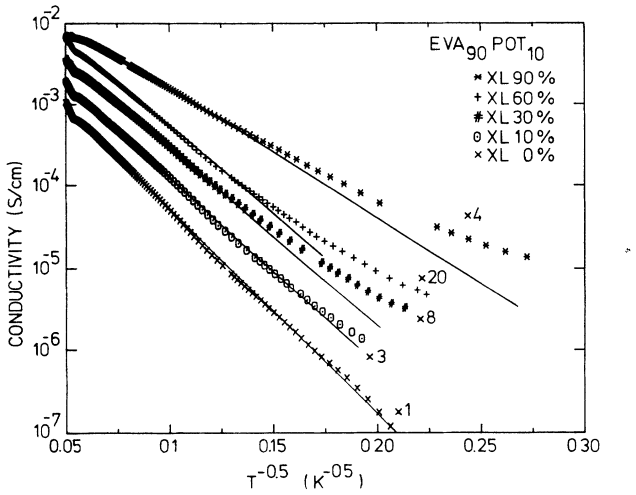

FIG. 2. $\sigma_{dc}(T)$ of $(EVA)_{90}(POT)_{10}$ at various degrees of cross linking. The solid lines correspond to the behavior of Eq. (1). The data points have been shifted by the factors indicated next to each curve.

10 to 450 K. Electrodes were made with carbon paste which gives an Ohmic contact to POT. The samples were attached to the sample holder by pressure contacts. Gold electrodes evaporated through identical masks were used when checking the slight changes in conductivity level due to polymer cross linking.

The electric field dependence of conductivity was measured using a single voltage pulse (0–100 V) applied across a resistor in series with the sample. The resistivity was measured perpendicular to the EVAPOT film in order to obtain high electric fields. The conductivity level was 10–100 times larger in the parallel direction which could be due to polymer chain orientation in the plane of the sheet. The size of the carbon paste contacts on both sides of the film was 0.1–0.2 cm^2. The voltage pulse across the sample was caught by a digital oscilloscope and the pulse width was determined by the RC time constant of the load (5–500 μs). Possible heating effects were checked by using 10 ms pulses but only a slight decrease of 1–2 % in comparison to the short-pulse resistance values was observed above 5000 V/cm.

RESULTS

Figure 2 shows the temperature dependence of dc conductivity at various degrees of cross linking in the sample $(EVA)_{90}(POT)_{10}$. The data have been fitted to

$$\sigma=\sigma_0 e^{-(T_0/T)^{0.5}}, \tag{1}$$

which gives the best agreement for the unirradiated sample. The fit corresponds to the model of charging-energy-limited tunneling (CELT) between small (2–20 nm) metallic particles in an insulating matrix.[8] The more the samples are cross linked the more the curves start deviating from the behavior of Eq. (1). In Fig. 3 the same data are applied to the model of thermal-fluctuation-induced tunneling (TFIT).[9] TFIT is applicable when the charging energy between the conducting particles becomes negligibly small, the size of the particles being typically of the order of micrometers. In this model the conductivity varies as

$$\sigma=\sigma_0 e^{-[T_1/(T_2+T)]} \tag{2}$$

if the potential-barrier shape between the conducting particles is assumed to be parabolic. A good agreement with TFIT in a large temperature range can be observed especially in the samples of more than 30% cross linking. The behavior of the conductivity above room temperature is related to conformational changes in the polymer backbone and to a loss of dopants which are not to be discussed here.

The data obtained from the samples $(EVA)_{70}(POT)_{30}$

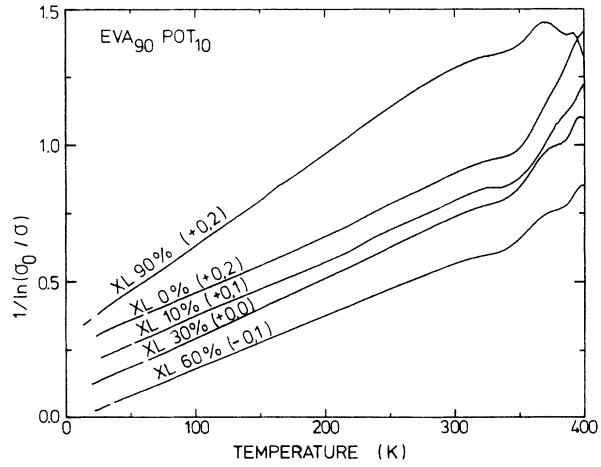

FIG. 3. $\sigma_{dc}(T)$ of $(EVA)_{90}(POT)_{10}$ at various degrees of cross linking. A straight line gives a perfect fit to Eq. (2) (TFIT) in this plot. The data points have been shifted by the increments indicated in parentheses.

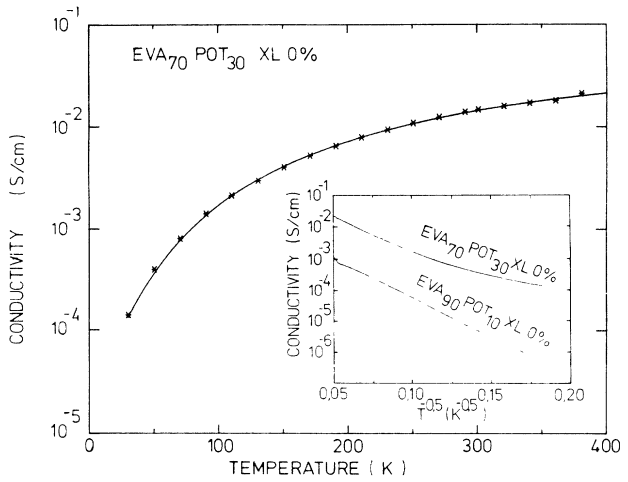

FIG. 4. $\sigma_{dc}(T)$ of $(EVA)_{70}(POT)_{30}$ XL 0%. The solid line is a fit to the TFIT model. Only every tenth data point is shown. The inset compares the data with the $\sigma_{dc}(T)$ of $(EVA)_{90}(POT)_{10}$ XL 0%.

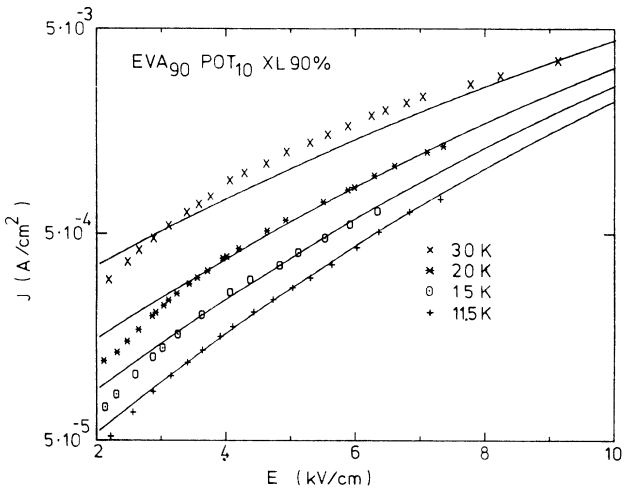

FIG. 6. $j(E,T)$ of $(EVA)_{90}(POT)_{10}$ XL 90%. The solid lines are fits to the TFIT model.

XL 0% fit the model of Eq. (2) in an excellent way as can be seen in Fig. 4. The inset compares the curve with the behavior of the sample $(EVA)_{90}(POT)_{10}$ XL 0%. Electron irradiation up to 45% cross linking did not cause any significant changes in the $\sigma_{dc}(T)$ data below room temperature in this sample of higher POT content.

Since no final conclusions can be drawn about the conductivity mechanism on the basis of $\sigma_{dc}(T)$ data alone the electric field dependence of σ was measured at various temperatures. If the tunneling conduction is charging energy limited the resistance in the sample varies as

$$R = R_0 e^{E_0/E} \tag{3}$$

in the high-field regime.[8] On the other hand if the charging energy is negligible and the tunneling is fluctuation induced the expression

$$j = j_0 \exp[-T_1/(T_2+T)(E/\epsilon_0 - 1)^2] \tag{4}$$

has been derived for the current density j when the electric field is high.[10] T_1 and T_2 can be determined from the $\sigma_{dc}(T)$ data. If this TFIT model is applicable the data measured at different temperatures in a given sample should fit Eq. (4) with the same parameter values j_0, ϵ_0. Figures 5 and 6 show that this indeed is the case in the samples of heavy cross linking or high POT content. In Fig. 5 the point of convergence (ϵ_0, j_0) seems to be reached at a lower field strength than in Fig. 6. This is related to the size of the conducting aggregates which is to be discussed later in this paper. The reason why j/j_0 is plotted instead of j in Fig. 5 is that in measuring the

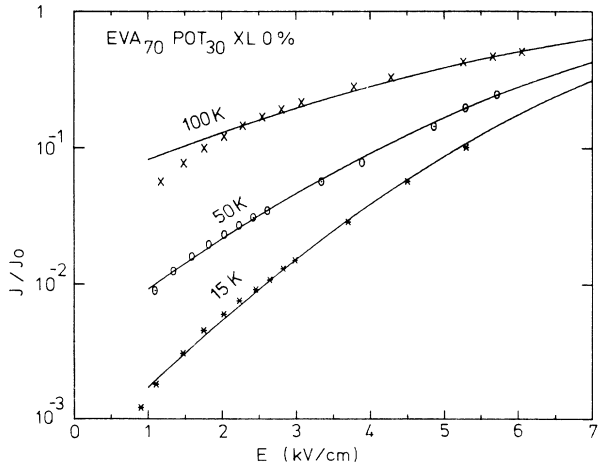

FIG. 5. $j(E,T)/j_0$ of $(EVA)_{70}(POT)_{30}$ XL 0%. The solid lines are fits to the TFIT model.

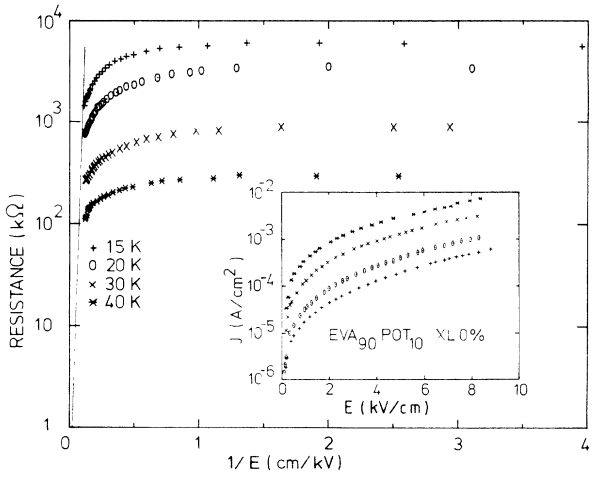

FIG. 7. ln$R$ of $(EVA)_{90}(POT)_{10}$ XL 0% as a function of $1/E$. The solid line shows the limiting behavior of Eq. (3) (CELT). The inset shows that there is no convergence of the data points $j(E,T)$ required by the TFIT model in this sample.

$j(E)$ curve at 15 K the electrode area was increased.

The size of the conducting particles is so much smaller in the sample $(EVA)_{90}(POT)_{10}$ XL 0% that the possible point (ϵ_0, j_0) lies far beyond the electric field strengths available in this study. This can clearly be seen in the inset of Fig. 7, where no convergence of datapoints is visible at high electric fields. If, however, $\ln R$ is plotted versus inverse electric field a tendency to the behavior of Eq. (3) can be seen (Fig. 7).

DISCUSSION

Sheng's model of fluctuation-induced tunneling has characteristic tunneling junction parameters V (barrier height), w (barrier width), and A (junction area). We use here the TFIT model with a parabolic-barrier approximation. The junction parameters cannot be determined uniquely on the basis of T_1, T_2, and ϵ_0. If we make an assumption about the barrier width or the barrier height the field ϵ_0 across the junction is given by

$$\epsilon_0=(T_1/T_2)^2\frac{2h^2}{\pi^4 mew^3}=(T_2/T_1)\frac{4\pi^2(2mV^3)^{1/2}}{he}\ , \qquad (5)$$

where m and e are the electron mass and charge, respectively. An estimate of the particle size can now be obtained by interpreting the ratio between ϵ_0 of the single junction given by Eq. (5) and the parameter $\epsilon_{0,\mathrm{fit}}$ used in fitting the experimental data as the ratio between the average junction width and the average size of the conducting particles.[11] Notice that in Eq. (5) ϵ_0 depends only on the ratio between T_1 and T_2. Thus a change in the slope of $\sigma_{dc}(T)$ does not necessarily imply an increase or decrease in the average particle size because usually when T_1 increases so does T_2 and vice versa.

Since ϵ_0 is a more slowly varying function of V than of w it is reasonable to try to give an estimation to V first. The TFIT model has been successfully applied to the case of highly doped polyacetylene[12,13] where the barrier heights were of the order of a few eV. A material having more resemblance to the EVAPOT polymer blend might be carbon-poly(vinylchloride) composite in Ref. 11 where a value of $V\approx 0.2$ eV was adopted. The high values of T_1 obtained from the $\sigma_{dc}(T)$ data indicate that the barrier has to be relatively high and that the model is applicable in a wide temperature range. Also the fact that the sample resistivities are frequency dependent at room temperature (to be reported later) implies that the electrons do not have enough energy to surmount the potential barrier and the conductivity is still fluctuation induced. Table I summarizes the values of the fitting parameters and the corresponding particle sizes obtained from the sample $(EVA)_{70}(POT)_{30}$ XL 0% and the samples $(EVA)_{90}(POT)_{10}$ XL 90% and XL 60%. The particle sizes have been calculated with three barrier heights: 0.1, 0.15, and 0.2 eV. Another way would be to estimate the cross-sectional area A as in Ref. 12 but here we have no extra information on the junction parameters.

The $\sigma_{dc}(T)$ data of the samples $(EVA)_{90}(POT)_{10}$ XL 60% and XL 30% fit the TFIT model well. The $j(E,T)$ data, however, indicate that the conducting aggregate size is smaller than in the sample $(EVA)_{90}(POT)_{10}$ XL 90% because the value of $\epsilon_{0,\mathrm{fit}}$ is larger. In the case of the sample $(EVA)_{90}(POT)_{10}$ XL 30% $\epsilon_{0,\mathrm{fit}}$ gets so large that no quantitative values can be given to the particle size.

The $\sigma_{dc}(T)$ and $j(E,T)$ data of the samples $(EVA)_{90}(POT)_{10}$ XL 0% and XL 10% are essentially the same. The CELT model explains the temperature dependence of σ and $\sigma(E,T)$ approaches the limiting behavior $\ln(\sigma/\sigma_0)=-E_0/E$. Although the maximum electric field was too low it is possible to give a rough estimate to the size of the conducting grain plus the insulating barrier (w').[8] The transition from low-field Ohmic behavior occurs at

$$\frac{eEw'}{kT}=1 \qquad (6)$$

at a point $\sigma(0,T)/\sigma(E,T)\approx\frac{1}{2}$. Using the value $E\approx 4000$ V/cm at 40 K in Fig. 7 we get $w'\approx 9$ nm. A comparison

TABLE I. The parameters used for fitting the TFIT model and the corresponding tunnel junction characteristics calculated with three different barrier heights. d is the particle size.

Sample	XL (%)	T_1 (K)	T_2 (K)	$\epsilon_{0,\mathrm{fit}}$ (V/cm)		
$(EVA)_{70}(POT)_{30}$	0	742	82	11 500		
$(EVA)_{90}(POT)_{10}$	90	295	28	22 000		
$(EVA)_{90}(POT)_{10}$	60	460	35	40 000		
Sample	**XL (%)**	**V (eV)**	**w (Å)**	**A (Å^2)**	**ϵ_0 (MV/cm)**	**d (nm)**
$(EVA)_{70}(POT)_{30}$	0	0.1	35	4200	1.1	330
		0.15	28	1500	2.1	510
		0.2	24	750	3.2	670
$(EVA)_{90}(POT)_{10}$	90	0.1	38	1700	1.0	170
		0.15	31	600	1.9	270
		0.2	27	300	2.9	360
$(EVA)_{90}(POT)_{10}$	60	0.1	48	3600	0.8	95
		0.15	39	1300	1.5	150
		0.2	34	650	2.3	200

between $\sigma_{dc}(T)$ and $\sigma(E,T)$ can now be made by using the estimate[8]

$$w' = \frac{kT_0}{4eE_0} , \tag{7}$$

where T_0 can be obtained from Eq. (1). From Fig. 2 we get $T_0 = 3300$ K and from Fig. 7 $E_0 \approx 70$ kV/cm. A substitution to Eq. (7) gives then $w' \approx 10$ nm, which is in good agreement with the previous estimate. If we assume that the barrier width is of the order of 3 nm as in Table I the conducting grain size becomes 6 nm. Barrier widths and conducting particle sizes of that order would point to a true molecular blend where the barrier could be formed at least partly from the octyl side groups having a length of about 1 nm.

As the material is irradiated by electrons the enlargement of the POT aggregates could be caused by a cross linking between sulphur atoms in the thiophene rings. The exact mechanism is not known, and therefore further research on the cross-linking properties of POT is in progress. Molecular enlargement has been observed during the heat treatment of POT with cross linking related to the residue of oxidant used for polymerization.[14] The important role of the considerable amount of synthesis-induced impurities in the cross linking of this material is supported by the fact that the TFIT model could not be applied properly to a cross-linked EVAPOT blend where the POT impurity concentration was much lower.

As a conclusion we may state that electron irradiation of EVAPOT has the effect of enlarging the conducting particle size by a factor of 10–50 as seen from the change from a charging-energy-limited tunneling to a thermal-fluctuation-induced tunneling of charge carriers between conducting particles.

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