Resonant Tunneling in a Polymer with Charge Injection Doping

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Abstract. It is shown that a supercurrent in disordered polymers placed between superconductor electrodes may be explained by resonant tunneling of Cooper pairs along polymer channels formed due to electrification effect. Polymer film thickness where supercurrent one may to observe depends on superconducting coherence length in superconductor. The more coherence length in superconductor electrode the more is a polymer film thickness where superconductor exists. Shapiro steps induced by microwave (\(f = 9.3 \text{ GHz}\)) radiation correspond to a single Josephson junction.

Keywords: disordered polymer systems, electrification, supercurrent, resonant tunneling, Shapiro steps.

Introduction

It is well known that all insulators and non-conducting polymers always accept a charge when they are in contact with metals. It has been shown that polymer electrification occurs due to the localized traps situated in the polymer in an energy interval close to the Fermi energy of the majority of the metals [1, 2]. The traps are the result of various kinds of defects, such as chemical groups, cavities and entanglements, unsaturated bonds. The defects can appear in the polymer due to aging with time or they can be specially created by UV irradiation and oxidation [3]. The experiment shows that the appearance of metallic conductivity in metal-polymers-metal sandwiches and a supercurrent in superconductor-polymer-superconductor sandwiches is inevitably linked to this electrification process [4,5 and references therein]. The thermal motion of the molecules also contributes to the generation of a static charge, as well as other mechanical action (i.e. contact movement) increases the electrification. This explains the switching of metal-polymer metal structures to a highly conductive state under pressure or the type of contacting – when touching or sliding contacts were placed between the metallic electrode and the polymer surface. Electrification of polymers in metal-polymer-metal constructions as well as the arising metallic conductive state is not possible if the polymer has a permanent conductivity, for example due to initial doping. In “perfect” polymers without any defects the electrification penetrates only into the polymer surface, up to about tens of nm. For that reason there is no metallic conductivity in a polymer with higher film thickness.

In accordance with [6] one mechanism for the switching of the polymer from the dielectric state to the high conductive state can be the following. Polarization of the polymer matrix by randomly distributed localized charges causes both a shift and a broadening of the orbital energies, so that some HOMO-levels may lie above the Fermi level of the contact metal and some LUMO - levels below it. This means that the contact between a metal and a polymer causes electrons from the metal to...
transfer to the LUMO, or electrons may transfer from the HOMO into the metal for separated polymer macromolecules which are closely located near the surface of metallic electrodes [6]. As a result, energy states with energies close to the Fermi energy of most metals form between HOMO and LUMO orbital of macromolecules. Only weak van der Waals forces hold the macromolecules together in the solid. In the case of a small distance \( r \) between the macromolecules neighboring bulk macromolecules can except a charge and also may create the spreading of the energy states around the Fermi level of the metal. That mechanism can produce percolation paths of conductivity from one electrode to the other. In a disordered polymer system the charge transport between separate macromolecules or macromolecules clusters may exist due to resonant tunneling\(^1\). Early it was experimentally shown that the depth of charge penetration due to electrification may reach several micrometers [1]. We consider resonant tunneling as main process for the charge transport over large distances in polymers with randomly distributed in space internal defects.

To test the resonant tunneling model we investigated the critical current \( I_c \) behavior, current-voltage characteristics (CVC) of Superconductor-Polymer-Superconductor (SPS) junctions under different uniaxial pressure as well as with irradiation with microwave radiation at low temperature. As polymers we used imid-siloxane, polyimide and polyamidine [8]. All investigated polymers were with defects.

In accordance with [9] resonance transport of Cooper pairs along the paths made up of periodically arranged impurity atoms results in a slower decrease of the critical current with increasing barrier thickness then occurs at direct tunneling. More over the action of localized states act as long metallic channels so that the junction is similar to a long superconductor-normal metal-superconductor (SNS) junction. In the frame of that model we may use the theory of the proximity effect by De Gennes. De Gennes attributed the proximity effect to Cooper pairs that propagate from a superconductor into normal metal. The critical current \( I_c \) for a SNS junction in that approach is the following [10]:

\[
I_c \propto \frac{\pi}{2eR_n} \frac{\Delta_n^2}{kT} \frac{d}{\xi_n} e^{-\frac{\Phi_s}{\xi_n}}
\]

Here are: \( I_c \) – critical current of weak link (normal metal \( N \)), \( R_n \) – resistance in normal state of \( N \); \( \Delta_n \) – superconducting gap at the normal interlayer interface, \( T_c \) – critical temperature of superconductor, \( d \) – the thickness of \( N \), \( l_n \) – the mean-free path in the normal metal, \( v_n \) – Fermi velocity in \( N \), \( \xi_n \) – the superconducting coherence length in \( N \).

The temperature dependence of \( I_c \) results from the temperature dependence of \( \xi_n \). For normal metal exist two limiting cases:

i) “clean limit” \( \xi_s << l_n \) (here \( \xi_s \) – the superconducting coherence length in superconductor). In this case one get \( \xi_n = \frac{\hbar v_n}{2\pi kT} \)

ii) “dirty limit” \( \xi_s >> l_n \)

In this case \( \xi_n = (\frac{\hbar v_n l_n}{6\pi kT})^{1/2} \)

The main predictions of the De Gennes theory are the following:

\(^1\) On the possibility of the resonant tunneling in Superconductor-Polymer-Superconductor sandwiches was firstly discussed in [7].
1) with increasing $d$ of the normal metal, $I_c$ should decrease exponentially at fixed $\xi_n$.
2) since $\xi_n$ depends on $T$, $I_c$ should exponentially decrease with increasing $T$ up to $T_c$ at fixed $d$;
3) $I_c$ does not depend directly on $\xi_s$ of the superconductor.

Before we proved experimentally the theoretical predictions for a SPS sandwich it should be noted the main dissimilarity to SNS which is that a polymer has no free carries as a normal metal. Hence the main problem of polymer in SPS construction with supercurrent is the value of superconducting coherence length ($\xi_p$) as well as its temperature dependence. When the LUMO of all macromolecules participate in the conductive paths from one electrode to another is aligned to the Fermi level then resonant tunneling of Coppers pars can exist in SPS. In this case the decay length of the superconductivity coherence length in polymers should be the same as in the superconductor electrodes, i.e. $\xi_p = \xi_s$. In this case $\xi_s$ should be replaced by $\xi_s$ in Eq. 1 and with decreasing $\xi_s$, $I_c$ should decrease exponentially in SPS at fixed polymer film thickness. The fundamental difference from normal metal is that $I_c$ of a SPS junction should depend on the type of superconductor.

**Experimental results and discussion**

The dependence $I_c$ versus film thickness $d$ (nm) for imid-siloxane is presented in Fig.1 at fixed $T$ and $\xi_p$. As seen from the figure the linear dependence of log $I_c$ against $d$ is in accordance with prediction Eq. 1. With increasing $d$ up to some critical thickness $d_c$ ($d_c < 5-10 \xi_s$) $I_c$ decay to zero at $T < T_c$. In this case for polymer thickness up to 2 microns we observed a constant resistance which did not depend on $T$ in a range between 1.8-3.4 K.

![FIGURE 1. Log$I_c$ dependence versus polymer film thickness $d$ for In-Imid-Siloxane-In at fixed $T_c$ close to $T_c = 3.4$ K. Contact areas between the polymer and superconductor are about the same.](image)

Figure 2 presents the dependence $R$ versus film-thickness for In-Polymer-In constructions at $T = 4.2$ K. One can see the linear dependence log$R$ against $d$ (nm). This behavior is also in agreement with the resonant tunneling prediction where $R \propto \exp(-r/a)$, here $r$ is a distance between localized states and $a$ is the radius of localization. It should be noted that the result for the $R(d)$ dependence obtained for imide-siloxane at low temperature differs from that obtained for
atactic polypropylene at room temperature where $R$ did not depend on $d$ [3]. Possibly the reason is connected with the much less value of the spreading resistance between the polymer channel and the metallic electrodes in our case. The spreading resistance decreased down to about 2 orders of magnitude in comparison to room temperature. This increased the measurement accuracy of the polymer resistance.

**FIGURE 2.** The dependence $R$ versus film thickness $d$ for In-P-In (P - imid-siloxane) sandwiches at fixed $T > T_c$.

Figure 3 shows the $I_c$ dependence versus superconducting coherence length of such superconductors as In, Sn, Nb in SPS constructions. As seen from Fig.3 $I_c$ obeys the Eq. 1 with $\xi_p = \xi_s$.

It follows as consequence that the detection of a supercurrent in high$T_c$-Polymer-high$T_c$ constructions would be impossible with polymer film thickness more then some nm because of the small value ($\xi_{highT_c} \sim 2$ nm).

**FIGURE 3.** Dependence $\ln I_c$ versus the inverse superconducting coherence length of some superconductors.

Figure 4 shows the CVC of Josephson type for the flexible polymer polyamide at small external pressure. As seen from the figure the CVC has a large hysteresis (indicated by the arrows). In accordance with resistively and capacitive shunted junction model the SPS junction with hysteresis loop has an essential capacitance [11]. The value of capacitance can be connected with the density of macromolecular chains in the polymer. The lower density of
macromolecular packing the larger is a distance between macromolecules which participate in the charge transport.

**FIGURE 4.** CVC of a S-P-S structure with high capacitance.

Figure 5 shows the dependence of the critical current $I_c$ versus $T$. The saturation $I_c$ at low temperatures is typical for a supercurrent transfer across a Josephson tunnel junction containing resonant localized impurity levels in the tunnel barrier [12].

**FIGURE 5.** The dependence $I_c$ against $T$ for S-P-S construction with high capacitance.
The CVCs for a hard polymer – polyimide at about the same external pressure with corresponding $I_c(T)$ dependence are shown in Fig 6. In this case CVC has no the hysterisis loop that points to a small value of capacitance. The $I_c(T)$ dependence was also transformed and became similar to $T$-dependence of point contact between two superconductors (Fig.7) in agreements with [12].

Figure 8 presents $I_c(T)$ dependence for the same polymer under different pressure. With increasing pressure the $I_c(T)$ dependence got linear. This means that polymer capacitance decreases due to the decreasing distance between the localized states.
FIGURE 8. Dependence $I_c$ versus $T$ for the same S-P-S structure under different pressures.

Figure 9 shows how the S-P-S junction with resonant tunneling responds to microwave radiation [13]. Sharp Shapiro steps with accuracy of 100 nV are seen at the voltage given by $V_n = n \frac{\hbar}{2e} f$ for $n = 1, 2, \ldots, 6$, here $f$ is frequency. This behavior is characteristically for a single Josephson junction. Current jumps are very sharp as observed in a homogeneous system. It must be emphasized that the existence of the Josephson effect and Shapiro steps in any junction are a direct proof for superconducting properties of the system.

A SPS junction is a very complex object because it consists a Superconductor-(Insulator-Macromolecule-Insulator)$_n$-Superconductor stack with a large number of $n$. Analysis of our experimental data in the frame of resonant tunneling model gave a satisfactory explanation of the dependence of $I_c$ on $\zeta$. We used the simple theoretical proximity model of superconductivity [10]. However, our results do not reject any existing intrinsic superconductivity in polymers [14]. But for this observation it is necessary to find out the preparation conditions of junctions on the base of polymers.
Acknowledgments

We wish to thank Dr. L.N. Ionov for assistance in microwave radiation experiments and Dr. D. Eagles and Prof. M. Yu. Kupriyanov for discussion.

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