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Study of the Conductance Characteristic of Doped Polymer by Monte Carlo Method*

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Abstract: The conduct mechanism of the doped polymer is considered. In an asymmetry system composed of high polymer and doping conductive matte, chain or congeries framework will be formed between the conductive particles to improve the conductance characteristic. In this procession, the conductive particles interact to each other. In this paper, we describe the conductance of the doped polymer by Monte Carlo method. The results accord with the experiments quite well. It can be concluded that there is an evident change of doped polymer from nonconductor to metal.

Key words: conductance, doping, polymer, Monte Carlo method

The methods to improve the conductance characteristic of macromolecule materials by doping are various. Such as the electrochemistry method, ion-spattering method, inducement method, soak method and so on. Among these methods, some can improve the conductance of these materials with several powers. When the impurity is removed, the conductance drops down immediately and sometime even down to a state of low conductance. Thus, it is called an insulator-metal phase change[1]. Now the Monte Carlo method we used to study the characteristics of polymer has attracted much attention of the world[2,3]. We improve the conductance characteristics of macromolecule materials by doping method and build a model of it in our research.

The system is calculated by using Monte Carlo method. The results indicate that the conductance of macromolecule materials breaks with an insulator-metal phase change along with the quantity of impurity. The results accord with the experimental data well.

1 Principles and Results of Experiments

Two kinds of specimens are studied in our experiments. One is film specimen and the other is block shaped by mould. The film specimen is thiophene polymer film made by blowing and extending method and doped by soaking in the iodin solution for more than ten minutes for iodin diffusing thoroughly. The block specimen is made by doping the conductive ethyne charcoal in the process of heating matrix of high polymer or the mixture of the high polymer and then shaped after ball grinding. The specimens are measured by the method of four-probe on the single line. As to the film specimen, the principle is shown in Fig.1.

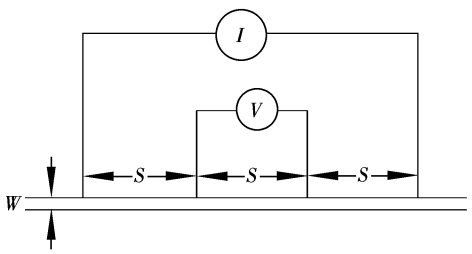

Fig.1 The sketch map of four-probe on a single line method

Compared with the specimen size, the thickness of the specimen can be ignored. And the specimen can be considered large and thin infinitely. According to the experience formula, the surface resistance R_s between two points on the specimen with a distance S is

$$R_s = \frac{V\pi}{I}\ln 2$$

Thus, the body resistivity of the materials is

$$\rho = R_s \cdot \omega = \frac{V\pi\omega}{I}\ln 2$$

The conductance is

$$\sigma = \frac{1}{\rho} = \frac{I}{\pi V\omega}\ln 2$$

The body resistivity of the block is also measured by the method above. It is shown in Fig.2.

The relationship of the conductance via the

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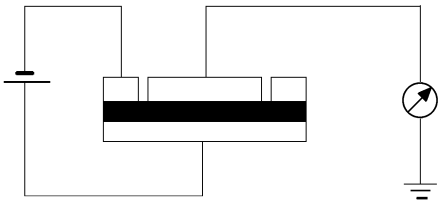

Fig.2 The measure principle for the body resistivity of block specimen

impurity concentration obtained from experiments is shown in Fig.3 and Fig.4.

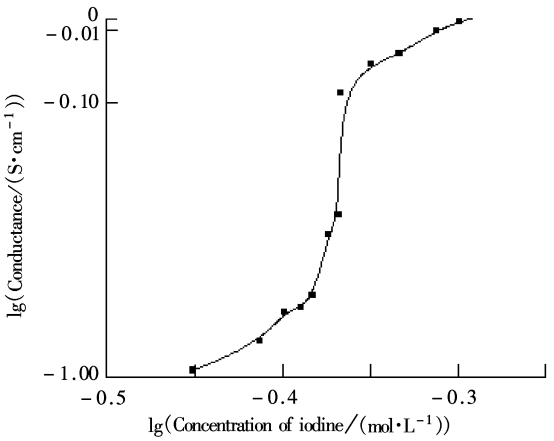

Fig.3 The conductance curve of thiophene polymer via density of iodin

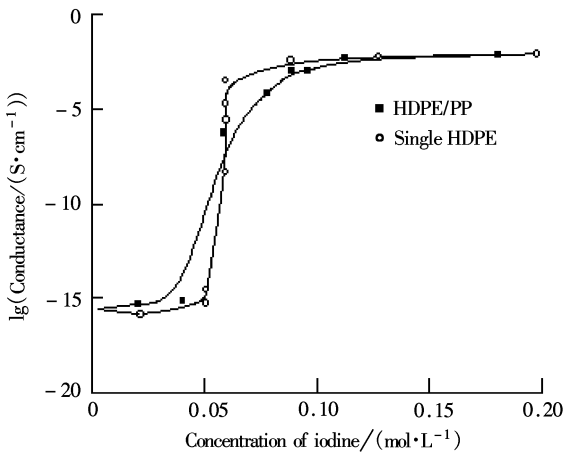

Fig.4 The curves of HDPE doped with conductive charcoal and the mixture of HDPE and PP doped with charcoal according to experiments

2 Conductive Model and Simulating by Monte Carlo Method

High polymer doping conductive impurity is a kind of asymmetry system. In this system, the conductive particles of the impurity interact to form a chain of congeries framework. Electrons can flow along the chain framework, showing conductive character of the materials. The conductance is determined by the capability of the impurity to form a chain framework and the distribution of the framework. The distance of the particles, the number of the contacted points and the distribution change along with the varies of the impurity's kind, quantity and compatibility with the high polymer. The mixture congregation of impurity separates in the mixture. Thus, generally conductive compound in the polymer comes into being when conductive particles are added to the polymer[4]. As to the specimen of iodin doping thiophene polymer film, iodin atoms obtain electrons from the polymer to become iodin ions, which exist in the conductive compound as I_2, I^- and I_3^-. We suppose that an electron can flow from one conductive compound system to another to form a conductive channel when the two conductive compound systems are near enough, even border upon. When the iodin concentration is very low, the conductive compound systems are dispersed so that the probability for them to border upon each other is low and only two-system conductive sets exist. The amount of the two-system conductive sets increase along with the iodin concentration increasing. Thus the probability for the conductive compound to border upon each other increases. And multi-system conductive sets can form so that longer conductive channel forms. But before a conductive channel between two poles comes into being, the conductance will not change. The whole piece of materials is still an insular. When the iodin concentration reaches a critical point, there will be complicated conductive channels and the conductance increases with several powers, called insular-conductor phase change. According to the analysis, we simulate the system by Monte Carlo method. For a thin film specimen, the film can be regarded as two-dimension. And we assume that the thiophene polymer molecules are arranged on the square grids orderly. Thus we can simulate the system conveniently and the results will not be affected. When calculating by Monte Carlo method, we suppose a 180 × 180 square grid, in which we set 1(conductor) or 0(insular molecule) randomly to form a distribution, according to the probability of conductors (iodin concentration). Then we calculate by typical Monte Carlo method (omitting the procession) and scan the distribution to seek an integrate conductive channel between two electrodes. Repeat several times to gain a statistic value of conductors probability at a certain iodin concentration and work out a curve shown in Fig. 5, similar with Fig.3.

The mechanism for doping high polymer or mixture of high polymers with charcoal is the same. When the

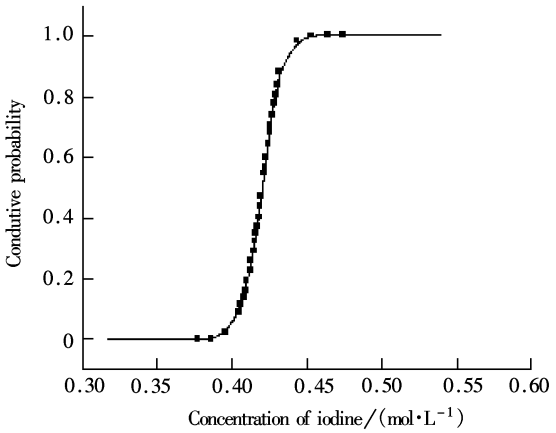

Fig.5 The conductive curve simulated by Monte Carlo method

charcoal ions are near enough to form a conductive channel, the probability for ions to connect to each other is determined by the concentration of the charcoal. Thus it can be simulated it by Monte Carlo method.

3 Discussion

1) Dealing the thiophene polymer film specimen with iodin can make the thiophene polymer molecules be oxidized. The energy band filled partly produces free electrons and holes. So the oxidized areas show metal nature and become conductors. However, the unoxidized areas distribute irregularly and become insular knots. Thus the conductors and insular knots correspond to the 1 states and 0 states in the model. The theory of swing and inducing is applied to explain this conductivity procession. The relationship between temperature and conductance is also discussed.

2) In the procession of doping high polymer or mixture of high polymers, just as doping HDPE or mixture of HDPE and PP with charcoal, the curve obtained in experiment, shown in Fig.4, is similar with the curve resulted from the Monte Carlo method, shown in Fig.5. So conclusion can be drawn that the conductivity in the procession of doping high polymer or mixture of high polymers can describe. There is a great break during the conductance change, which is called insular-metal phase change.

3) The study in this paper is meaningful for macromolecule conductive materials. Also it can be used to improve the application of conductive shield, tiny-liquid wave absorbing and resist-static materials.

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掺杂法提高聚合物电导率的蒙特卡洛法讨论

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摘 要 掺杂法提高聚合物电导的机理是考虑导电填充物和高聚物所构成的不均匀体系中,导电颗粒间会形成链式组织或聚集体组织而提高导电性能,在此过程中导电颗粒有相互作用.本文是采用蒙特卡洛法对掺杂高分子材料的电导特性作了研究,研究结果与实验符合较好,并得出存在剧变特征的所谓绝缘体——金属相变特性的计算结果.

关键词 电导,掺杂,聚合物,蒙特卡洛法

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