CONDUCTING POLYPARAPHENYLENE PREPARED BY HIGH TEMPERATURE DOPING

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Abstract. This paper describes a method of preparing a high-conductivity and high stability conductive polymer – polyparaphenylene (PPP) by a high temperature (250–600°C) doping method. The doping process at the controlled sample temperature and the dopant activity provide an attractive method for electron material technology control. The mechanism and the kinetic analysis of the doping process are discussed. The analysis of the diffusion coefficients and activation energies permits to conclude that, in general, the process of halogen diffusion in PPP is in agreement with the diffusion of impurities in amorphous bodies.

Key words: high temperature doping, high stability, conductive polymers, doping kinetics, diffusion process, diffusion coefficients, activation energies.

1. INTRODUCTION

The physical and chemical properties of solid materials depend strongly on the defect structure. The main problem in semiconductive material technology is the preparation of the materials with well-defined physical and chemical properties, determined by the defect-structure of these materials.

The basic principles of defect-structure studies, first presented by F. Kröger, were also used to investigate A_2B_6 semiconductive materials [1]. Recently, a new group of semiconductive materials – conductive polymers – has attracted special attention [2]. Conductive polymers are generally inexpensive, readily shaped electric materials with easily controllable chemical, physical, mechanical, and electrical properties. Besides polyacetylene, there are polypyrrole, polythiophene and polyaniline, to name a few of the most commonly studied materials.

Furthermore, for the conductive polymers, the dependence of the physical properties on the technological parameters (temperature, vapour pressure) is still open. Though conductive polymers and A_2B_6 semiconductive materials are structurally different, it is possible to point out some similarities in the technology of these material groups. For example, the usual method for the doping of polymer materials is doping from the solutions or electrochemical doping rather than gas-phase doping, typically

used for doping A_2B_6 semiconductive materials. All the doping procedures for the polymer materials described were conducted at room temperatures. This paper describes a method of polyparaphenylene (PPP) doping at high temperatures for preparing a high-stability conductive polymer. In addition, the kinetics of the doping process was investigated.

Most of the experimental results of our doping kinetics studies were presented in [3], where we characterised the kinetics of doping of the PPP doped with iodine and bromine at temperatures ranging from 300 to 600°C and with potassium at 250°C. However, mathematical analysis of the process was not made. In this paper, we will give a detailed analysis of the reasons and mechanism of the conductivity increase in PPP, doped by high temperature doping with halogens and alkali metals.

2. EXPERIMENTAL

PPP was prepared according to the procedure of Kovacic. Presumably the most successful and economical method for PPP preparation is the oxidative cationic polymerisation of benzene [4, 5]. Benzene is polymerised directly to PPP by use of a Lewis acid catalyst $-AlCl_3$ and an oxidising agent – $CuCl_2$. This method makes a polymer particularly suited to giving highly conductive material on doping. Since PPP is an insoluble non-melt-processible polymer, it is generally handled as a free-flowing powder or as pellets compacted from powder under high pressure. For the doping and conductivity investigations, pellets were pressed from the PPP powder. Compacted powder pellets were then annealed in vacuum at high temperature for 24 h. In addition to increasing the crystalline perfection of the polymer, this process apparently opens up some voids in the pellet (via loss of volatiles, such as chlorine and low molecular weight oligomers), a process facilitating dopant penetration.

2.1. Doping process

The halogen doping of PPP was done by exposing the polymer to halogen vapour at temperatures from 300 to 650°C by various doping times. Figure 1 shows the apparatus for doping. PPP pellets were loaded into one end of the quartz tube, halogen into the other end. Next, the tube was evacuated, sealed and loaded into the double-zone furnace. PPP and halogen temperatures were controlled separately by the temperatures of zones [6–8].

Since the gas-phase doping was performed in a closed system, the process was accompanied by the generation of by-products that are also gases at doping temperatures. To investigate the influence of these possible by-products to the doping process, a step-by-step doping was performed. It means that after every hour of doping, the by-products were removed from the system, after the gas-phase removal, the ampoule was resealed, and the process of doping continued. Upon doping, pellets changed their colour from brown to dark also with a metallic hue. In the case of doping with potassium and sodium, the PPP pellets and alkali

metal were loaded into a one-zone tube, the doping was performed at 250 °C. The alkali metal-doped polymer is extremely air and water sensitive and was handled using dry box (helium) techniques.

The halogen content in the doped samples was determined by the Leipert–Münster method and the content of the potassium by the flame emission technique. The dopant content is expressed as the number of dopant atoms per 100 PPP monomer units.

2.2. Conductivity measurements

The electrical conductivity of doped samples was measured at room temperature. The four-in-line probe was used to measure the conductivity of doped samples. A special probe head, containing four equally spaced spring-loaded electrodes, was lowered onto the sample until the four probes were in close contact with the sample. A constant current source was used to pass a steady current through the outermost probes, and the voltage drop across the inner two contacts was measured. Our measurement system facilitated measurement of the electrical conductivity during the doping process. The measurement system and the ampoule used are illustrated in Fig. 1.
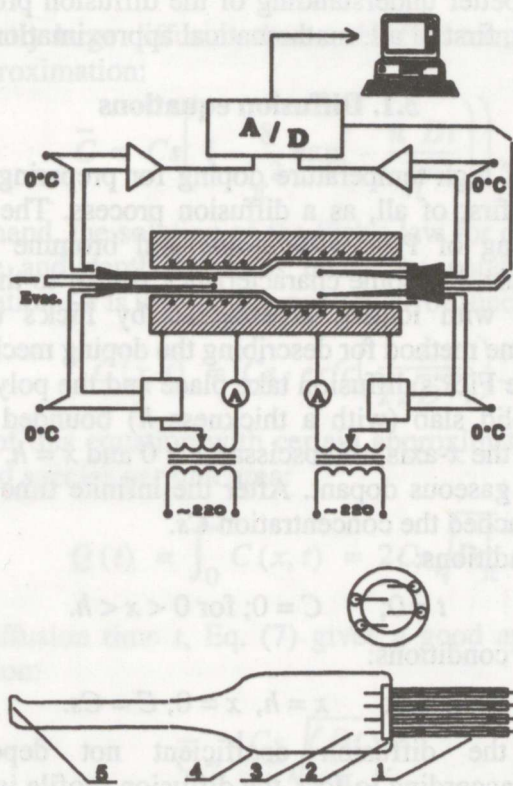

Fig. 1. The system for doping and conductivity measurements and the ampoule for high-temperature conductivity measurement. 1 – quartz removals for the electrodes, 2 – PPP sample, 3 – tungsten electrodes, 4 – quartz tube, 5 – doping component reservoir.

The ampoule for the conductivity measurement had four sealed electrodes, and the four-probe method was used. Since the sample thickness was comparable to the probe spacing, the van der Pauw method was used to determine sample conductivity.

During the measurement or doping process, the condition between the component temperature *Tcomp* and the semiconductive material temperature *Tsem* (*Tsem* ≥ *Tcomp*) was provided.

The measurement and the doping process control were based on the AD/DA converter connected to a PC [9].

3. RESULTS AND DISCUSSION

The process of the conducting PPP preparation is usually described by the electrical conductivity dependence on the doping temperatures, and furthermore, in the form of kinetic dependence as the mean concentration of the dopant as the function of the doping time. Most of these results were described in our earlier investigations, however, without the mathematical characterisation of the doping process [3]. This study gives a detailed analysis of the reasons and mechanism of the conductivity increase in PPP, prepared by the high temperature doping with halogens and alkali metals.

To achieve a better understanding of the diffusion process during the gas-phase doping, first of all, mathematical approximations are necessary.

3.1. Diffusion equations

The method of high temperature doping for preparing conducting PPP was determined, first of all, as a diffusion process. The kinetics of high temperature doping of PPP with iodine and bromine as well as with potassium, as a rule, has some characteristics similar to the doping kinetics of polyacetylene with iodine, investigated by Fick's diffusion [10, 11]. Therefore, the same method for describing the doping mechanism was used.

We assume the Fick's diffusion take place and the polymer sample be a homogeneous solid slab (with a thickness *h*) bounded by two parallel planes normal to the *x*-axis, of abscissae $x = 0$ and $x = h$. The sample is in contact with the gaseous dopant. After the infinite time of doping t, the PPP will have reached the concentration *Cs*.

The initial conditions:

$$t = 0; \quad C = 0; \text{ for } 0 < x < h.$$

The boundary conditions:

$$t > 0; \quad x = h, \ x = 0; \ C = Cs.$$

Considering the diffusion coefficient not depending on the concentration C, according to Jost, the diffusion profile is [11]:

$$C = Cs\left(1 - \frac{4}{\pi}\sum_{v=0}^{\infty}\frac{1}{(2v+1)}\sin\frac{(2v+1)\pi x}{h}\exp\left(-\left(\frac{(2v+1)}{h}\right)^2 Dt\right)\right). \quad (1)$$

Equation (1) gives the local concentration of the dopant C as a function of time. It was difficult to measure the diffusion profile of the dopant along the samples, therefore we obtained only the total amount of the dopant M picked up by the PPP sample:

$$M = \int_0^h C \cdot dx = 2 \int_0^t -D\left(\frac{\partial C}{\partial x}\right)_{x=0} dt. \tag{2}$$

The mean dopant concentration $\bar{C}$ presents the average concentration of the dopant along the sample:

$$\bar{C} = \frac{M}{h}. \tag{3}$$

It can be derived at once from the measurements of the dopant content in samples.

A general solution for the diffusion process is described by Eq. (4):

$$\bar{C} = Cs\left(1 - \frac{8}{\pi^2} \sum_{v=0}^{\infty} \frac{1}{(2v+1)^2} \exp\left(-\left(\frac{(2v+1)\pi}{h}\right)^2 Dt\right)\right). \tag{4}$$

For a sufficiently large diffusion time t, the first term in the series (4) gives a good approximation:

$$\bar{C} = Cs\left(1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{h^2}\right)\right). \tag{5}$$

On the other hand, the solution of the Fick's law for concentration as a function of time and depth variables under the condition of constant surface concentration Cs is the complementary error function:

$$C(x, t) = Cs \cdot erfc\left(\frac{x}{2\sqrt{D \cdot t}}\right). \tag{6}$$

The integration of this equation with certain approximation gives for the amount of infused species per unit area:

$$Q(t) = \int_0^\infty C(x, t) = 2Cs\sqrt{D\frac{t}{\pi}}. \tag{7}$$

For the small diffusion time t, Eq. (7) gives a good approximation for mean concentration:

$$\bar{C} \approx \frac{4Cs}{h}\sqrt{\left(\frac{Dt}{\pi}\right)}. \tag{8}$$

As we have shown earlier, the the results of conductivity investigation, in general, were in agreement with the dependence of the dopant content

on the doping time. Therefore, they were used to characterise doping kinetics and dopant diffusion [3].

The density of the conductive paths is determined by the attachment of dopant atoms, so that the conductivity can be expressed:

$$\sigma(t) = \sigma_0 + K\sqrt{D \cdot t}, \tag{9}$$

where K is a constant depending on the geometrical form and parameters of the sample. The significance of this result is that once the surface saturation concentration has been achieved, a plot of conductivity against $t^{1/2}$ must be linear and by substituting the value of the diffusion coefficient D, expressed in the Arrhenius law mode, into Eq. (9) should yield a value of activation energy Ea'' of conductive defect formation (Eq. 11).

3.2. Experimental results

Most of our experimental results for the doping kinetics were described in our previous investigation [3]. But according to the mathematical model, presented in this paper, these results need additional comments. Figures 2–4 show the kinetics of halogen doping for PPP. These data are analysed according to Eq. (8) and plotted $\bar{C}/Cs$ vs $t^{1/2}$.

Figures 5–7 show a semilogarithmic plot of $(Cs - \bar{C})/Cs$ as a function of doping time. These data are calculated according to Eq. (5).

As we can see from Figs. 2, 4, 5 and 6, it is possible to describe the doping process by different subprocesses. All these subprocesses are presented for iodine doping at doping temperatures above 500°C (Fig. 2).
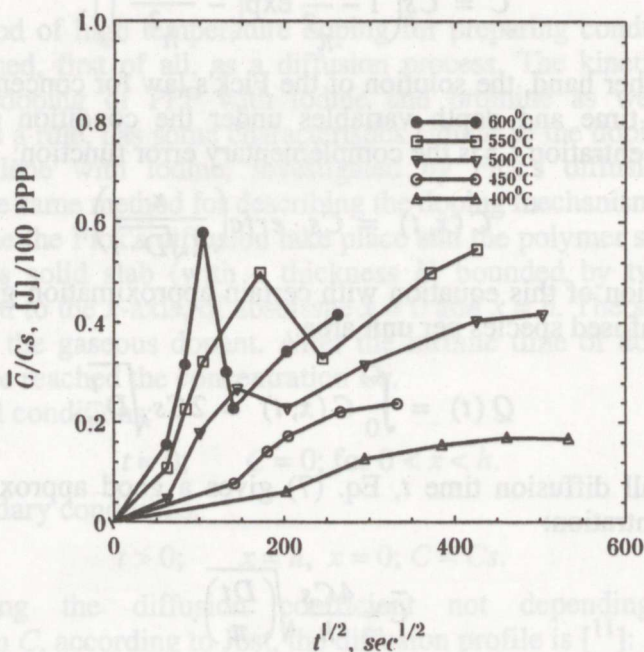

Fig. 2. The kinetics of iodine doping for PPP, presented as $\bar{C}/Cs$ function of doping time ($t^{1/2}$). $Cs = 30$ iodine atoms per C_6H_4 monomer.

It should be noticed that during the preliminary period, the gaseous iodine comes into contact with the PPP surface most effectively. The short preliminary period is followed by the period which is characterised by an increase close to linear in the mean concentration of iodine on $t^{1/2}$.

With an increase in the doping time, a short period follows during which the mean concentration of iodine in PPP decreases, and then, the process of doping is transferred into the normal exponential function in the course of which the equilibrium condition between the sorption and desorption of the dopant is reached. The saturated concentration value of iodine in PPP (Cs) which, as literary data and experimental material show, cannot considerably exceed 30 iodine atoms per C_6H_4 monomer.

The level of the saturated concentration of iodine and the rate of the doping depend heavily on the temperature.
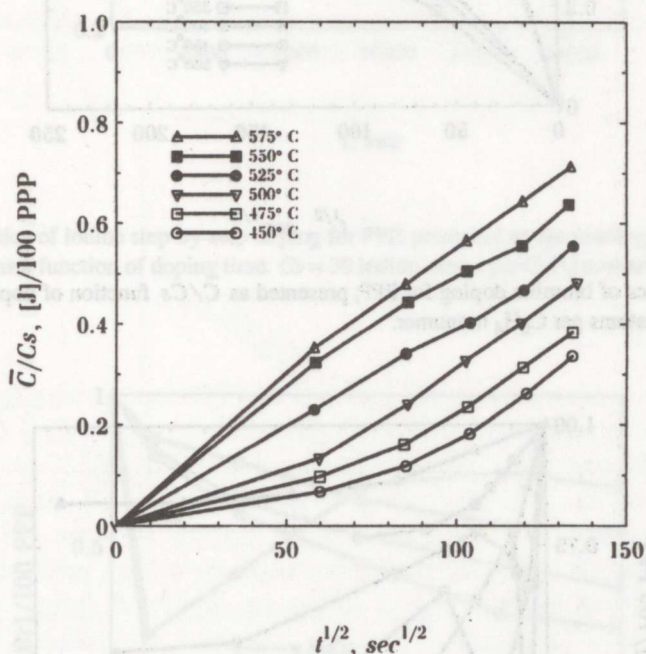

Fig. 3. The kinetics of iodine step-by-step doping for PPP, presented as $\bar{C}/Cs$ function of doping time ($t^{1/2}$). $Cs = 30$ iodine atoms per C_6H_4 monomer.

As Fig. 3 shows, for the step-by-step doping of PPP with iodine, the rate of diffusion is significantly higher, and the process proceeds without the desorption period similarly to continuous doping (Fig. 2). Furthermore, at doping temperatures below 500°C, the dopant content increases to concentrations which were practically unattainable by the usual doping technology, the preliminary period at temperatures 450–475°C is short and at temperatures above 500°C, it is not appreciable.

Figure 4 shows the ability of bromine to dope more actively than iodine. The doping process at 350°C and above has, in general, the same character

as iodine doping at 400–450°C. Moreover, at 300°C, the period of decrease in bromine concentration proceeds after the fast preliminary period.
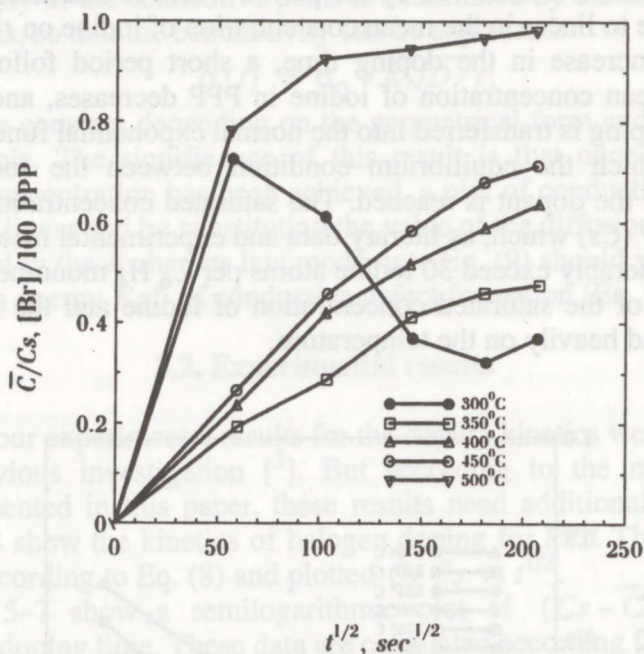

Fig. 4. The kinetics of bromine doping for PPP, presented as $\bar{C}/Cs$ function of doping time ($t^{1/2}$). $Cs = 55$ bromine atoms per C_6H_4 monomer.
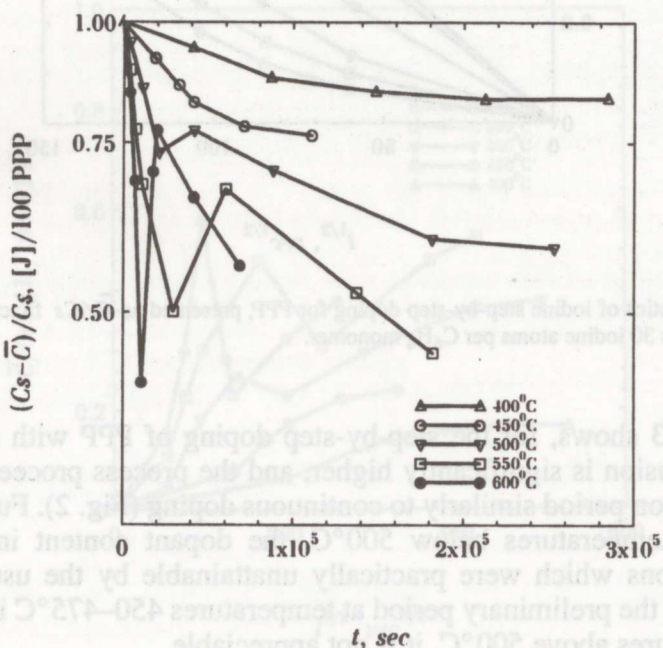

Fig. 5. The kinetics of iodine doping for PPP, presented as the semilogarithmic plot of $(Cs - \bar{C})/Cs$ as a function of doping time. $Cs = 30$ iodine atoms per C_6H_4 monomer.
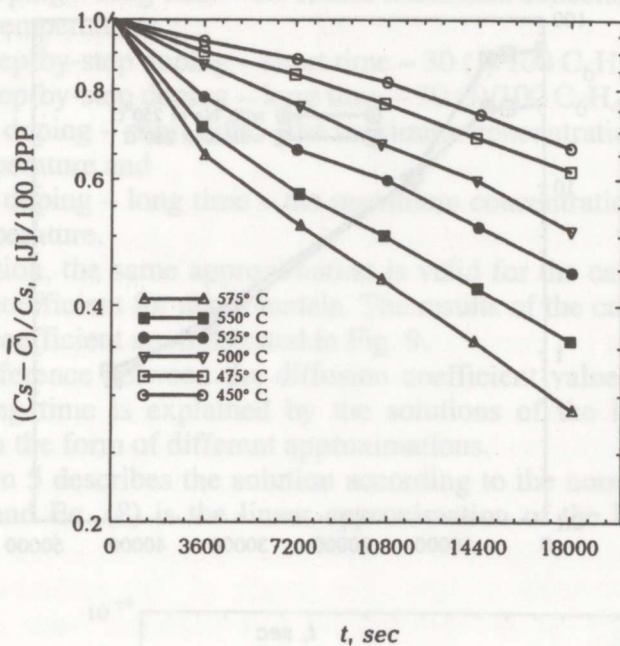
Fig. 6. The kinetics of iodine step-by-step doping for PPP, presented as the semilogarithmic plot of $(Cs - \bar{C})/Cs$ as a function of doping time. $Cs = 30$ iodine atoms per C_6H_4 monomer.
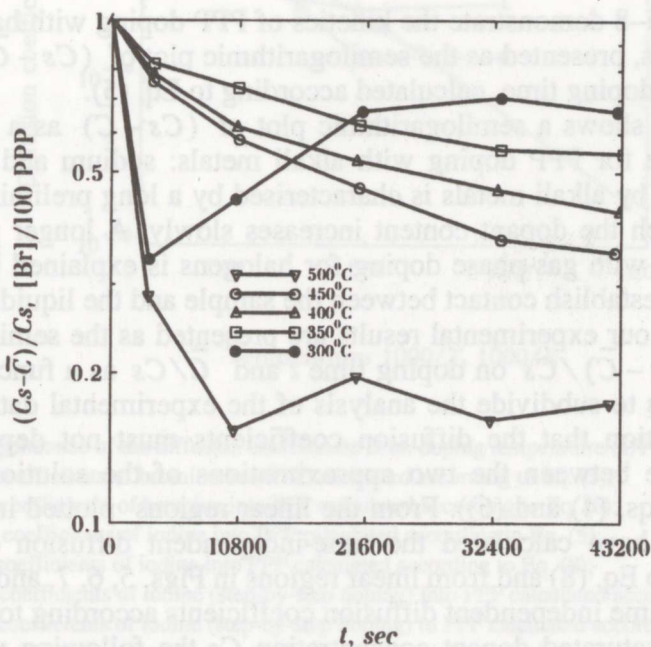

Fig. 7. The kinetics of bromine doping for PPP, presented as the semilogarithmic plot of $(Cs - \bar{C})/Cs$ as a function of doping time. $Cs = 55$ bromine atoms per C_6H_4 monomer.
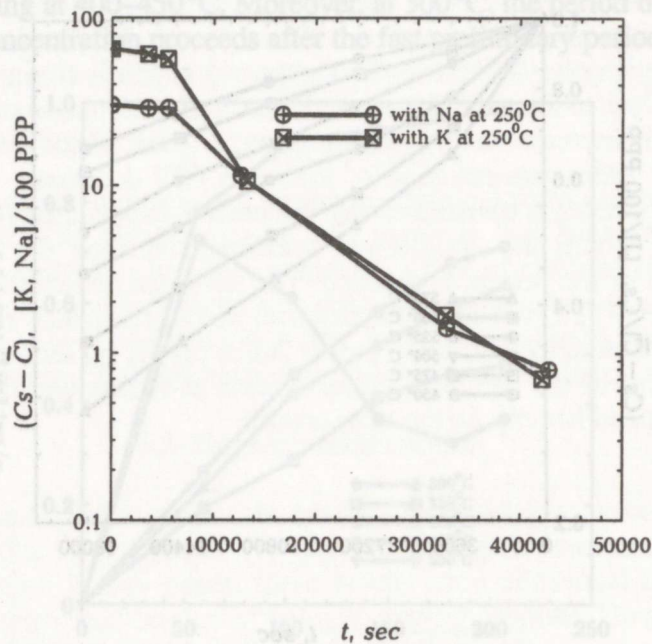
Fig. 8. The kinetics of doping with alkali metal sodium and potassium for PPP, presented as the semilogarithmic plot of $(Cs - \bar{C})$ as a function of doping time. The saturated dopant concentration value $Cs = 54$ for potassium doping and $Cs = 20$ for sodium doping.

Figures 5–8 demonstrate the kinetics of PPP doping with halogens and alkali metals, presented as the semilogarithmic plot of $(Cs - C)/Cs$ as a function of doping time, calculated according to Eq. (5).

Figure 8 shows a semilogarithmic plot of $(Cs - C)$ as a function of doping time for PPP doping with alkali metals: sodium and potassium. The doping by alkali metals is characterised by a long preliminary period during which the dopant content increases slowly. A longer preliminary period than with gas-phase doping for halogens is explained by the time required to establish contact between the sample and the liquid dopant.

Because our experimental results are presented as the semilogarithmic plot of $(Cs - \bar{C})/Cs$ on doping time t and $\bar{C}/Cs$ as a function of $t^{1/2}$, the aim was to subdivide the analysis of the experimental data, based on the assumption that the diffusion coefficients must not depend on the doping time between the two approximations of the solution of Fick's equation (Eqs. (4) and (6)). From the linear regions plotted in Figs. 2, 3, and 4, we have calculated the time-independent diffusion coefficients according to Eq. (8) and from linear regions in Figs. 5, 6, 7, and 8, we have calculated time independent diffusion coefficients according to Eq. (5).

For the saturated dopant concentration Cs the following values were used:
– iodine doping – short time – 30 (J)/100 C_6H_4 and

– iodine doping – long time – the iodine maximum concentration value for the given temperature;

– iodine step-by-step doping – short time – 30 (J)/100 C_6H_4 and

– iodine step-by-step doping – long time – 30 (J)/100 C_6H_4;

– bromine doping – short time – the maximum concentration value for the given temperature and

– bromine doping – long time – the maximum concentration value for the given temperature.

In addition, the same approximation is valid for the calculation of the diffusion coefficient for alkali metals. The results of the calculation of the diffusion coefficient are illustrated in Fig. 9.

The difference between the diffusion coefficient values for short and long doping time is explained by the solutions of the Fick's diffusion equation in the form of different approximations.

Equation 5 describes the solution according to the normal exponential function, and Eq. (8) is the linear approximation of the Fick's diffusion equation.
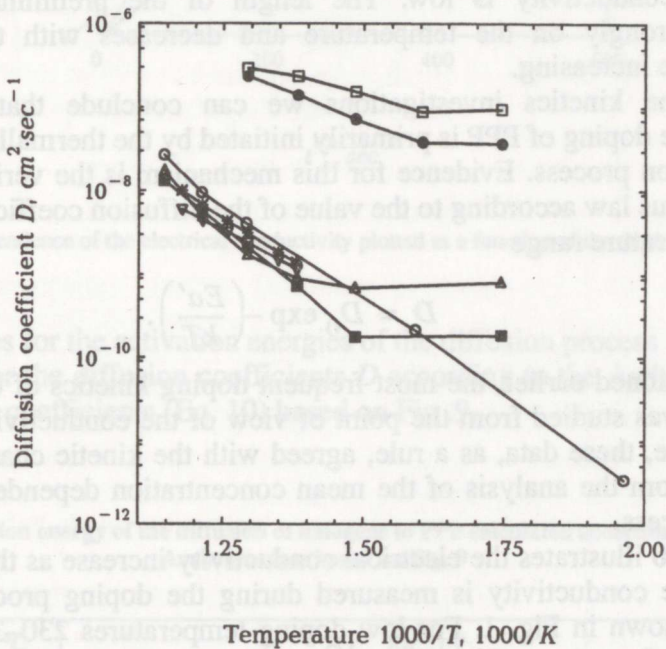

Fig. 9. The dependence of the diffusion coefficients D on doping temperature ($1/T$):

□ – diffusion coefficients of bromine into PPP calculated according to Eq. (5);

● – diffusion coefficients of bromine into PPP calculated according to Eq. (8);

△ – diffusion coefficients of iodine into PPP calculated according to Eq. (5);

■ – diffusion coefficients of iodine into PPP calculated according to Eq. (8);

∗ – diffusion coefficients of iodine (step-by-step doping) into PPP calculated according to Eq. (5);

∇ – diffusion coefficients of iodine (step-by-step doping) to PPP calculated according to Eq. (8);

○ – diffusion coefficients calculated on the basis of the initial and final concentrations according to Eq. (9) for different diffusion times t obtained from the linear regions (cf. Fig. 10).

117

As the diffusion coefficient values and the kinetical dependence show, a difference exists in the results obtained below and above 500°C for iodine doping, and the same is valid for bromine, but at 350°C. For iodine doping below 450°C, the diffusion coefficient is practically independent of temperature. It can be explained by a slow incorporation of the dopant, probably when no electrically active defects are generated. The main part of the dopant must be in an electrically inactive form. This is also confirmed by the low value of the electrical conductivity – close to the undoped PPP conductivity value. Earlier, in our electrical conductivity and Hall effect investigations we made the same conclusions [6, 12]. An active incorporation of the dopants and a conductivity increase take place above 500°C, explained by the thermal destruction of the polymer [3].

The difference between the values of the diffusion coefficient obtained by Eqs. (5) and (8) can be explained by the existence of the preliminary period which is important mostly at lower temperatures. During the preliminary period, only an active dopant sorption to the PPP surface takes place, the incorporation of the dopant into the polymer is not active, and electrical conductivity is low. The length of the preliminary period depends strongly on the temperature and decreases with the doping temperature increasing.

From the kinetics investigations we can conclude that the high temperature doping of PPP is primarily initiated by the thermally activated incorporation process. Evidence for this mechanism is the verification of the Arrhenius law according to the value of the diffusion coefficient D in a wide temperature range

$$D = D_0 \exp\left(-\frac{Ea'}{kT}\right). \tag{10}$$

As mentioned earlier, the most frequent doping kinetics of conducting polymers was studied from the point of view of the conductivity change. Furthermore, these data, as a rule, agreed with the kinetic characteristics obtained from the analysis of the mean concentration dependence in the doping process.

Figure 10 illustrates the electrical conductivity increase as the function of $t^{1/2}$. The conductivity is measured during the doping process in the ampoule shown in Fig. 1. For low doping temperatures 230–350°C, the linear plot of conductivity against $t^{1/2}$ yields a straight line. Therefore we can calculate the diffusion coefficients on the basis of initial and final concentrations (Ci and Cf) according to Eq. (8). Ci and Cf were obtained by chemical analysis before and after the conductivity measurements. For the conductivity investigations above 500°C, the measurements began from the undoped form of PPP ($Ci = 0$), and Cf was obtained also by chemical analysis. The diffusion time values were obtained from the linear regions of the curves in Fig. 10. Therefore, we can calculate the diffusion coefficients on the basis of the initial and final concentrations according to Eq. (8) for different diffusion times t obtained from the linear regions in Fig. 10 and from temperatures. The D values obtained by this method are

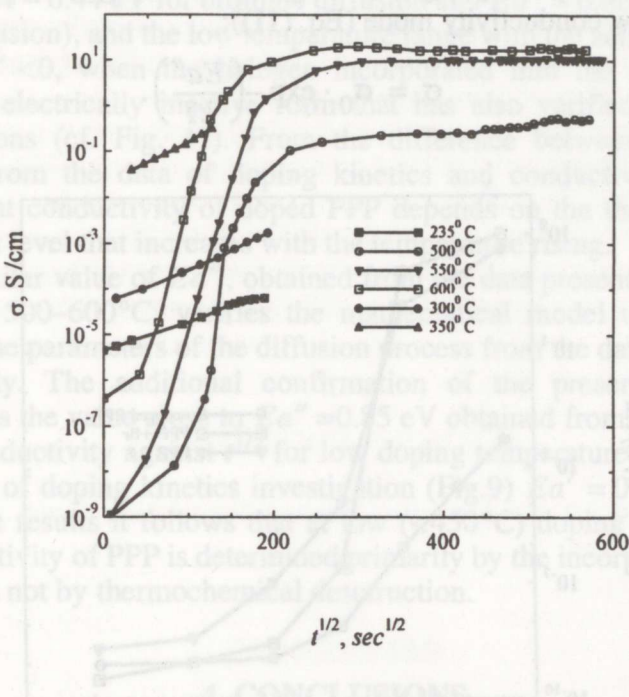slightly higher than D values obtained from the kinetics investigations (Fig. 9 – graph. symbols ○).

Fig. 10. The dependence of the electrical conductivity plotted as a function of the doping time ($t^{1/2}$).

The values for the activation energies of the diffusion process Ea' were calculated for the diffusion coefficients D according to the Arrhenius law for diffusion coefficients (Eq. 10) based on Fig .9.

Table 1

The activation energy of the diffusion of halogens to PPP calculated according to the Arrhenius law based on Fig. 9

Temp. range, °C	Ea', eV						
230–600							0.96*
300–350	<0	<0			<0	<0	
350–500					0.44	0.34–0.24	
400–600	1.05						
450–575		0.92	0.86	0.92			
450–600		0.92–0.98					
Graph symbol	■	△	▽	*	●	□	○

* at lower temperatures the samples were predoped.

The values for the activation energies of the conductive defect formation Ea'' were obtained by the Arrhenius law for diffusion coefficients (Eq. 10) substituted into Eq. (9) from the data presented in Fig. 10 and also by analysing the data presented in Fig. 11 according to the Arrhenius law conductivity mode (Eq. (11)):

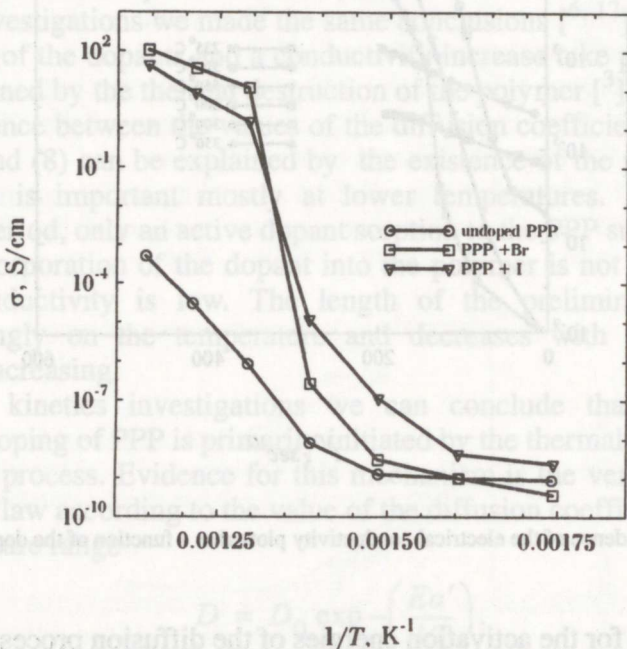$$\sigma = \sigma_0 \cdot \exp -\left(\frac{Ea''}{kT}\right). \tag{11}$$

Fig. 11. The dependence of the electrical conductivity plotted as a function of temperature ($1/T$).

Table 2

The activation energies for conductive defect formation Ea''

Temp. range, °C	Ea'', eV			
	from Fig. 11			from Fig. 10
230–350				0.85
500–600	1.98	1.54	3.6	1.98
Graph symbol	▽	□	○	○ ● ▽ △ □ ■

The calculated values of the activation energies show that it is possible to divide the diffusion of halogens into PPP on two different temperature

120

ranges. The high temperature range (>350°C for bromine, >400°C for iodine doping) when the diffusion process is a thermally activated adsorption process is characterised by the activation energy values ($Ea' = 0.24 - 0.44$ eV for bromine diffusion and $Ea' = 0.86 - 1.05$ eV for iodine diffusion), and the low temperature range with the activation energy values $Ea' < 0$, when the halogen incorporated into the PPP structure mainly in electrically inactive form that has also verified conductivity investigations (cf. Fig. 11). From the difference between Ea' values obtained from the data of doping kinetics and conductivity results, it follows that conductivity of doped PPP depends on the thermochemical destruction level that increases with the temperature rising.

The similar value of Ea'', obtained from the data presented in Figs. 10 and 11 at 500–600°C, verifies the mathematical model used by us to calculate the parameters of the diffusion process from the data of electrical conductivity. The additional confirmation of the presented diffusion equations is the value close to $Ea'' = 0.85$ eV obtained from a straight line plot of conductivity against $t^{1/2}$ for low doping temperatures (Fig.10) and the results of doping kinetics investigation (Fig.9) $Ea' = 0.86 - 1.05$ eV. From these results it follows that at low (<450°C) doping temperatures, the conductivity of PPP is determined primarily by the incorporated part of dopant and not by thermochemical desctruction.

4. CONCLUSIONS

High temperature doping facilitates preparation of the conductive polymer – polyparaphenylene – with high electrical conductivity and high stability. The doping process at the controlled sample temperature and the dopant activity provides an attractive method for electron material technology control. The temperatures of the practical application of the PPP increase with high temperature doping, and therefore PPP can be regarded as a prospective conductive polymer material for very high temperature applications. The high temperature doping procedure is accompanied by the thermal destruction of the polymer but it is not the only reason of the increase in electrical conductivity. The main reason for the conductivity increase is the incorporation and distribution of the dopants like in classical semiconductive materials, but the thermal destruction of the polymer affects the incorporation process.

In general, the conductivity level obtained depends on the incorporated dopant amount at doping temperatures 500 °C when the main part of the dopant is incorporated in an electrically active form, and the influence of the preliminary period is not essential. The thermochemical destruction can be controlled by using the step-by-step doping method, and for bromine, lower bromine pressures are recommended, for instance, bromine doping of PPP at dopant pressure −0.15 atm gives more controllable conductivity results [8]. By the step-by-step doping method, we can also obtain higher dopant concentrations than by the continuous doping at the same temperatures. Bromine is more easily diffused into the

PPP than iodine, the activation energy and diffusion coefficient values provide evidence of this. The alkali metal doping process, in general, is in good agreement with the presented diffusion model. But the main problem for the PPP doped with alkali metals is the instability in air.

The importance of the result for the technological application of PPP is in the calculation of the values for the diffusion coefficient and activation energy for the halogen doping process.

Based on our kinetics analysis of the doping process, we can conclude that by the electrical conductivity data analysis, it is possible to calculate the parameters of the diffusion process.

As a result of the analysis of the diffusion coefficients and activation energies, we can conclude that, in general, the process of halogen diffusion in PPP is in agreement with the diffusion of impurities in amorphous bodies.

ACKNOWLEDGEMENTS

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JUHTIVA POLÜPARAFENÜLEENI VALMISTAMINE KÕRGTEMPERATUURSE LEGEERIMISE ABIL

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On esitatud hea elektrijuhtivuse ja stabiilsusega juhtiva polümeeri – polüparafenüleeni – saamise meetod kõrgtemperatuurse (250–600°C) legeerimise abil. Legeerimisprotsessi kontroll polüparafenüleeni temperatuuri ja lisandi aktiivsuse kaudu loob efektiivse võimaluse elektronmaterjalide valmistamise tehnoloogia juhtimiseks. On analüüsitud legeerimisprotsessi mehhanismi ja kineetikat. Arvutatud difusioonikoefitsientide ja aktiveerimisenergiate alusel võib järeldada, et halogeenide difusiooniprotsess polüparafenüleenis allub lisandi difusiooni seaduspärasustele amorfsetes kehades.