Exchange of Dopant Ions in Polyacetylene

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The spontaneous exchange of dopant ions in polyacetylene is demonstrated, providing a route to the synthesis of polyacetylenes with different dopant ions but exactly the same doping level; the process is thermodynamically controlled and does not occur if it is thermodynamically disfavoured, as in the case of exchange of I_3^- for BF_4^- ions.

Polyacetylene, $[CH]_x$, is an organic semiconductor with room temperature conductivity values, σ_{RT}, of *ca.* 10^{-6} and 10^{-11} Ω^{-1} cm^{-1} for the *trans*- and the *cis*-polymer, respectively. Doping, which increases Ω_{RT} up to 10^3 Ω^{-1} cm^{-1}, can be achieved by chemical[1] or electrochemical oxidation (*p*-doping) or reduction (*n*-doping), which creates positive and negative charge carriers, respectively, and introduces oppositely charged counter- or 'dopant' ions. Although the effect of dopant level on conductivity has been carefully studied,[2] the role of the dopant ion itself in conduction is not well understood. Experimental results[3] on $[CH]_x$ and theoretical calculations on conducting polymers with explicit consideration of the doping agents[4] suggest that the nature of the dopant ion can have a marked influence on conductivity. However, it is not clear that different conductivities are not a result of different experimental conditions, since the conductivity of $[CH]_x$ is an extremely sensitive function of the doping level.[5] Thus, in comparing samples of $[CH]_x$ with different dopant ions it is essential that the doping level remain the same. Here we report the use of spontaneous solution ion-exchange,[6] a physical process driven by concentration gradients, to vary the counter-ion in the same sample of $[CH]_x$.

A dopant ion exchange process can be empirically represented by equation (1), where $(A)_{y_i}$ is the mole fraction of initial dopantion A^- in $[CH]_x$, $(B)_{z_f}$ is the final mole fraction of exchanging ion B^-, and $(A)_y$ and $(B)_z$ are the intermediate stoicheiometries of A^- and B^-, respectively. Since this is a spontaneous physical process and there are no chemical reactions, doping level remains constant; thus, after complete exchange, $(A)_{y_i} \equiv (B)_{z_f}$. Assuming, for the initial boundary conditions,[6] that A is homogeneously distributed throughout polyacetylene film of thickness h, that the diffusion coefficient (D) is constant, and that the concentration of B^- in the solution is in large excess over the amount of A^- in the doped polyacetylene, we can derive, for the initial time interval,[7] equation (2), where $y_i - y_t$ is the quantity of A^- which has left, or of B^- which has entered, the polyacetylene fibrils in time t.

$$CH(A)_{y_i} + B^- \rightleftharpoons CH(A)_y(B)_z \rightleftharpoons CH(B)_{z_f} + A^- \quad (1)$$

$$\frac{y_i - y_t}{y_i} = \frac{4}{\pi^{\frac{1}{2}}}\left(\frac{Dt}{h^2}\right)^{\frac{1}{2}} \quad (2)$$

Films of *cis*-$[CH]_x$, *ca.* 100 μm thick, prepared by the method of Ito *et al.*,[8] were homogeneously oxidized by electrochemical means[9] to $y_i = 0.055$ and 0.0294 of ClO_4^-. Several pieces of doped films, *ca.* 10 mg each, were immersed in a 100-fold excess of 1 M-$LiAsF_6$ (USS Agrichemicals) in propylene carbonate (Burdick and Jackson) in a dry box. Films were removed at various intervals, rinsed with toluene, pumped dry, and analysed for chlorine. Figure 1 shows the progress of exchange for $[CH(ClO_4)_y]_x$ with doping levels, y, of 0.055 and 0.0294 and initial conductivities of 550 and 60 Ω^{-1} cm^{-1}, respectively. For the more highly-doped $[CH]_x$,

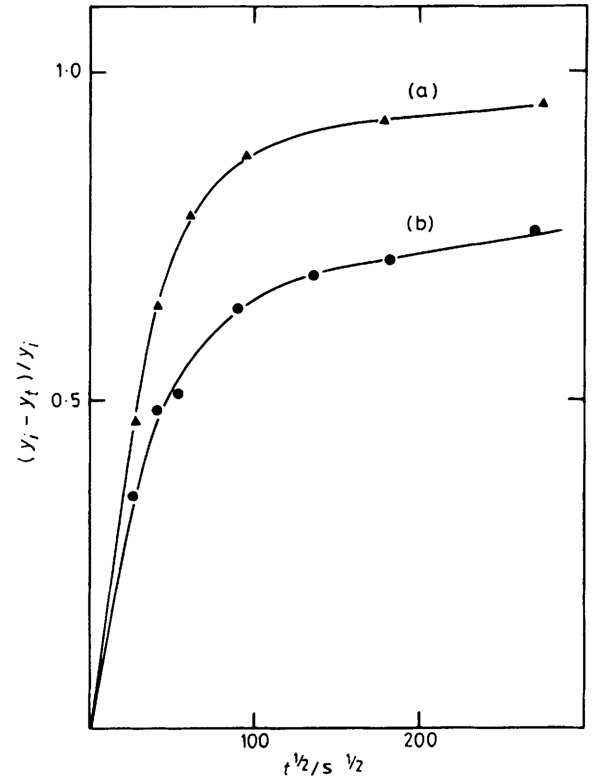

Figure 1. Fractional exchange of perchlorate dopant ion with hexafluoroarsenate ion *vs.* $t^{1/2}$ for perchlorate-doped $[CH]_x$ in 1 M-$LiAsF_6$ in propylene carbonate at 30 °C; (a) y_i 0.055, (b) y_i = 0.0294.

exchange is nearly quantitative after a few hours. After exchange the conductivity had decreased by only 10%, probably as a result of slight spontaneous undoping since AsF_6^--doped $[CH]_x$ showed a similar decrease in conductivity upon exchange with ClO_4^- and the conductivity of ClO_4^--doped $[CH]_x$ decreases by the same amount when kept in perchlorate electrolyte. From equation (2) a diffusion coefficient for diffusion through 100 μm films of about 5×10^{-9} cm^2 s^{-1} was obtained from the initial (short time) portion of the exchange curves.

Other experiments show that the exchange is completely reversible with respect to the initial dopant ion, in that the original ion may be reintroduced by soaking an exchanged sample in a solution of the original ion. Elemental analyses for chlorine and arsenic on exchanged samples show that exchange is quantitative when one ion is in great excess. Exchange performed with an excess of tetrafluoroborate ion in solution instead of AsF_6^- shows similar kinetics.

We also attempted ion exchange with iodine vapour-phase doped $[CH]_x$ and found that the exchange of dopant ions is thermodynamically controlled and may not occur when it is thermodynamically disfavoured. Polyacetylene doped slowly to a level of 6 mol % iodine by the method of Chiang *et al.*[3] was immersed in 0.35 M-$LiBF_4$ in propylene carbonate. Eight samples, allowed to exchange for times from 0 to 9 days, showed a constant concentration of iodine by elemental analysis of (37 ± 3)% [$y(I_3^-)$ = 0.02], indicating that negligible exchange had occurred, even on this extended time scale.

The explanation for the lack of exchange is provided by thermodynamic considerations. It has been shown that the potential of polyacetylene depends on the degree to which it has been oxidized.[10,11] The formal potential for the couple $[CH^+]_x + xe^- \rightleftharpoons [CH]_x^0$ is about 0.6 V *vs.* reference hydrogen electrode.[12,13] The anion present in iodine-doped polyacetylene is mainly I_3^- rather than I^-.[14] If I_3^-, an oxidizing agent itself, were to be displaced from polyacetylene in the course of an ion exchange, an additional redox couple would have to be considered, namely $I_3^- + 2e^- \rightleftharpoons 3I^-$ in the solvent phase. In terms of the Nernst equation for the potential, $E = E^0 + (RT/nF) \log (a_{I_3^-}/a_{I^-})$, E will become more positive as more I_3^- is released. The potential for the polyacetylene couple does not vary during the exchange because the degree of oxidation remains constant. Therefore, there would be an overall net increase in electrochemical potential (a positive change in free energy) if I_3^- were to exchange. The process is therefore not spontaneous, *i.e.* exchange does not occur. This explanation does not rule out self-exchange between I_3^- in solution and I_3^- in the polymer. Our results clearly show that exchange systems are easier to analyse if the complicating redox reactions of a reactive counter ion, such as I_3^-, can be avoided by the use of inert ions such as ClO_4^-, AsF_6^-, or BF_4^-.

In conclusion, we have demonstrated, for the first time, spontaneous ion exchange in a doped, highly conducting organic polymer. This phenomenon represents a novel way of introducing different counter ions into polyacetylene and may prove valuable in assessing conduction mechanisms.

This work was supported by grants from N.S.F. and Stauffer Chemical.

Received, 27th January 1987; Com. 106

References

1 H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, 578.
2 J. C. W. Chien, 'Polyacetylene—Chemistry, Physics and Material Science,' Academic Press, New York, 1984.
3 C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, 1978, **100**, 1013.
4 J. L. Bredas, B. Themans, J. G. Fripiat, J. M. Andre, and R. R. Chance, *Phys. Rev. B.*, 1984, **29**, 6761.
5 J. C. W. Chien, J. M. Warakomski, F. E. Karasz, W. L. Chia, and C. P. Lillya, *Phys. Rev. B*, 1983, **28**, 6937.
6 F. Helfferich, 'Ion Exchange,' McGraw-Hill, New York, 1962.
7 J. Crank, 'The Mathematics of Diffusion,' Clarendon Press, Oxford, 1956, p. 66.
8 T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 11.
9 J. R. Reynolds, J. B. Schlenoff, and J. C. W. Chien, *J. Electrochem. Soc.*, 1985, **132**, 1131.
10 P. J. Nigrey, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1979, 594.
11 K. Kaneto, M. Maxfield, D. P. Nairns, and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans. 1*, 1982, **78**, 3417.
12 A. F. Diaz and T. C. Clarke, *J. Electroanal. Chem.*, 1980, **111**, 115.
13. A. G. MacDiarmid, R. J. Mammone, J. R. Krawczyk, and S. J. Porter, *Mol. Cryst. Liq. Cryst.*, 1984, **105**, 89.
14 T. Matsuyama, H. Sakai, H. Yamaoda, Y. Maeda, and H. Shirakawa, *Solid State Commun.*, 1981, **40**, 563.