Charge Transport in Polyimines Containing *trans*-1,2-Bis-9-carbazolylcyclobutane

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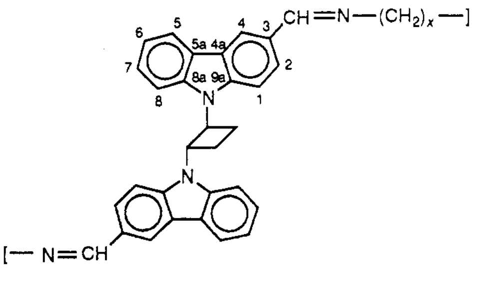
Introduction

We have previously described[4] the synthesis of a series of polyimines containing *trans*-1,2-bis-9-carbazolylcyclobutane (TBCC) and methylene spacers of variable length and studied their charge-transfer interaction with small molecular electron acceptors. A brief review of prior research on polymers based on TBCC was also included in our previous publication. As mentioned there, it has been documented that the peculiar spatial arrangement of the carbazole rings in TBCC prevents excimer formation and leads to better photoconductivity in polymer films doped with TBCC, as well as better photoconductivity in the charge-transfer complexes of the TBCC-containing polymers.

This paper presents NMR spectral evidence for the arrangement of carbazole rings in the polyimines and compares hole mobility in a polyimine film with hole mobility in a poly(*N*-vinylcarbazole) [PVK] film, confirming previous experimental data.

Experimental Part

The synthesis of the polyimines is described in our previous publication.[4] The polymers have the following general formula (the numbering of carbons/protons is used for NMR identification):



NMR spectra were recorded on a Bruker AM-400 spectrometer in chloroform solutions using standard conditions. Assignments were decided on the basis of two-dimensional COSY and HETCOR spectra, run with the software provided by Bruker.

Hole mobility was determined by the time-of-flight (TOF) technique, which has been widely used in the study of charge transport in several different materials.[5–7] The device consists of a generation layer (about 0.5 μm) of vanadylphthalocyanine and a thicker charge-transport layer (about 15 μm) of the analyzed polymer. The charge transport layer is coated from a solution of 10 wt % of the polymer in dichloromethane. The charge-generation layer is used to generate a set of charge carriers and their transit time across the transport layer is measured to determine the hole mobility.[6]

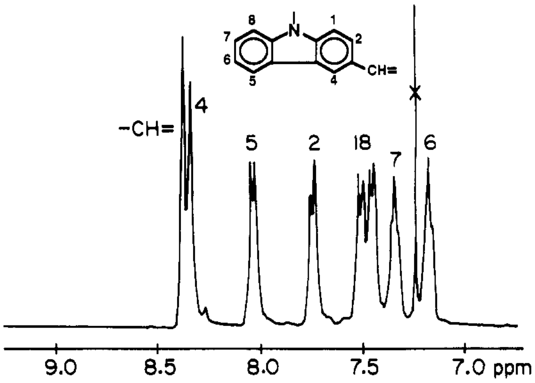


Figure 1. Aromatic part of the ^{1}H NMR spectrum of PI-12 in CDCl$_3$. The assignments of the signals correspond to the numbering on the formula.

Results and Discussions

The aromatic part of the ^{13}C NMR spectrum of PI-8 (as an example) is very similar to the aromatic part of the ^{13}C NMR spectrum of PVK. The imine carbon resonates at 161.0 ppm. The aromatic carbons resonate at 141.2 (8a), 140.4 (9a), 128.3 (3), 126.2 (7), 126.1 (2), 123.9 (5a), 123.6 (4a), 120.8 (5), 120.7 (4), 120.0 (6), 109.8 (8), and 109.6 ppm (1). These resonances are fairly similar to those of the aromatic carbons of PVK,[8] the obvious difference being carbon 3. It is shifted downfield in the polyimine because of the directly bonded imine carbon.

The proton NMR spectrum (aromatic region) of PI-12 is presented in Figure 1. The assignments are given in the figure. This spectrum proves the great differences in terms of orientation of the carbazole rings in the polyimines as compared with PVK. In PVK, the range of chemical shifts of the aromatic protons is between 8 and 5 ppm, while the polyimines show resonances between 8.5 and 7 ppm, approximately. This is the first indication of much less shielding in the polyimines. The most shielded proton in PVK was proton 1, and the next was proton 2. These protons fall in the middle of the shielding cone of a neighboring carbazole unit, independent of the chain configuration. The bulky carbazole ring is so close to the main chain that the only conformation this chain may take allows the formation of stacks of carbazole rings. This was proven by molecular modeling.[8] In fact, proton 1 resonates at an unusually high field for an aromatic proton (about 5 ppm). In comparison, proton 1 resonates very close to proton 8 in the polyimine, at about 7.5 ppm, as shown in the figure, indicating no stacking of the carbazole rings in this polymer. The absence of carbazole stacks in

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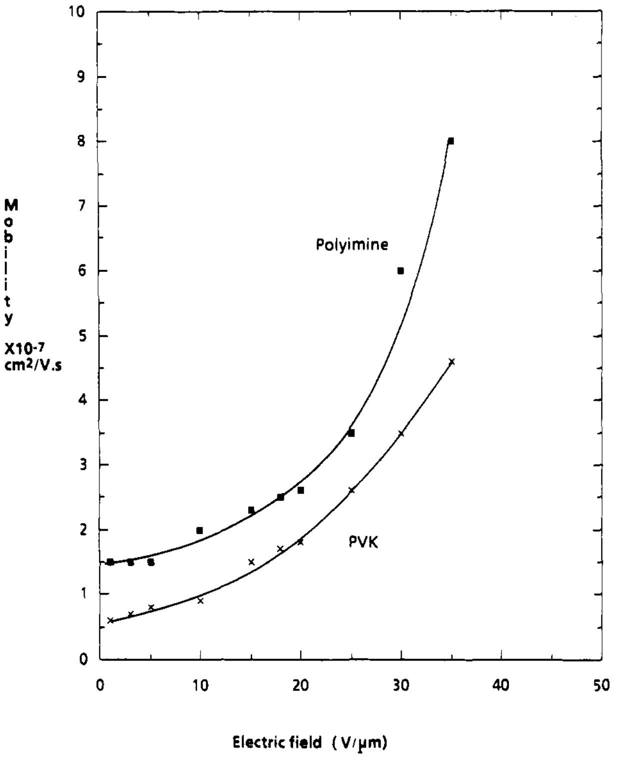

Figure 2. Hole mobility dependence on electric field for PI-6 and PVK obtained in the conditions described in the text.

the "normal" polyimine conformation clearly proves that there is no spatial incentive to form excimers, as PVK provides.[9]

The results of the electric field dependence of the hole mobility are shown in Figure 2. The polyimine sample is a film of PI-6. Also shown for comparison are the results obtained with a PVK film. It is clear that the hole mobility is higher in the polyimine than in PVK. The improvement in the hole mobility could be due to one or many of the factors that affect mobility: a decrease in the extent of conformational trapping;[10] a narrower energy distribution of hopping sites;[11] subtle differences in the polarizability of the medium;[12,13] a reduction of excimer-forming trapping sites.[9]

Conclusions

Improved hole mobility in polyimines containing TBCC in comparison to hole mobility in PVK can be attributed to a decrease of trapping sites in the polyimines. This decrease can be correlated to the NMR spectral evidence for lack of a stacked arrangement of the carbazole rings. Such a stacked structure is present in PVK.

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