Preparation and Conductivities of Fullerene-doped Polyanilines

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Upon doping with C_{60}–C_{70} (75 : 25 by mole) or by C_{60} (>99%) in N-methylpyrrolidin-2-one–toluene solution at room temperature, conductivities of the emeraldine base of polyaniline as free-standing solution-cast films were found to increase significantly to ca. 10^{-4} S cm^{-1} at a fullerene content of ca. 1 mol%.

Since the discovery[1] and development of a large-scale method for the preparation[2] of fullerenes (including buckminsterfullerene, C_{60}), the physical and chemical properties of this new allotropic carbon form have been investigated extensively.[3] In particular, fullerenes exhibit very intriguing electronic properties. For examples, C_{60} was found to form a charger-transfer (CT) complex with N,N-diethylaniline[4] and to increase the photoconductivities of polyvinylcarbazole significantly.[5] Upon doping with alkali metals, C_{60} is reduced and becomes a superconductor at low temperatures.[6] In all these cases, the fullerene functions as a good electron acceptor.

Recently, we have been interested in the use of C_{60} to dope p-type conducting polymers, especially polyanilines. We anticipated that neutral polymers (e.g. emeraldine base of polyanilines[7,8]) could be doped by C_{60} to give higher conductivities through the formation of CT complexes between the polymer as the electron donor and C_{60} as the acceptor. During the preparation of this paper, reports have appeared in the literature on C_{60} doping of poly(3-alkylthiophene)s[9] and on photoinduced electron transfer from a conducting polymer to C_{60}.[10] The conductivities of poly(3-alkylthiophene)s doped with C_{60} were found to be about one order of magnitude higher than the undoped polymers.[9] In this communication, we present our preliminary results on doping emeraldine base (EB) of polyanilines (i.e. polyaniline and polytoluidine) with fullerenes, including C_{60} (purity >99%) and a mixture of C_{60} and C_{70} (75:25 by mole), in N-methylpyrrolidin-2-one (NMP)–toluene (50:50 by volume) solution at ambient temperature. The conductivities and spectroscopic properties of the fullerene-doped polyanilines are also reported.

Fullerene-containing soot (SES Research) was extracted with toluene. The extract was concentrated by evaporating toluene and the resulting fullerene solution was characterized by UV–VIS–near-IR absorption spectroscopy on a Perkin-Elmer Lambda-2 spectrophotometer. The molar absorptivities ($\varepsilon[\lambda]$) at 338 and 384 nm for C_{60}($\varepsilon[338]$ 51000 and $\varepsilon[384]$ 7860 dm^3 mol^{-1} cm^{-1}) and C_{70} ($\varepsilon[338]$ 27100, $\varepsilon[384]$ 26400 dm^3 mol^{-1} cm^{-1}) were used in a two-component Lambert–Beer analysis to yield concentrations of C_{60} and C_{70} in the solution of extract from measured absorbances. The results were $[C_{60}]$ = 2.6 × 10^{-3} and $[C_{70}]$ = 8.4 × 10^{-4} mol dm^{-3}, corresponding to a 75:25 molar ratio of C_{60} : C_{70} as expected in the extract. C_{60} with less than 1% C_{70} was subsequently obtained from the extract by preparative chromatography on neutral alumina.[11] EBs of polyaniline and polytoluidine were synthesized following the literature procedures.[7,8] To prepare the fullerene-doped EB free-standing films, a 3% (by mass) EB of polyaniline solution in NMP was mixed with the fullerene solution in toluene. The resulting solution had a fullerene content of 0.39, 0.78 or 1.0 mol% per nitrogen ring unit of the EB. This solution was cast into a clean glass plate and the solvents were allowed to evaporate at room temperature. The casting process was repeated several times in order to obtain films with thickness of 0.003 to 0.03 mm. The coated glass plate was placed in a propanol–water (50:50 by volume) mixture and the film was lifted off the glass. The free-standing film was then dried under vacuum at room temperature for 48 h. The conductivities of the free-standing films were measured using the standard four-probe method.
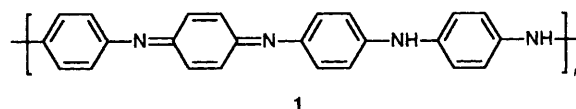

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Table 1 Conductivities of fullerene-doped EB films of polyaniline

Entry	C_{60}–C_{70}/ molar ratio	Mol% fullerene in the film	Conductivity/ S cm^{-1}	Film thickness/ mm
1	—	0	≪1 × 10^{-5}	0.030
2	75:25	0.39	5.3 × 10^{-5}	0.014
3	75:25	0.78	2.2 × 10^{-4}	0.022
4	75:25	1.0	2.3 × 10^{-4}	0.004
5	>99:1	1.0	6.5 × 10^{-4}	0.004
6	—	0	1.6[a]	0.025[a]

[a] Data for EB film doped with HCl from ref. 12(b).

The EB form of polyaniline can be schematically represented by formula 1 with quinoid and benzene rings as well as imine and amine units. The undoped EB film is an insulator with conductivities of ca. 10^{-8} S cm^{-1}.[7,8] Upon doping with the fullerenes (C_{60}–C_{70} = 75:25), the conductivities increased significantly to ca. 10^{-4} S cm^{-1} at a fullerene content of ca. 1 mol% (i.e. 1 fullerene per 100 nitrogen ring units). As shown in Table 1 (entry 5), C_{60} appears to be a better dopant because the EB film cast with pure C_{60} exhibits a somewhat higher conductivity than those with C_{60}–C_{70}. However, the EB films doped with the fullerenes seem to have lower conductivities than those conventionally doped with protonic acids, iodine or iron(III) chloride.[7,8,12] For example, the conductivities of polyaniline doped in 1 mol dm^{-3} HCl aqueous solution are generally in a range of 1–10 S cm^{-1} at ca. 50 mol% acid dopant per nitrogen ring unit. EB films with higher fullerene contents could not be obtained because of technical difficulties in casting films resulting from the limited solubility of the fullerenese in NMP–toluene. It should be noted that further increases in fullerene content may not necessarily improve the conductivity to the values obtained from the conventional doping process. The conductivities are essentially the same at the fullerene contents of 0.78 and 1.0% (Table 1, entries 3 and 4). Morita and coworkers also observed that conductivity of the C_{60}-doped polythiophenes reached a maximum value of ca. 10^{-6} S cm^{-1} at a C_{60} content of 5 mol% followed by a decrease at higher C_{60} concentrations.[9] This could be attributed to the relatively large sizes of the fullerene molecules, which, as dopants, might result in distortion of the conjugation and coplanarity of the polymer backbones and in an increase in the interchain distance. Thus, both intra- and inter-chain CT processes would be hindered, leading to a lower conductivity.

The significant increase in conductivity of the EB films by the fullerene doping could be explained tentatively on the basis of formation of CT complexes. Fullerenes (C_{60} and C_{70}) are known to be good electron acceptors [e.g. $E_{1/2}$ = −0.4 V vs. saturated calomel electrode (SCE) for the formation of C_{60}^{1-} ion[13]], while the EB of polyaniline is a good electron donor ($E_{1/2}$ = 0.13 V vs. SCE[7]). Therefore, there should be a CT interaction between the fullerenes and EB. The electron

transfer from EB to the fullerenes would form positive polarons in the conjugated polymer chains, which would result in the increased conductivity of the EB films. However, attempts to obtain definitive spectroscopic evidence for such CT interactions proved difficult. Solutions (10^{-3} mol dm^{-3}) of the fullerene-doped EB of polyaniline in NMP–toluene were too weak to show a significant CT band, although a new 585 nm excited fluorescence maximum at 760 nm with a shoulder at 790 nm was observed. Diffuse reflectance FTIR spectra of the fullerene-doped films showed shifts of less than 2 cm^{-1}.

To enhance the effects, the EB of polytoluidine (0.72 mmol) was doped with C_{60} (0.09 mmol) in benzene by refluxing the solution for 16 h under argon. The brown, insoluble precipitate was exhaustively washed with benzene and diethyl ether and dried under dynamic vacuum at 75 °C. The diffuse reflectance FTIR spectrum of this product showed the four characteristic bands of the C_{60} IR-active vibrational modes[14] at 1435, 1187, 572 and 524 cm^{-1}, shifted from 1433, 1183, 576 and 528 cm^{-1}, respectively, for pure C_{60}. Similar results were obtained for the EB of polyaniline. It was reported that many amines such as n-propylamine, tert-butylamine, n-dodecylamine and morpholine react as nucleophiles with C_{60} to afford amino addition products.[15] Therefore, the IR spectral results could reflect either CT interactions or the nucleophilic addition of the N–H groups of the EB of polyanilines to C_{60} molecules. Elemental analyses revealed that the composition of this C_{60}-doped polytoluidine corresponds to about one C_{60} molecule per eight nitrogen ring units in the polymer chain. Since up to six N–H bonds could be added to one C_{60} molecule, the C_{60}-doped polytoluidine might exist as a highly crosslinked material.

In summary, we have found that upon doping with fullerenes (C_{60} or C_{60}–C_{70}), the conductivities of emeraldine base of polyaniline increase significantly to ca. 10^{-4} S cm^{-1}. The IR spectra of the fullerene-doped polyaniline and polytoluidine exhibit some changes from those of the fullerenes and of the polymers. The preliminary spectroscopic data could be interpreted by CT interactions between the fullerenes as electron acceptors and the polymers as electron donors, or by nucleophilic addition of the N–H groups in the polymers to the fullerene molecules.

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