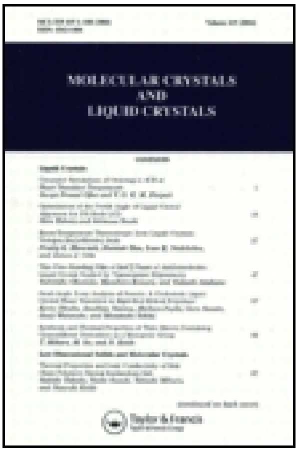

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Infrared Spectra and Photoinduced Absorption of C_{60} Doped Polyhexylthiophene

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INFRARED SPECTRA AND PHOTOINDUCED ABSORPTION OF C_{60} DOPED POLYHEXYLTHIOPHENE

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Abstract We report the IR spectra and the photoinduced absorption of polyhexylthiophene(PHT) doped with C_{60}. The presence of C_{60}^{-n} anions is observed in the IR spectra by a mode at 1383 cm^{-1} and a broad electronic transition at 1.2 eV, while most of the C_{60} molecules stay neutral. This is indicative that for a small fraction of C_{60} molecules, charge transfer occurs in the ground state .

The photoinduced absorption spectra display a sharp transition at 1.15 eV peculiar to C_{60} monoanion, the spectral features change with fullerene concentration. The intensity of the polymer photoinduced bands increases 5-10 times due to photoinduced charge transfer to C_{60}.

INTRODUCTION

PHT doped with various concentrations of C_{60} has been studied in previous works with several techniques. ESR , conductivity [1] , cyclic voltammetry [2] and Vis. absorption spectroscopy [3] measurements have been discussed in terms of an electron charge transfer from the polymer valence band to the LUMO level of C_{60} , leading to charged excitations (polarons) P^+ and C_{60}-1. C_{60} is a weak dopant for PHT, much different from conventional dopants like iodine, BF_4 and AsF_6, because fullerene molecules are mainly in neutral state.

Upon photoexcitation there is a quenching of the luminescence and an enhancement of photoconductivity [3,4] which has been explained by dissociation of the exciton and reduction of the intrachain electron-hole geminate recombination of PHT, due to an electron transfer from the excited state of the polymer to the LUMO level of C_{60}.

A similar photoinduced electron transfer mechanism has been proposed for other composites of fullerene and conjugated polymers, like soluble polyphenylenevinylene

(PPV) [5], polyoctylthiophene (POT) [5], poly- octadecylthiophene [4]. These polymers do not show, with the exception of POT, any ground state wave functions mixing with C_{60}. In POT composites the charging of C_{60} in the ground state has been questioned since the ESR of C_{60}^{-1} has not been observed [5].

For soluble PPV composites, the photoinduced absorption spectra obtained with cw photomodulation, have directly monitored the presence of photoinduced electron transfer, displaying in the spectra the first transition of long lived metastable C_{60}^{-} anions. For POT the measurements have been interpreded in terms of a reversible photodoping process; the electronic transition of the photoinduced C_{60}^{-} anions was not detected by cw photomodulation technique [5] but appears in the FTIR photoinduced spectra [6]. The photoconductivity [4,7] and the rectifying properties of Schottky diodes of poly-alkylthiophenes doped with C_{60} [8] have suggested that the efficiency of the photoinduced electron transfer is dependent on fullerene concentrations.

In this work we report new spectroscopical evidences of the electron transfer from PHT to fullerene both in the ground state and in the excited state. We have studied the IR absorption spectra and the photoinduced absorption spectra as a function of fullerene concentration.

EXPERIMENTAL

Both poly(3-hexylthiophene) and C_{60} of appropriate molar ratio were dissolved in toluene and then the samples were obtained by casting the solution on Kbr crystals substrates for the infrared absorption spectroscopy. Details of the preparation and purification method and procedures are reported in previous papers [1,3]. The photoinduced absorption measurements and part of the IR absorption spectra were performed on KBr pellets, prepared by a carefull dispersion of free standing cast films in KBr . Samples at the following C_{60} concentration have been compared : 0, 0.1, 0.2 , 0.5 , 2 , 5 , 10 % M.

The absorption and the photoinduced absorption spectra has been obtained with a Bruker IFS66 FTIR spectrometer equipped to cover a spectral range from 400 cm^{-1} (0.05 eV) to 15000 cm^{-1} (1.85 eV). The absorption measurements have been performed at room temperature. The photoinduced absorption spectra have been obtained with the sample at 80 °K by measuring the fractional changes in transmission in response to an external laser incident on the sample for 10 s (70 mW/cm^2 of a 488 nm Ar^+ laser line).

RESULTS AND DISCUSSION

The IR absorption results may be summarized as follows:

i) The IR bands of PHT are not affected by the presence of fullerene and are indicative of some conformational disorder [9].

ii) There are five bands increasing with C_{60} concentration at 526 cm^{-1}, 576 cm^{-1}, 1181 cm^{-1}, 1383 cm^{-1} and 1427 cm^{-1} (see Fig.1). Their narrow bandwidths suggest that they are related to fullerene rather than to the polymer charged excitations (IRAV modes) [10]. Their frequencies correspond, with the exception of the 1383 cm^{-1} mode, to fullerene bands, thus probing the presence of neutral C_{60} into the samples. The 1383 cm^{-1} mode is peculiar to the doping process. By increasing C_{60} concentration, the 1383 cm^{-1} mode is enhanced with respect to the polymer and to C_{60} bands and it has been observed an electronic transition at 1.2 eV, scaling with the 1383 cm^{-1} band. It may be inferred from the vibrational and electronic properties of alkali-C_{60} compounds (A_nC_{60} , A=K, Rb) [11] that this band is due to fullerene monoanions.

The IR spectra of the composites in KBr pellets are displayed in Fig. 1 for various concentration of fullerene C_{60} , increasing from the bottom to the top, from 0 to 10 % M.

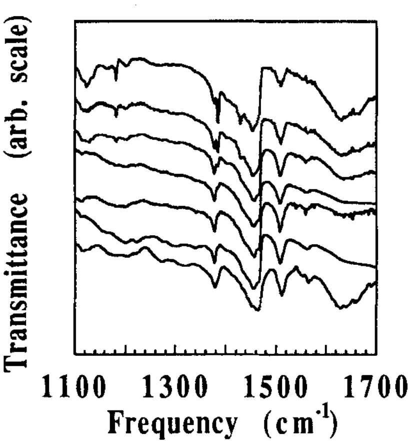

FIGURE 1

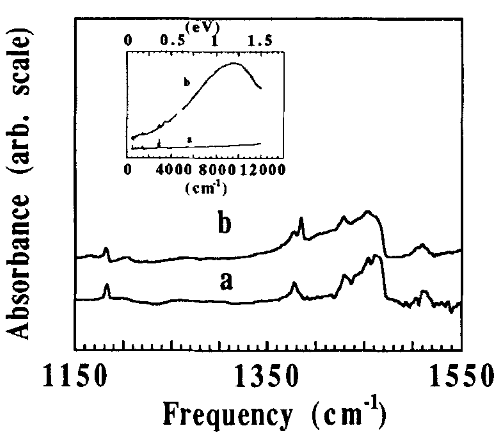

FIGURE 2

Fig. 2 shows the spectra of a 10 % M sample prepared as a solution cast film (*a*) and as a KBr pellet (*b*). In the cast film the 1383 cm^{-1} band is a weak shoulder of the alkyl CH_3 umbrella deformation (1377 cm^{-1}) while it grows in intensity in the pellet. This enhancement scales with a broad electronic band peaked at 1.2 eV which appears over an intense background due to the opalescence of the pellet. In the cast film the electronic transition is such a weak feature that it can be barely detectable. The same spectral features have been also observed for the 2% and the 5% M samples. An extrinsic effect like the direct interaction between C_{60} , KBr and moisture may lead in principle to C_{60} anions, but it is unlikely as we checked experimentally that the IR spectrum of a KBr pellet of C_{60} alone , embebbed of moisture for several days, does not display evidences of C_{60} anions formation. The 1383 cm^{-1} band is neither indicative of PHT degradation. Thus the enhancement of this band is due to a more efficient doping in KBr pellets which may be explained by the dishomogeneity of the cast films: at 10 % level, a large part of C_{60} are in aggregates due to low solubility of C_{60}. The extension of fullerene domains depends on the net C_{60} concentration and it is reduced by grinding the films with KBr, leading to an effective increase of the concentration of "single" C_{60} molecules. Therefore in the pellet there is an increase of the polymer- C_{60} contacts and a more efficient polymer-fullerene electron transfer in the ground state.

There are not clear spectroscopical evidences for polaron formation into the conjugated polymer. If polaron formation occurs, its vibrational features differ at least in intensity from the IRAV modes obtained with conventional dopants. The high polarizability of C_{60} may probably account for this result either by influencing polaron formation or by reducing the intensities of the polaron IRAV mode due to inhomogeneous broadening.

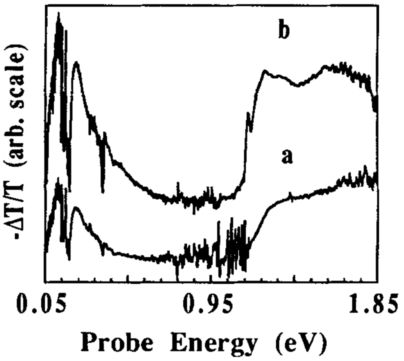

FIGURE 3

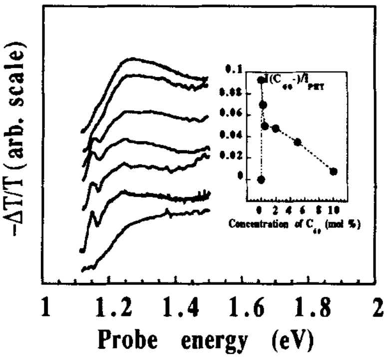

FIGURE 4

Fig. 3 shows the photoinduced absorption of the neutral polymer (**a**) and of a 0.1 % mol. C_{60} doped polymer (**b**).The spectral features of the neutral polymer are peculiar to poly-3-alkylthiophenes [10,12]. PHT bands are not significantly affected by the presence of C_{60}. A new sharp band appears at 1.15 eV whose intensity depends on C_{60} concentration. This band, in agreement with previous results on soluble PPV composites [5] and with recent results on POT composites [6], is the spectral signature of photoinduced fullerene anions (C_{60}^{-1}).

The NIR photoinduced spectra are compared in Fig. 4 for the following fullerene concentrations: 0, 0.1,0.2, 0.5, 2, 5, 10 % M from the bottom to the top. The intensity of each spectrum has been scaled arbitrarly and the inset displays the changes with concentration of the intensity ratio of the photoinduced C_{60}^- transition to the PHT 1.25 eV transition. It can be seen that this ratio has a maximum at .1% M and thendecreases with C_{60} concentration. At low fullerene concentrations the spectra display a structure (at 1.2 eV, 1.25 eV) superimposed to the PHT photoinduced band which corresponds nicely with the weak transitions detected in the absorption spectra of monoanion C_{60}- solutions [13].

The photogeneration is reversible as we checked by comparing the absorption spectra before and after several hours of exposure to the laser pump.

In the MIR region it is possible to scale the PA intensity at each concentration normalizing the PA signal to the number of photons absorbed by each sample.[14]. Fig. 5 shows these changes with fullerene concentration. The PA intensities are normalized to the PA signal of the neutral polymer. Even at very low concentrations (.1 % mol) we find a strong enhancement of the photoinduced activity which quickly saturates. If a monomolecular recombination mechanism for the charged species is assumed, there is a ten times enhancement of the PA activity while a bimolecular recombination mechanism leads to a 5 times enhancement.

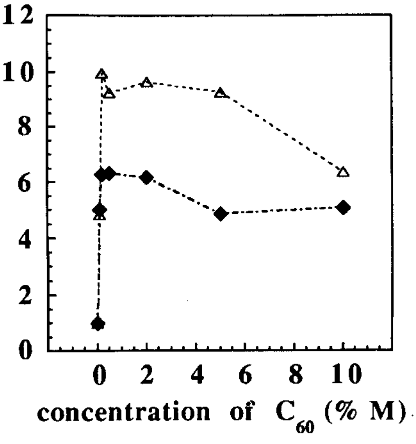

FIGURE 5

CONCLUSIONS

These IR data bring evidence for a ground state electron transfer from poly-3-hexylthiophene to C_{60}.

The data suggest that C_{60} segregation strongly affects the efficiency of the electron charge transfer in the ground state. This observation may partially explain the differences in the results obtained in different polyalkylthiophene- C_{60} composites.

The PA results show that a reversible electron transfer from the excited state of the conducting polymer into fullerene takes place. The spectral features changes with fullerene concentration and the data may possibly suggest a more efficient electron transfer at very low concentrations. There are however several other factors changing with the concentration of fullerene: bulk effects on the oscillator strength of the 1.15 eV may occur; the polymer PA bands may increase in intensity as partial ground state charge transfer is inducing charged defects which may act as trapping centers for the polymer photoexcitations. The polymer photoinduced activity is drastically enhanced by a small amount of C_{60} and saturates for higher concentrations. In terms of a more efficient charge transfer at low concentration, this result may be possibly explained as follows:

a) The intrachain electron-hole recombination is reduced by photoinduced electron transfer thus leading to higher densities of the polymer photoexcitations. (this accounts for the features at low C_{60} concentration)

b) The doping effect and the polymer chain disorder due to fullerene are leading to trapped photoexcitations with longer lifetime and thus to higher photoinduced absorption. (this accounts for the features at high C_{60} concentration)

REFERENCES

1 S. Morita, A.A. Zakhidov, T. Kawai, H. Araki, K. Yoshino Jpn.J.Appl.Phys., 31, L890 (1992)

2 S. Morita, S. Kiyomatsu, A. A. Zakhidov and K. Yoshino J.Phys.: Condens.Matter 5 , L103 (1993)

3 S. Morita, A.A. Zakhidov, K. Yoshino Solid State Commun. 82, 249 (1992)

4 K. Yoshino, X.H. Yin, S. Morita, T. Kawai, A.A. Zakhidov Solid State Commun. 85, 85 (1993)

5 L. Smilowitz, N.S. Sariciftci, R. Wu, C. Gettinger, A.J. Heeger and F. Wudl Phys.Rev.B 47 , 13835 (1993)

6 K. Lee, R.A.J. Janssen, N.S. Sariciftci and A.J. Heeger, Phys.Rev.B 49 , in press

7 C.H. Lee,G. Yu, D. Moses, K. Pakbaz, C. Zhang, N.S. Sariciftci, A.H. Heeger, F. Wudl Phys.Rev.B 48 15425 (1993)

8 C.S. Kuo, F.G. Walkim, S.K. Sengupta, S.K. Tripathy Solid State Commun. 87, 115 (1993)

9 G. Zerbi, B. Chierichetti, O. Inganas J. Chem. Phys. 94, 4641 (1991)

10 Y.H. Kim, D. Spiegel, S. Hotta, A.J. Heeger Phys. Rev.B 38, 5490 (1988)

11 K.J. Fu, W.L. Karney, O.L. Chapman, S.M. Huang, R. Kaner, F. Diederich, K. Holczer, R.L. Wetten Phys. Rev.B. 46, 1937 (1992)

12 C. Botta, S. Luzzati, R. Tubino, A. Borghesi Phys. Rev.B 46, 13008 (1992)

13 M. Baumgarten, A. Gugel, L. Gherghel Adv.Mater. 5, 458 (1993)

14 S. Luzzati et al. , to be published