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Electronic structure of some conjugated polymers for electron transport

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Abstract

The chemical and electronic structure of three different, strictly alternating copolymers, poly(2,5-diheptyl-1,4-phenylene-*alt*-1,4-naphthylene) (P14NHP), <math>poly(2,5-diheptyl-1,4-phenylene-*alt*-2,6-naphthylene) (P26NHP) and <math>poly(2,5-diheptyl-1,4-phenylene-*alt* $-9,10-anthrylene) (P910AHP), have been studied by photoelectron spectroscopy and optical absorption spectroscopy. The experimental results have been analyzed using the results of quantum chemical calculations. In the geometrical structure of all three of the polymers there are large torsion angles between the phenylene unit and the naphthylene or anthrylene units. These large torsion angles lead to localization of the <math>\pi$ -electron wave functions, and minimal conjugation along the polymer backbone. For all three polymers, the highest occupied molecular orbital is completely localized to the naphthylene or anthrylene unit. The frontier molecular orbital wave functions are very reminiscent of the highest occupied orbitals of the isolated naphthalene or anthracene molecules. The optical absorption spectra of all three polymers of all three polymers verify the existence of large optical band gaps, consistent with the large torsion angles. The first several optical transitions in the polymers are also very reminiscent of the transitions in single naphthalene and anthracene molecules. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Much research has been done in order to improve the performance for polymer-based LEDs. For example, multilayered structures may be employed, incorporating electron or hole transport layers [1]. Alternatively, polymer blends may provide enhanced properties of charge transport and localization in single layer devices [2]. In addition, a range of colors may be made available, and the quantum efficiencies tuned, by adjusting the electronic structure of the conjugated polymers, through molecular engineering of the geometric structures of the polymer chains [3]. In real conjugated polymers, the highest occupied electronic states extend over many repeat units of the polymer backbone. In the polymer, such electronic delocalization results in a smaller electronic band gap than for the monomeric repeat units themselves. On the other hand, steric effects may inhibit a planer geometry of the polymer backbone. Large

^{*}Corresponding author. Tel.: +46-13-288916; fax: +46-13-137568. *E-mail address*: jbi@ifm.liu.se (J. Birgerson). torsion angles may then occur, which serve to reduce conjugation along the backbone of the polymer chain, there by localizing to some extend the frontier electronic states. In copolymers with carefully chosen monomeric units, steric effects may be employed to create desired localized electronic states. The monomeric units can be chosen to provide, for example, desired electronic transport properties, while the polymer form may provide desired processing and mechanical properties [4]. Polymer systems can be designed and synthesized with specific local variations, along the polymer chain, of, for example, the π - π^* electronic energy gap. The localized electronic structure may be designed, for example, to act as traps for electrons or for holes in such a way as to increase the quantum efficiency for polymer-based LEDs [2].

In this work, three different strictly alternating conjugated copolymers, specifically designed to exhibit certain electronic localization properties, have been studied. The chemical structures of the three different polymers, poly(2,5-diheptyl-1,4-phenylene-*alt*-1,4-naphthylene) (P14NHP), poly(2,5-diheptyl-1,4-phenylene-*alt*-2,6-naphthylene) (P26NHP),



Fig. 1. The chemical structure of poly(2,5-diheptyl-1,4-phenylene-*alt*-1,4-naphthalenyl) (P14NHP), poly(2,5-diheptyl-1,4-phenylene-*alt*-2,6-naphthalenyl) (P26NHP) and poly(2,5-diheptyl-1,4-phenylene-*alt*-9,10-anthrylene) (P910AHP).

poly(2,5-diheptyl-1,4-phenylene-*alt*-9,10-anthrylene) (P910AHP) are displayed in Fig. 1.

The electronic structure of these polymers was studied by ultra violet photoelectron spectroscopy (UPS) and optical absorption spectroscopy. The polymers were prepared with the idea of incorporating certain small fused ring aromatic molecules directly in the polymer backbone, along with alkyl-substituted phenylene moieties, in order to provide both solution processing and electronic transport properties in one and the same polymer film. The experimental results have been analyzed with the help of the results of quantum mechanical calculations using the Valence Effective Hamiltonian (VEH) model [5]. Recently, new molecular materials for electron transport in organic-molecule-based light emitting devices, o-LEDs, have been patented [6,7]. The chemical structures of certain of these molecules are very similar to the monomeric repeat units of the polymers studied in this present work. These polymers present a combination of features of the new transport molecules, with the advantages of polymer processing and film stability.

2. Experimental details

The alternating copolymers were synthesized using the Suzuki reaction of 2,5-diheptylbenzene-1,4-bis(trimethylene boronate) with 1,4-dibromonaphthalene,2,6-dibromonaphthalene and 9,10-dibromoanthracene, in presence of a palladium catalyst as described elsewhere [8]. The samples were prepared for study by dissolving the polymers in chloroform. Films for photoelectron spectroscopy were prepared by spin-coating the polymer solutions onto silicon substrates, and for optical absorption spectroscopy on quartz substrates. Final film thicknesses were about 10 nm (photoelectron spectroscopy) or 200 nm (optical absorption), as determined by using a Sloan Dektak 3030 profilometer. After insertion into the vacuum system of the photoelectron spectrometer, the samples were heated for 1 h at 100°C to remove any absorbed water vapor and/or any residual solvent. The photoelectron spectra were taken at Beam Line I411 at the Swedish National Synchrotron Radiation Laboratory (MAX laboratory), Lund, Sweden. Beam line I411 is equipped with an undulator and a modified Zeiss SX-700 plane grating monochromator. The spectrometer portion is

equipped with a SCIENTA SES-200 electron energy analyzer. Optical absorption spectra were recorded in air at room temperature using a Perkin-Elmer Lambda-9 spectrometer.

3. Theoretical methodology

Geometrical input into the VEH calculations was generated using the semi-empirical Hartree-Fock Austin Model 1 (AM1) technique [9]. The optimization of the geometry's were performed on oligomers of the different polymers, where the geometry of the central part then was used as the unit cell for the polymer system. The electronic structure, the set of energy-versus-momentum curves [5], was calculated on single isolated polymer chains using the nonempirical pseudo-potential Valence Effective Hamiltonian (VEH) model [5]. The density-of-valence-states (DOVS) curves are derived in the standard manner, from the inverse of the derivative of the electronic band structure with respect to momentum. The bare DOVS was then convoluted with Gaussian functions (FWHM of 0.7 eV) in order to more closely approximate the experimental UPS data. The spectra were also contracted by the standard factor of 1/1.3 along the energy axis, in order to compensate for the lack of electronelectron correlation in the Hartree-Fock-based VEH model. To compensate for solid state polarization effects, the spectra are shifted towards lower binding energy [10]. The calculations of the optical absorption spectra were carried out by using the Intermediate Neglect of Differential Overlap (INDO) method with single excited configuration interaction (INDO/SCI [11]. The singly excited configurations were generated on the basis of the upper 50 occupied and lower 50 unoccupied molecular orbitals. The theoretical optical spectra were simulated by convolution with Gaussian functions (FWHM of 0.4 eV).

4. Results and discussion

The X-ray core level photoelectron spectra, not shown here, indicate that all three polymers are of good quality. No oxygen was detected. The UPS valence band spectra, along with the corresponding DOVS, of the three polymers are shown in Fig. 2. The spectra are plotted with the energy axis



Fig. 2. Photoelectron spectra of the polymers P14NHP, P26NHP and P910AHP, taken with a photon energy of 85 eV, and the corresponding VEH DOVS curves. The vacuum level is the energy reference level.

relative to the vacuum level. The agreement between the experimental spectra and the theoretical DOVS spectra is obviously very good, even as seen in the wide over view of Fig. 2. There are, however, some minor disagreements for the relative intensities in the spectra. This is mainly because of two effects. First, differences in photoionization crosssections will affect the relative intensities in the spectra. Second, in the calculations, the diheptyl group is replaced

with a methyl group to save computational time. This replacement does not change the value of the calculated binding energies, but does affect the observed relative intensities. It can also be seen that the agreement between the experiment spectra and the theoretical DOVS is worse for higher binding energies. This is because the VEH model is not parameterized for high binding energies, and because of the presence of many-body (electron-correlation) effects in the UPS spectra at high binding energies, leading to deviations from the DOVS of the neutral system in the ground state [5]. The optimized geometrical structures, from the AM1 calculations, of all three polymers, obtained for isolated polymer chains, have large torsion angles between the naphthylene or anthrylene groups and the substituted phenylene group. In actual polymer films, lower values are expected to occur because of solid state packing effects.

4.1. Electronic structure of P14NHP

In Fig. 3a is shown the lower binding energy portion the UPS spectrum of P14NHP, compared with the original energy band structure and the calculated DOVS. The agreement is excellent, enabling a discussion of the origin of the structure. The five highest occupied bands are π -like, and localized to the aromatic moieties. Localization is obvious from the fact that the "bands" are not dispersed (are flat).

The theoretical torsion angle for P14NHP is 90°. This large angle arises from steric hindrance between the naphthylene unit and the heptyl group on the phenylene moiety. For a torsion angle this large, the π -wave functions are localized to the individual aromatic groups, and the "bands" are flat. This localization can be seen in the highest occupied molecular orbital, and some of the next highest orbitals, HOMO, H-2, H-4, which are completely localized to the naphthylene unit, HOMO, as shown in Fig. 4a. These



Fig. 3. The lower binding energy portion of the UPS spectra and the corresponding VEH DOVS calculations are shown for: (a) P14NHP; (b) P26NHP, and (c) P910AHP. The vacuum level is taken as reference.



Fig. 4. (a) HOMO for P14NHP; (b) HOMO for P26NHP; (c) HOMO for P910AHP; (d) HOMO-1 for P14NHP; (e) HOMO-1 for P26NHP.

molecular orbitals also have symmetries very similar to the three highest occupied molecular orbitals of isolated naphthalene molecules. In addition, H-1 and H-3 are localized to the phenylene part of the polymer. The first dispersed state is the σ -band "H-5". From the cut-off energy of the secondary electron spectrum in the UPS spectrum of the polymer film, the ionization potential of the polymer is approximately -7.8 eV. The value of the ionization potential for an isolated naphthalene molecule in gas phase is -8.15 eV [12].

4.2. Electronic structure of P26NHP

The chemical structure of P26NHP is very similar to that of P14NHP, but with the naphthylene group inserted into the backbone in a slightly different configuration. In P26NHP, the connection between the phenylene group and the naphthylene unit is at the carbon atom number 2 and 6 in the naphthylene unit. This results less steric hindrance and a smaller torsion angle than for P14NHP. The geometry optimization results indicate a torsion angle of about 49°, even though 49° is still rather large, the smaller torsion angle means that the wave functions of the HOMO for P26NHP are at least some what less localized than for P14NHP, and that the ionization potential should be slightly lower. The measured ionization potential is about -7.6 eV, while the corresponding value for P14NHP is -7.8 eV. In Fig. 3b, the lower binding energy part of the measured UPS spectra and calculated DOVS are shown together with the calculated energy band diagram. The agreement is very good. The five highest occupied orbitals are π -orbitals. Because of the large torsion angles, the HOMO, H-2, H-4 are almost completely localized to the naphthylene units. The symmetries for these molecular orbitals are also very similar to the three highest occupied molecular orbitals of an isolated naphthalene molecule. The HOMO for P26NHP is illustrated in Fig. 4b. The H-1 and H-3 are localized to the phenylene part of the polymer. H-5 is the first real dispersed band, corresponding to a σ -band delocalized along the polymer backbone. The effect of the smaller torsion angle, compared to P14NHP, may be seen in the band diagram in Fig. 3b. HOMO for P26NHP is more dispersed along the chain axis because of the orientation of the naphthylene unit. The dispersion arises from both the smaller torsion angle as well as the fact that the naphthylene unit lies bonded into the chain in the direction of the polymer backbone.

4.3. Electronic structure of P910AHP

Polymer P910AHP contains an anthrylene unit in the backbone, but oriented perpendicular to the axis of the backbone, as may be seen in Fig. 1. This arrangement leads to large steric hindrance effects. The AM1 results indicate a torsion angle of about 84° for the isolated polymer chain. The effect of the large angle can also be seen in Fig. 3c where the lower binding energy portion of the UPS spectra and the corresponding VEH DOVS calculations are shown. The five highest occupied molecular orbitals have π -like symmetry. As shown in Fig. 4c, the HOMO, H-2 and H-4 are all localized to the anthrylene units. These three orbitals have symmetries similar to the three highest occupied

orbitals for isolated anthracene molecules. H-1 and H-3 are localized to the phenyl unit. H-5 is the first real dispersed band. The experimental ionization potential is about -7.1 eV for P910AHP. The value for an isolated anthracene molecule in the gas phase is -7.47 eV [12]. Note that for a condensed molecular solid film of only anthracene molecules, the ionization potential measured by UPS is 6.0 eV for molecules in the bulk and 6.3 eV for molecules on the surface [13]. Compared with the value of about 7.5 eV [12], these values are higher than for the present case of anthrylene units chemically bonded in the polymer chain.

4.4. Optical absorption

In Fig. 5, the optical absorption spectra for the three different polymers are shown. The experimental spectra are compared with theoretical spectra calculated from the INDO/SCI. The agreement between experimental and simulated optical absorption spectra is very good for all the three polymer systems.

For P14NHP, the experimental values of the first three optical transitions are 4.07, 5.55 and 6.27 eV. The theoretical values are 4.17, 5.67 and 6.33 eV. An analysis of the nature of the transitions shows that the first peak (4.07 eV) corresponds mainly to a transition from the HOMO to the LUMO. The second peak (5.55 eV) corresponds mainly to transitions from the HOMO to the L + 1 as well as from the H-2 to the LUMO. These values can be compared to the energies for the first two transitions in isolated naphthalene molecules, which occur at 4.34 and 5.61 eV [14]. These spectra verify



Fig. 5. Optical absorption spectra of the polymers P14NHP, P26NHP and P910AHP and the corresponding curves for the ZINDO calculations.

the fact that the electronic properties of this polymer are dominated by the electronic structure of the naphthylene units, and are similar to those of a condensed molecular solid film of naphthalene molecules.

For P26NHP, the first optical transitions occur at 4.07, 4.69 and 5.5 eV. The theoretical values are 4.10, 4.67 and 5.5 eV. An analysis of the nature of the transitions shows that the first peak (4.07 eV) corresponds mainly to a transition from the HOMO to the LUMO. The second peak (4.69 eV) corresponds to transitions from H-1 to LUMO. The third peak (5.5 eV) is a combination of many different optical transitions, which may also be seen in the width of the peak. As in the case of P14NHP, these optical transitions are very similar to those of isolated naphthalene molecules. In naphthalene, the first two transitions are at 4.34 and 5.61 eV [14], which correspond to the first and third transitions in P26NHP. In the second optical transition of P26NHP, both the phenylene and naphthylene parts of the polymer are involved. In Fig. 4, the difference between the H-1 for P14NHP and for P26NHP can be seen. For P14NHP, H-1 is completely localized to the substituted phenyl unit. The H-1 of P26NHP is strongly localized to the (substituted) phenyl unit, but with some small wave function intensity on the naphthylene unit. These differences account for the extra optical transition observed in P26NHP as compared with P14NHP.

Finally, for P910AHP, the experimental value of the first optical transition, 3.28 eV, can be compared with the theoretical value of 3.36 eV, which corresponds mainly to a transition between the HOMO and the LUMO. There are also some vibrational features visible in the first transition. The second transition at 4.81 eV corresponds to transitions between H-2 and the LUMO as well as the HOMO and L + 1. The theoretical value is 5.07 eV. These two first transitions involve only the anthrylene part of the polymer, and can be compared with the experimental value of the two first optical transitions in isolated anthracene molecules, where the first two optical transitions are at 3.31 and 4.84 eV, respectively [14]. The experimental values for the remaining two transitions are 5.56 and 6.36 eV, while the corresponding theoretical values are 5.64 and 6.29 eV. The first of these two transitions (5.56 eV) corresponds to a transition between the H-2 and the L + 1, which is also localized to the anthrylene part of the polymer.

5. Summary and conclusions

The electronic and chemical structure of three different copolymers, poly(2,5-diheptyl-1,4-phenylene-*alt*-1,4-naphthylene) (P14NHP), poly(2,5-diheptyl-1,4-phenylene-*alt*-2,6-naphthylene) (P26NHP), poly(2,5-diheptyl-1,4-phenylene-*alt*-9,10-anthrylene) (P910AHP) have been studied by photoelectron spectroscopy and optical absorption measurements. The results of quantum chemical calculations agree well with the experimental results. The AM1 geometries

show that all of the polymers have very large torsion angles that will reduce, or even break, the conjugation over the polymer backbone. There is a strong localization of the electrons in the HOMO to the naphthylene/anthrylene units. The ionization potentials for the polymers are comparable to the ionization potentials for the pure naphthalene/anthracene molecules, which is in agreement with the optical absorption spectra, compared with the results of the ZINDO calculations.

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