Confined and delocalized polarons in \( \pi \)-conjugated oligomers and polymers: A study of the effective conjugation length

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We studied optical absorption of polarons in \( \pi \)-conjugated oligomers and polymers using the photoinduced absorption technique as well as chemical doping spectra from the literature. We find that the photon energy of the polaron low-energy transition obeys a relationship that depends only on the oligomer-length in a wide class of unsubstituted and substituted oligomer solutions and films. Based on this observation, we show that polarons in polymer films can be either confined as in oligomers or quite delocalized, depending on the individual \( \pi \)-conjugated semiconductor. In high mobility polymer films polarons may be delocalized over several chains.

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\( \pi \)-conjugated semiconductors have been used to manufacture promising thin film devices such as organic light-emitting diodes and field-effect transistors. It is well-known that chemical doping or electrical charge injection results in the formation of polarons in these systems.\(^1\) Figure 1 shows a comparison between different models that have been used for describing polarons in \( \pi \)-conjugated semiconductors. Panel (a) depicts the electron–phonon (e–p) or Su-Schrieffer-Heeger (SSH) model.\(^1\)–\(^3\) It predicts that the e–p coupling causes a gap between valence and conduction band. In the singly charged system two localized polaron levels appear inside the gap. Experimentally one finds two optical transitions\(^4\) that are interpreted as the \( P_1 \) and \( P_2 \) transitions. Panel (b) depicts the molecular orbital picture where HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals, respectively. These models are usually applied to a single, isolated chain; the effects of interchain interaction on polarons\(^5\)–\(^8\) in real sample films are however not yet sufficiently understood.

\( \pi \)-conjugated oligomers are often used as model compounds instead of \( \pi \)-conjugated polymers because they can be obtained with a well-defined chemical structure. Although the molecular weight of polymers is typically much larger than that of oligomers, nevertheless it is established that the polymer should be viewed as a string of effectively independent segments, separated by chemical or physical defects. The length of these segments is called the conjugation-length (CL).

We have used the continuous wave photoinduced absorption (PA) and the Fourier-transform infrared photoinduced absorption (FTIR-PA) spectroscopies to study the polaron optical transitions in films of \( \pi \)-conjugated polymers and oligomers. The PA spectroscopy has been widely used in \( \pi \)-conjugated materials, and experimental details were described previously.\(^4\) The PA spectrum, \( \Delta \alpha(\omega) \) is obtained by dividing \(-\Delta T/T\), where \( \Delta T \) is the pump laser induced change in transmission. We extended the probe photon energy down to 0.05 eV using a FTIR spectrometer in combination with a deuterated triglycine sulfide (DTGS) detector. The FTIR-PA setup is described in more detail in Ref. 6.

Figure 2 shows the PA spectra of two \( \pi \)-conjugated polymer films, namely methylated ladder-type poly-paraphenylene [mLPPP, panel (a)] and poly-phenylene-vinylene [PPV, panel (b)] and that of an alkyl-substituted oligothiophene film [12T, panel (c)]. All these spectra show three optical transitions (it is known that the high energy transition in PPV is actually composed of two bands\(^9\)). It is well-established\(^4\) that these transitions are due to triplet exciton absorption (\( T_1 \)) and polaron absorption (\( P_1 \) and \( P_2 \)).

Figure 3 shows the peak photon energies of the \( P_1 \) transition in a large variety of oligomers versus the oligomer-length, \( L \).\(^10\) We note that the \( \Delta \), \( \Theta \), \( \Theta \), and \( \Theta \) data were taken from the literature.\(^11\)–\(^15\) It is seen that the \( P_1 \) transition in each of the oligomer classes redshifts as \( L \) increases; specifically \( P_1 = P_1 \text{,} \text{ + const/} \text{L} \). This observation in itself is not novel. In fact this scaling relation is ubiquitous in oligomers: the optical gap (i.e., the singlet exciton energy),\(^16\) triplet exciton energy,\(^17\) and also the \( P_2 \) transition each obey such a scaling relation. The striking observation is that if the \( P_1 \) data for the various oligomers are plotted versus \( L \) rather than the number of repeat-units (as it is usually done) and combined into a single graph, we find that the \( \Delta \), \( \Theta \), \( \Theta \), \( \Theta \), and \( \Theta \) data points all fall on a "universal" line. This observation is fully appreciated when compared to similar plots

FIG. 1. Models used to describe polaron levels and optical transitions depicted here for the positive polaron. (a) Electron–phonon (SSH) model. (b) Molecular orbital picture.
oxidized using SbCl₃, see inset.

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carried by alkoxy substitution.

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5T.

Ftigure 3 encompasses both anion and cation data. This
suggests that anion and cation absorption are very similar.
Indeed, in 3PV it was found that the difference between an-
ion (reduced using potassium in THF solution), and cation
(oxidized using SbCl₃ in CH₂Cl₂) absorption bands is less
than 10 meV.¹⁸ Since both unsubstituted and alkyl-
substituted oligomers display the same trend in Fig. 3, this
indicates that alkyl-substitution has only minor effects on P₁.
Alkoxy-substitution on the other hand results in a major
change of the cation absorption in OPV.¹³ This observation
can be explained by the localizaton of the positive charge
caused by alkoxy substitution.¹³ We may therefore conclude
that the P₁ band scal is universal for both anions and
cations in a wide class of unsubstituted and alkyl-substituted
oligomers.¹⁹ By extrapolation we find that P₁,∞=0.25 eV for
the infinite oligomer.

In order to further expand the domain of validity of the
“universal” scaling law for P₁, PA measurements of P₁ in
films of alkyl-substituted OT were performed and added to
Fig. 3. It is seen that (a) the linear relationship for P₁ con-
tinues at least to OT with 17 repeat units, (b) interchain
effects apparently do not play a significant role in OT, and
(c) the fact that both positive and negative polarons are
present in PA studies does not lead to a significant change of
P₁. These observations, together with the identification that

FIG. 2. PA spectra of π-conjugated polymer and oligomer films.
(a) mLPPP (the chemical structure is given in the inset), (b) PPV
(see inset), and (c) 12T (see inset). The spectra were measured at
80 K under excitation by an argon-ion laser (typically 100 mW)
and modulated by an optical chopper (typically at 1 kHz). The T₁
transition is due to triplet-triplet absorption, whereas P₁ and P₂ are
due to polaron absorption bands.

for the optical gap, where large differences between the vari-
ous oligomer classes exist (e.g., 4 eV for 5P, but 3 eV for
5T). However, the data for the alkoxy-substituted OPV ap-
parently do not follow the “universal” scaling law.

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FIG. 3. The peak photon energies of the P₁ polaron transition in
a variety of oligomers, namely solutions of (unsubstituted) oli-
gophenyls [OP, △, radical anion (RA)], alkyl-substituted (AS)
oligophenylene-vinylenes [OPV, ○, radical cation (RC)], alkoxy-
substituted OPV (●, RC), end-capped oligothiophenes (OT, □,
RC), films of AS OT [□, PA], AS oligothienylene-vinylenes (OTV,
△, RC). The solid line is a fit to the data excluding △.

the CL of a polymer is the length of the “equivalent” oligo-
mer, clearly suggest that P₁ can be used as a universal and
sensitive measure of the CL of polymer films (caution is
ecessary when dealing with alkoxy-substituted polymers).
Specifically, we may use the following method for obtaining
the effective CL of polymer films: we measure P₁, say by
using the PA technique, then invert the universal relation
P₁(CL).

This procedure is the basis for the presentation of the
polymer P₁ data in Fig. 4, where crosses mark the data for a
certain polymer (name is assigned). The y-coordinate of the
crosses is equal to the measured P₁ using the PA technique,
whereas the x-coordinate then yields the CL obtained by in-
version of P₁(CL). We find that some polymer films [poly-
phenylene-ethenylene (PPE), PPV and regio-random poly-3-
hexyl-thiophene (RRa-P3HT)] have a short CL and behave
rather like oligomers, whereas in poly[2-methoxy, 5-(2’-ethyl-hexyloxy)-p-phenylene-vinylen] (MEH-PPV)
we find that the polarons are considerably more delocalized
than in oligomers. In addition, it is seen that this procedure
does not yield a meaningful result for the CL for some poly-
mer films for which P₁ < P₁,∞. These polymers are regio-
regular poly-3-hexyl-thiophene (RR-P3HT), mLPPP and
poly(9,9-dioclyfluorene (PFO).²⁰ We note that the spectrum
of PFO is for the so-called β-phase.²¹,²² It is clear that some-
thing interesting occurs in the these samples. Before continu-
in this discussion, however, a closer look at the FTIR-PA
spectra (Fig. 5) for these three polymers is in order.

It is seen that the P₁ transition is superimposed by narrow
bands with some resemblance to the infrared active vibra-
vibrational spectrum. We find that experimental findings are in stark contrast to this prediction; this is particularly so for the sharp antiresonances (ARs) that are due to Fano-type interactions. Indeed, it has been shown that the sharp ARs are due to Fano-type interferences that occur when the $P_1$ transition overlaps with the vibrational spectrum. The $P_1$ transition is therefore given as the envelope of the measured spectrum, indicated by the dotted lines in Fig. 5.

We start our discussion with the SSH or e–p model that yields the $P_1$ transition in a variety of $\pi$-conjugated polymer films, the names of which are assigned. The crosses mark the intersect with the linear fit to the oligomer data in Fig. 3; the $y$-coordinate therefore gives the measured $P_1$ peak photon energy, whereas the $x$-coordinate gives the effective conjugation length.

The model yields for the "$P_1$" transition

$$P_1 = \frac{1 - \frac{1}{\gamma}}{2} E_g \times f(\gamma).$$

Here $A$ quantifies the $e$–p coupling strength (e.g., in eV/nm), $M$ is the ionic mass, $\omega_E$ is the Einstein phonon frequency, and $W$ is the band width before inclusion of $e$–p coupling. The term in the bracket is the energy, $V$ associated with the $e$–p coupling. The observation of the universal scaling law, $P_1 = P_{1,\pi} + \text{const}/L$ translates into the following statements. $W$ is similar for a wide class of $\pi$-conjugated polymers and oligomers. Since $W$ increases only weakly with $L$, then $V$ is considerable larger in short oligomers but does not vanish even in the infinitely long oligomer. We note that a recent theoretical paper concluded that $V = \text{const}/N$ in a more or less universal manner in acenes and fullerenes with various numbers, $N$ of $\pi$-bonds.

The inclusion of interchain interaction in theoretical calculations is generally found to destabilize the polaron since the amplitude of the $e$–p interaction decreases with increasing number of atoms involved. However, even in the presence of interchain interaction it is also expected that polarons are restabilized by defects or finite CL. One therefore expects that this destabilization is only effective in high purity, ordered and rigid systems. We recall that mLPPP and $\beta$-phase PFO (Refs. 21 and 22) are particularly rigid polymers and that RR-P3HT forms nanocrystal lamellae because of its high regioregularity. It has been predicted that, for $t_{\perp}$ on the order of 0.15 eV, the polaron excitation substantially delocalizes over adjacent chains. This leads to the expectation that the $P_1$ transition of a delocalized polaron (hereafter referred to as $DP_1$) is redshifted compared to the (hypothetical) value without interchain interaction. Therefore
delocalization as a result of interchain interaction can naturally explain the observation that $P_1 < P_{1,\infty}$. However, interchain interaction in the form of (transition) dipole-dipole interaction leads to a level-splitting and may result in a blueshift compared to the transition without level splitting.\(^5\)\(^,\)\(^8\)

Nevertheless, an overall red-shift is consistently found in calculations.\(^5\)\(^,\)\(^8\) We may therefore conclude that $P_1 < P_{1,\infty}$ is the signature of delocalized polarons in RR-P3HT, mLPPP, and PFO. Since charge carrier mobilities in RR-P3HT, mLPPP, and PFO (Ref. 29) are orders of magnitude larger than in PPV and RRA-P3HT films, it appears that delocalized polarons may be a necessary prerequisite for high mobility in polymers. We note that whereas evidence for delocalized polarons in RR-P3HT was found earlier,\(^6\)\(^,\)\(^27\)\(^,\)\(^30\) the present work succeeds to embed these results into a more general framework.

It has been predicted\(^25\) that the polaronic effect may entirely disappear because of interchain interaction unless stabilized by defects or small CL. In this case the absorption of charge carriers would have to be described in a picture similar to that used for amorphous semiconductors.\(^31\) In this picture “$D P_1$” is a transition between localized states below and extended states above the mobility edge, respectively, and therefore a measure of the energy difference between quasi-Fermi level and mobility edge, respectively.

In summary, we found that the polaron $P_1$ transition obeys a universal relationship that depends only on the oligomer-length in a wide class of oligomer solutions. Employing the PA technique, we generalized this result to films of oligomers and polymers. We have therefore discovered a simple and sensitive method for measuring the effective CL in polymer films. Applying our methods to polymers, we find that polarons may be as confined as in oligomers in some systems, but may even be delocalized over several chains in high mobility polymer films.

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\(^1\)A. J. Heeger et al., Rev. Mod. Phys. 60, 781 (1988).

10 OP-lengths are based on quaterphenyl (Ref. 32); intra-ring bond =1.4 Å; inter-ring bond=1.45 Å. OP-lengths are based on trans-stilbene (Ref. 33); intra-ring bond=1.39 Å; inter-ring single (double) bond is 1.45 Å(1.33 Å). OT-lengths are based on quaterthiophene (Ref. 34); intra-ring C-C bond=1.411 Å; inter-ring bond=1.45 Å. OTV length is based on thiophene ring and the vinyl bond length.

19 We limit our discussion to oligomers of nondegenerate ground-state polymers. In polyenes (oligomers of the degenerate ground state polymer polyacetylene), the $P_1(L)$ scaling is a little steeper than that of the oligomers reported here, and $P_{1,\infty}=0.1$ eV (Ref. 35). This may be interpreted as evidence that the polarons are somewhat more extended in polyenes.
20 RR-P3HT is closely related to the alkyl-substituted OT, whereas mLPPP and PFO are related to the OP; their $P_1$ should therefore follow from extrapolation of the OT and OP data, respectively.