Charge Mobilities in Organic Semiconducting Materials Determined by Pulse-Radiolysis Time-Resolved Microwave Conductivity: π-Bond-Conjugated Polymers versus π−π-Stacked Discotics

John M. Warman,* Matthijs P. de Haas, Gerald Dicker, Ferdinand C. Grozema,
Jorge Piris, and Michael G. Debije

Radiation Chemistry Department, IRI, Delft University of Technology,
Mekelweg 15, 2629 JB Delft, The Netherlands

Received March 14, 2004. Revised Manuscript Received July 2, 2004

A review is given of the one-dimensional, intrachain and intracolumnar, charge mobilities, $\Sigma\mu_{1D}$, determined for π-bond-conjugated polymeric and for π−π-stacked columnar discotic materials using the pulse-radiolysis time-resolved microwave conductivity technique. The largest values, on the order of 10 cm^2/(V s), are found for single-crystal polydiacetylenes polymerized either thermally or with low doses of radiation. Much lower values of $\Sigma\mu_{1D}$, covering the range from 0.009 to 0.125 cm^2/(V s), are found for solution-synthesized conjugated polymers for which six different backbone structures have been investigated. This is attributed mainly to their complex morphology and the resulting static disorder in the backbone structure. The highest mobilities for this class of material, ca. 0.1 cm^2/(V s), are found for liquid crystalline derivatives of polyfluorene and poly(phenylenevinylene). Larger mobilities are found for discotic materials, with maximum values close to 1 cm^2/(V s) in both the crystalline solid and liquid crystalline phases. This is attributed to their self-organizing nature and hence higher degree of structural order, which compensates for the weaker electronic coupling between monomeric units in the discotics compared with the covalently bonded conjugated polymers.

Introduction

A parameter of prime importance in determining the successful technological application of organic compounds as the active layers in the rapidly advancing area of molecular (opto)electronics is the mobility of charge within these materials. This parameter controls, for example, the switching speed of field effect transistors, the intensity of light-emitting diodes, and the separation of charge in photovoltaic cells. In this paper we present a combined review of mobility determinations that we have made using the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique for two of the leading contenders for application in organic (opto)electronic devices, π-bond-conjugated polymers and π−π-stacked discotic materials.

Because of their complex molecular and morphological structures, organic polymeric or (liquid) crystalline discotic materials cannot readily be subjected to "classical" dc methods of measuring their charge-transport properties.[1] Mobilities determined by time-of-flight methods or from the *I*/*V* characteristics of field effect transistors are most often dominated by effects due to domain or grain boundaries, structural disorder, and chemical or physical defects. Additional complications can arise from the occurrence of chemistry or interdiffusion at the organic/metal-electrode interface. Improvements in the purity and structural organization of organic semiconductor materials in recent years have resulted in a gradual increase in the mobilities achieved in dc device structures. The most recent estimates actually begin to approach those, on the order of 1 cm^2/(V s), determined some time ago for organic single crystals at room temperature.[2] The necessity of applying electrode layers prevents however the general and ready applicability of dc measurement techniques to the determination of the intrinsic charge mobilities in the large number and great variety of organic materials which are presently available.

Some time ago, we adapted an *electrodeless* technique that we had successfully applied to the study of electronic charge carriers in dielectric liquids[3,4] for the study of morphologically more complex solid materials. This "PR-TRMC" technique was initially applied to the study of charge transport in ethylenic hydrocarbon polymers and biopolymers and inorganic semiconductors. More recently, our attention has focused on conjugated polymers and columnarly stacked discotic materials, both of which are potential candidates for device applications. It is the purpose of the present paper to review the information that we have obtained on these two categories of organic semiconductors. The results presented will concentrate on the *mobilities* determined in bulk materials to the exclusion of data on the decay kinetics via trapping and charge recombination, which are also obtained using PR-TRMC.[5,6] The reader is also referred

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* To whom correspondence should be addressed. Fax: +31 15 2787421. E-mail: Warman@IRI.TUDelft.nl.

10.1021/cm049577w CCC: $27.50

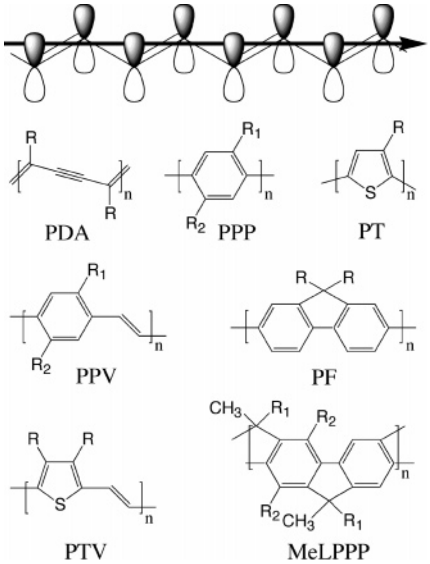

Figure 1. Backbone structures of the conjugated polymers investigated using the PR-TRMC technique with the position of backbone substituents indicated by R.

to separate publications for results obtained on isolated polymer chains in dilute solution[7−9] and aligned thin films using a flash-photolysis modification of the technique.[10,11]

While it is acknowledged that the PR-TRMC technique has its limitations, for example, the individual contribution of the positive and negative charge carriers cannot be separately determined, it is a method that can be readily applied to any material irrespective of its morphology or optical properties, thus allowing a large number and variety of materials to be investigated and compared. Because of the low electric field strength (<100 V/cm) and the ultrahigh frequency (ca. 30 GHz), the random diffusional motion of charge carriers is only slightly perturbed. This, together with the nanosecond time response of detection, ensures that the mobilities determined are effectively zero-field, trap-free values, characteristic of the most well-organized (highest mobility) domains within a sample. In an attempt to obtain better insight into the underlying mechanism of charge transport in these materials, we are at present carrying out PR-TRMC measurements in which both the real and the imaginary microwave conductivities are measured. In the work presented here only changes in the real component have been investigated.

Materials

Results are presented on two, quite different types of carbon-based compounds, both of which have been proposed as organic semiconductor materials for application in plastic electronic devices, conjugated polymers, and columnar discotics. The molecular structures of the compounds investigated are illustrated in Figures 1 and 2.

Conjugated polymers depend for their semiconductive properties on the interaction between half-filled p-orbitals on adjacent carbon atoms along the polymer backbone. Rather than resulting in equidistance between the carbon atoms and metallic behavior, as might be expected, Peierls distortion leads to pairing of electrons and the creation of a chain of alternating single, σ, and double, π, bonds (in the terminology of organic chemistry), hence the generic name π-bond-conjugated polymers. While for isolated chains charge transport will, of necessity, be highly one-dimensional along the backbone, in aggregated solids interchain charge transfer may also contribute to the mobility.

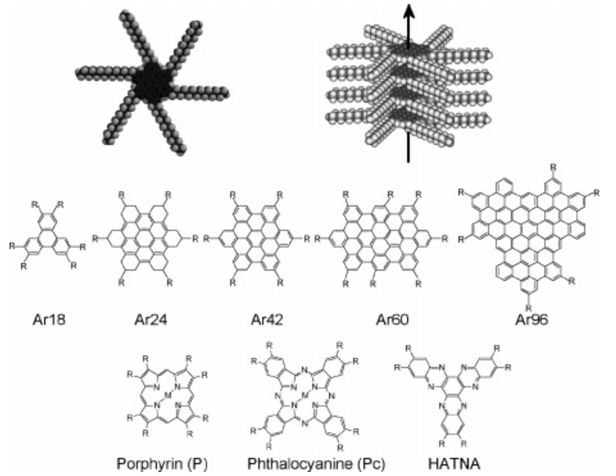

Figure 2. Structures of the discotic cores investigated using the PR-TRMC technique with the position of peripheral substituents indicated by R.

The backbone substituents, indicated by "R" in Figure 1, usually contain long, aliphatic hydrocarbon chains. These were initially introduced to increase the solubility of the (otherwise intractable) polymer, thus allowing more rigorous purification and better processability. These "passive" substituents can however also influence other physical and morphological properties relevant to their application as semiconductor materials, including liquid crystalline behavior.

The discotic materials derive their name from the presence of a central, planar core which usually consists of an aromatic moiety with delocalized π-orbitals above and below the plane. The peripheral substituents, R, are introduced in this case with the deliberate aim of inducing liquid crystallinity, although ease of purification and processing is an important secondary consideration. In the liquid crystalline phases of discotic compounds, the peripheral aliphatic chains are effectively molten and the central cores form extensive columnar stacks with the plane of the cores orthogonal to the columnar axis. The interaction between the π-orbitals of adjacent cores provides the pathway for charge migration in this case. The presence of the surrounding insulating hydrocarbon mantle results in highly one-dimensional charge transport, as recently experimentally demonstrated for aligned thin films.[11] In the crystalline solid phase of discotics, an underlying columnar structure remains but the cores are tilted (often at close to 45°) with respect to the columnar axis.

Experimental Section

A much simplified schematic of the PR-TRMC apparatus is shown in Figure 3. Only a brief outline of the measurement procedure and data analysis will be given here since extensive descriptions have appeared in previous publications.[6,12]

The material of interest is contained in a microwave cell consisting of a 14 mm long piece of microwave

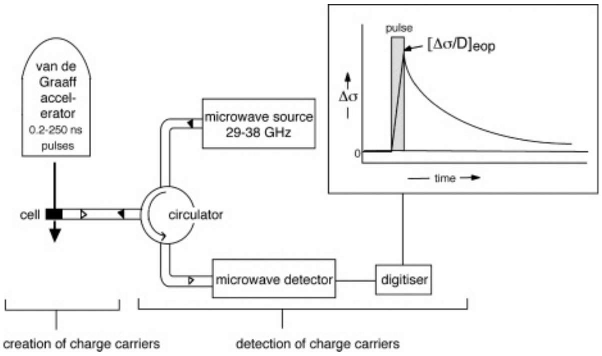

Figure 3. A much simplified schematic representation of the pulse-radiolysis time-resolved microwave conductivity equipment.

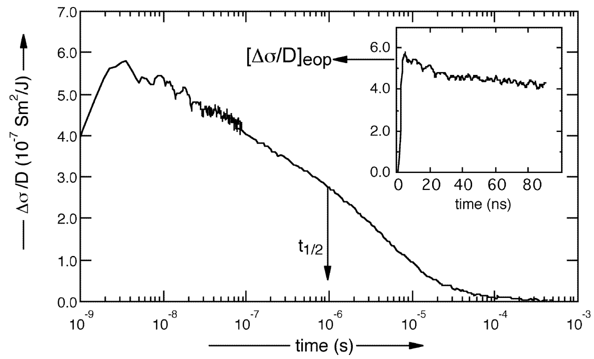

Figure 4. Typical conductivity transients monitored using a logarithmic (main figure) or linear (inset) time base.

waveguide of internal cross section 3.55 × 7.1 mm^2. For most of the samples the grain or domain dimensions were much smaller than those of the cell, resulting in a random orientation of the underlying microstructure. In the case of polydiacetylenes, some compounds were obtained in the form of single crystals of millimeter dimensions with well-defined crystal axes. For these samples a special cell was constructed which allowed the crystals to be rotated through 360° with respect to the highly polarized microwave electric field vector.[13] In this way information could be obtained on the anisotropy of charge transport.

The samples are uniformly ionized with a single nanosecond pulse of 3 MeV electrons from a Van de Graaff accelerator. The energy absorbed by the sample (the dose, D, J/m^3) is accurately known from dosimetry and results in the formation of charge carrier pairs with a concentration, N_p, on the order of micromolar (ca. 10^{21} m^{-3}). If the charge carriers formed are mobile, an increase in the conductivity of the sample, $\Delta\sigma$, occurs which is monitored as a decrease in the microwave power reflected by the cell. Typical conductivity transients are shown in Figure 4, one taken on a short, linear time scale for accurate measurement of the dose-normalized end-of-pulse conductivity, $[\Delta\sigma/D]_{eop}$, and the other taken on a logarithmic time scale. The latter provides information on the after-pulse decay resulting from trapping and/or charge recombination. Only the first aspect, from which mobility estimates can be obtained, will be considered in this review.

The conductivity is related to the carrier-pair concentration, N_p, and the sum of the positive and negative carrier mobilities, $\Sigma\mu = [\mu(+) + \mu(-)]$, by

$$\Delta\sigma = eN_p\left(\sum\mu\right) \tag{1}$$

with e the elementary charge (1.6×10^{-19} C). The initial concentration of pairs formed during the pulse, $N_p(0)$, can be calculated from the dose in the pulse and the average pair-formation energy, E_p (in electronvolts), according to

$$N_p(0) = D/eE_p \tag{2}$$

From (1) and (2), the following expression can be derived for the mobility in terms of the measured quantity $[\Delta\sigma/D]_{eop}$:

$$\sum\mu = E_p[\Delta\sigma/D]_{eop}/W_{eop} \tag{3}$$

In (3), W_{eop} is the fraction of initially formed charge carrier pairs which survive charge recombination within the pulse.

For high-energy radiation, the value of E_p can be estimated using the semiempirical expression derived by Alig et al.:[14]

$$E_p \approx 2.73E_I + 0.5 \tag{4}$$

In (4), E_I is the ionization onset energy for molecular materials or the band gap for semiconductor materials. (4) is found to be quite universal, providing reasonable estimates of E_p for materials varying from low-band-gap semiconductors with E_I as low as ca. 1 eV to saturated hydrocarbon liquids for which E_I is closer to 10 eV. If a reasonably good estimate of E_I is available, then (4) should give a value of E_p which is good to within ±20%.

If a medium consists of different molecular components, the fraction of energy deposited initially in a given component, n, is proportional to its fractional contribution to the total electron density, $\Delta Z(n)$. In the present materials, for example, we can differentiate between the σ-bonded components, R in Figures 1 and 2, with an $E_I(\sigma)$ value close to 8 eV and the π-bonded polymer backbones or discotic cores with $E_I(\pi)$ values closer to 4 eV. The effective overall value of E_p is then given by

$$E_p = [\Delta Z(\sigma)/E_p(\sigma) + \Delta Z(\pi)/E_p(\pi)]^{-1} \tag{5}$$

The values of E_p calculated for the present compounds using (5) lie within the range 11−18 eV.

The remaining unknown parameter in (3) is the end-of-pulse survival probability, W_{eop}. If no estimate of W_{eop} is available, a lower limit to the mobility, $\Sigma\mu_{min}$, can be derived by assuming that all initially created charge carriers survive to the end of the pulse, i.e., $W_{eop} = 1$, giving

$$\sum\mu_{min} = E_p[\Delta\sigma/D]_{eop} \tag{6}$$

The results for the polymeric materials have usually been presented as $\Sigma\mu_{min}$ values in the past.

The actual value of W_{eop} will be determined to a large extent by the average thermalization distance of electrons from their sibling positive ion, $\langle r_{th}\rangle$, and the diffusional escape probability of charges separated by this distance. In high-energy irradiated organic materials, $\langle r_{\mathrm{th}} \rangle$ has been found to be close to 50 Å and escape probabilities are usually between 1% and 10% at room temperature,[15] even for low-dielectric-constant, saturated hydrocarbon media. A thermalization distance of 50 Å is considerably greater than the distance between the polymer chains in the present materials. There is therefore a high probablity that the electron and hole of an initial charge carrier pair become situated on different, widely separated polymer chains after thermalization. Because of this, we believe that the survival probability of initial charge carriers on a nanosecond time scale should be at least 10% and possibly closer to unity. We consider it therefore extremely unlikely that the actual values of the mobility sum would be an order of magnitude larger than the values of $\Sigma\mu_{\mathrm{min}}$ calculated as described above.

For the discotic materials, a method of estimating W_{eop} has been presented and is fully discussed in previous publications.[5,16] The values of W_{eop} derived lie within the range from 0.3 to 0.6 for the discotic compounds investigated. In presenting the data for discotic compounds, the reasonable assumption is made that charge transport is highly one-dimensional along the axis of the columnar stacks;,an assumption that is based on the insulating mantle of saturated hydrocarbon surrounding the cores. This has been substantiated recently by the large anisotropy in the photoconductivity found for aligned thin films of discotics.[11] In the PR-TRMC experiments the organized domains are randomly oriented, and the mobility measured will be an effective isotropic value. Since the interest is in the one-dimensional, intracolumnar mobility, the data are usually presented as $\Sigma\mu_{\mathrm{1D}} = 3(\Sigma\mu)$, with $\Sigma\mu$ the value derived using (3).

For the conjugated polymers the assumption of highly one-dimensional charge transport, in this case along the polymer backbone, is less well-founded since $\pi-\pi$ interactions could result in interchain charge transfer making a significant contribution to the overall charge migration process. Anisotropy measurements on polydiacetylene single crystals,[13] and on aligned films of a polyfluorene derivative,[10] do however lend support to this assumption for most, if not all, of the polymers investigated. For more ready comparison with the values for the discotic materials, we have therefore chosen to present the mobility values for the conjugated polymers also as effective one-dimensional values given by $\Sigma\mu_{\mathrm{1D}} = 3(\Sigma\mu_{\mathrm{min}})$.

Results and Discussion

Conjugated Polymers. *Polydiacetylenes (PDAs).* PDAs were the first class of conjugated polymers which could be produced in a pure form, by thermal or radiation-induced polymerization of the corresponding monomeric crystals.[17] In this respect they remain unique. But, despite initial high expectations, they have been found to be unsuitable for device applications even though soluble derivatives have been prepared. The availability of relatively large single crystals did however make possible mobility measurements using dc photoconductivity and time-of-flight techniques, which provided the fundamental impetus for subsequent studies of conjugated polymers as active materials in electronic devices.

Table 1. One-dimensional Charge Mobility, $\Sigma\mu_{\mathrm{1D}}$, and Chain Length for Selected Polydiacetylene Derivatives and Different Methods of Polymerization

R (in Figure 1)	method of polymerization (dose)	chain length (no. of monomer units)	$\Sigma\mu_{\mathrm{1D}}$ [cm^2/(V s)]
pTS	thermal		7.6,[a,b] 1.0–3.5[c,d]
pTS	γ-ray (>100 kGy)		0.36[c]
3BCMU	γ-ray (>100 kGy)		0.12[c]
4BCMU	γ-ray (>100 kGy)		0.06[c]
9BCMU	γ-ray (>100 kGy)		0.06[c]
pTS	HE electrons (<100 Gy)		7[a]
3BCMU	HE electrons (<100 Gy)	1000[a]	10[a]
4BCMU	HE electrons (<100 Gy)	2400[a]	11,[a] 8,[c,e] 15[f]
9BCMU	HE electrons (<100 Gy)	4700[a]	42[a]

[a] Reference 21. [b] Reference 24. [c] Reference 22. [d] Reference 12. [e] Reference 25. [f] Reference 23.

The majority of the mobility values previously determined for PDAs lie within the range from 1 to 100 cm^2/(V s),[18] with the outstanding exception being the estimate of greater than 2×10^5 cm^2/(V s) by Donovan and Wilson.[19] At the present time there would appear to be a broad consensus which would agree with the conclusion reached in the exhaustive review of PDA mobility values by Bässler,[20] that "there is no need to invoke a mobility greater than about 100 cm^2/Vs for carrier transport along a defect-free PDA chain". In light of recent experiments on photoelectron emission from organic polymers,[21] it seems likely that the ballistic transport observed by Donovan and Wilson was in fact due to photoelectrons ejected into the vacuum space between the electrodes.

Because of the lack of necessity of electrode contacts, three unique types of measurement on PDAs are possible using the PR-TRMC technique. First, mobility estimates can be made on polycrystalline or microcrystalline-powder samples. Second, the mobility within polymerized regions can be determined in situ as a function of the extent of polymerization using the high-energy (HE) electrons of the accelerator to induce polymerization of initially pure monomeric crystals. Third, because of the highly polarized electric field vector of the microwaves, the angular dependence (anisotropy) of the mobility can be determined by rotating a single, millimeter dimension crystal within the irradiation cell.

Some representative PR-TRMC mobility values are given in Table 1 for the (frequently studied) *p*-toluenesulfonate (pTS) and the (dissolvable) *n*-alkoxycarbonylmethylurethane (*n*BCMU) derivatives.[13,18,22–26] For the BCMUs it was possible to determine the average length of the polymeric chains, i.e., the length to which the chains propagate after initiation before the strain built up in the crystal lattice retards further reaction.[13,22] These values are also given in the table since they may be related to the magnitude of the mobilities measured.

As can be seen the values of $\Sigma\mu_{\mathrm{1D}}$ for thermally polymerized samples of pTS-PDA lie within the range from 1 to 7.2 cm^2/(V s), i.e., close to the majority of previous values determined using dc techniques. The values obtained for radiation-polymerized materials are however much lower. This is undoubtedly due to the extremely high doses (>100 kGy) routinely used to produce "fully polymerized" samples and is presumably the result of eventual chain scission and/or the buildup

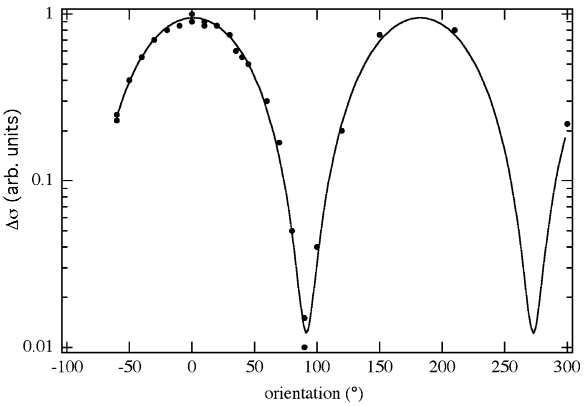

Figure 5. Dependence of the radiation-induced conductivity of a single crystal of pTS-PDA on the orientation of the backbone axis with respect to the microwave electric field vector.

of chemical or physical trapping sites. ESR measurements on PDA samples prepared by γ irradiation have shown there to be a concentration of free-radical sites present of ca. 3×10^{17} per gram or close to millimolar.[27] The possible presence of additional, zero-spin radiolytic trapping sites could not be detected using this technique.

The negative effect of an elevated dose has been demonstrated by PR-TRMC measurements on initially pure monomeric samples which were subjected to an increasing accumulated dose delivered in situ by the accelerator. This clearly showed that the mobility within polymerized regions of the sample decreased considerably even for doses 2 orders of magnitude lower than those which at the time were conventionally used.[13,24] The limiting, low-dose mobility values (corresponding to less than 10% conversion of the monomer) are seen in Table 1 to be comparable with or even higher than the values found for the thermally polymerized pTS samples. Furthermore, there is a tendency for the mobility to increase with increasing chain length as might be expected since this reflects decreasing strain within the crystal lattice and hence smaller perturbation of the backbone structure. The absolute magnitudes of the low-conversion mobilities are within the same range as those determined in the majority of TOF measurements,[18] and tend to support the proposition of Bässler of a maximum mobility for PDAs on the order of 100 cm^2/(V s).[20]

The highly one-dimensional nature of charge transport in PDAs is shown by the angular dependence of the radiation-induced microwave conductivity for a single-crystal, millimeter dimension pTS sample shown in Figure 5. Analysis of the data, taking into account the shape of the crystal, resulted in an estimate of a factor of approximately 100 in favor of charge migration along the polymer backbone,[13] in agreement with the large anisotropies previously measured using dc techniques.[18]

Poly(phenylenevinylenes), PPVs. PPV derivatives, which are synthesized in solution, differ dramatically from the topologically polymerized single-crystal PDA materials discussed in the previous section. For example, the solid dialkoxy-PPV materials listed in Table 2, as freshly prepared, are characterized by fibrous, polycrystalline, or waxlike, textures, indicative of different and imperfect structural ordering. The more than 1 order of magnitude difference in mobility values for compounds with almost identical conjugated backbone structures is considered to be the result of differences in the degree of static disorder within the polymer backbones. This is supported by the observation that high-temperature annealing can have a marked positive effect on the mobility, particularly for the lowest mobility materials. Even after annealing, however, the range of mobility values remains large, from 0.0075 to 0.108 cm^2/(V s). Recent PR-TRMC measurements on a series of symmetrically substituted dialkyl-PPV derivatives by Krebs and Jorgensen[28] show a similar range of values for $\Sigma\mu_{1D}$, from 0.02 to 0.18 cm^2/(V s), when analyzed in the same way as for the present results.

Table 2. Room-Temperature Values of $\Sigma\mu_{1D}$ for Dialkoxy-PPV Derivatives Freshly Prepared and after Annealing at 150 °C for ca. 1 h

			$\Sigma\mu_{1D}$ [cm^2/(V s)]	
pseudonym	R$_1$	R$_2$	fresh	annealed
MEH	methoxy	2-ethylhexoxy	0.0036	0.0075
dMOM	methoxy	3,7-dimethyloctoxy	0.0054	0.0240
(dMO)$_2$	3,7-dimethyloctoxy	3,7-dimethyloctoxy	0.042	0.045
(DD)$_2$	dodecoxy	dodecoxy	0.030	0.030
(OD)$_2$	octadecoxy	octadecoxy	0.060	0.108

Even the maximum mobility value for the PPVs is 1−2 orders of magnitude lower than found for the PDAs. The question is whether this is a result of an intrinsically better conductive pathway along the PDA backbone or is due to greater residual backbone disorder in the PPVs even after annealing. Theoretical calculations suggest that much larger mobilities should be possible along a completely planar PPV chain,[29] and we are of the opinion that values on the same order as for PDAs would be found if a rigid, planar backbone organization could be achieved.

The asymmetrically dialkoxy-substituted derivatives MEH- and dMOM-PPV display mobilities which are considerably lower than those of the symmetrically substituted compounds. Interestingly, the mobilities, even after annealing, show an inverse relationship with the solubility in organic solvents such as benzene. Thus, both the MEH and dMOM derivatives can be readily dissolved in benzene, but the dMOM compound gradually aggregates at room temperature to form a gel while MEH-PPV solutions are stable. The (dMO)$_2$ and (DD)$_2$ derivatives are only slightly soluble, and (OD)$_2$-PPV is completely insoluble. This trend can be understood in terms of an increasing tendency toward interchain π−π-stacking, which results in a stronger tendency toward aggregation and hence a lower solubility. As a corollary, the precipitated solid materials of the least soluble compounds would be expected to have the highest degree of structural order and hence the largest mobilities, as is observed. It might be inferred from this that interchain charge transfer makes an important contribution to the overall mobility. This conclusion is however not necessarily correct since the π-stacking of adjacent chains most probably results in a more rigid and coplanar backbone structure which would be expected to have a positive influence on intrachain charge delocalization and migration.

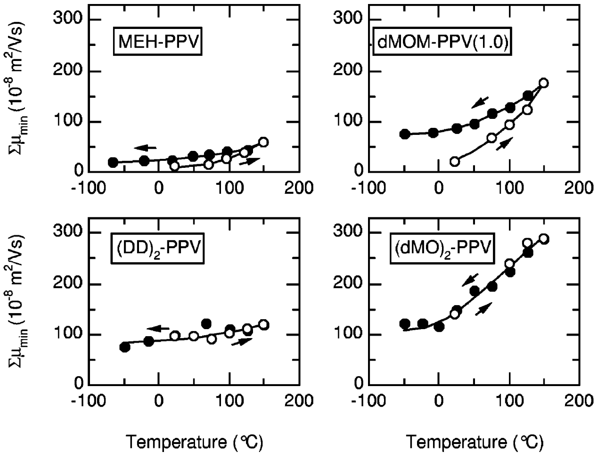

Figure 6. Temperature dependence of the isotropic charge mobility for the first heating (open circles) and cooling (filled circles) trajectories of the phenylenevinylene polymers shown.

As a result of the annealing effect, the temperature dependence of the mobility for the first heating and cooling trajectories can appear complex, as shown in Figure 6. Considering only the cooling behavior after annealing, only a relatively low activation energy of the mobility of ca. 0.1 eV or less is found for all compounds.

The temperature dependence of the mobility for $(OD)_2$-PPV (not shown in Figure 6) is particularly interesting since this compound becomes a free-flowing liquid for temperatures just below 200 °C.[6] Even in this highly mobile phase, however, the mobility remains high with a $\Sigma\mu_{1D}$ value of ca. 0.05 cm^2/(V s). This material can therefore be considered to be the first example of a liquid organic semiconductor. On cooling from the liquid phase, a lamellar liquid crystalline phase is entered in which the molecules can be aligned by shearing to produce a highly dichroic film. Unfortunately the insolubility of $(OD)_2$-PPV makes processing of this interesting material for applications in device structures, via, for example, spin-coating or ink-jet-printing, impossible.

The degree of conjugation of π-bond-conjugated polymers is an important parameter in determining their physical properties such as solubility, optical absorption, and conductivity. A series of dMOM-PPV compounds have been investigated by PR-TRMC in which the conjugation was broken by allowing a known fraction, X, of the vinylene residues to remain saturated (methanolated) in the final stage of synthesis. In this way polymers with a degree of conjugation $(1 - X)$ of >0.98 (nominally “fully conjugated”), 0.96, 0.87, and 0.6 have been obtained and investigated.[6] The corresponding values of $\Sigma\mu_{1D}$ found for thermally annealed samples were 0.024, 0.005, 0.003, and 0.001 cm^2/(V s), respectively; clearly indicating the importance of this parameter in determining the conductive properties, as expected.

Miscellaneous Polymers. Values of $\Sigma\mu_{1D}$ for other types of conjugated polymers that have been investigated using the PR-TRMC technique are given, at room temperature and 100 °C, in Table 3 together with values for those PPV derivatives with the highest and lowest mobilities. A general observation is that the mobility for all compounds is only weakly thermally activated with an activation energy of ca. 0.1 eV at most. The absolute values do however vary considerably.

Table 3. Values of $\Sigma\mu_{1D}$ at Room Temperature (rt) and 100 °C for Thermally Annealed Samples of the Conjugated Polymers Shown

pseudonym	backbone	R$_1$, R$_2$ in Figure 1	$\Sigma\mu_{1D}$ [cm^2/(V s)] rt	$\Sigma\mu_{1D}$ [cm^2/(V s)] 100 °C
PF2,6	fluorene	2-ethylhexyl	0.125	0.200
$(OD)_2$-PPV	phenylene-vinylene	octadecoxy	0.108	0.102
rrPHT	thiophene	hexyl	0.042	0.057
PTV	thienylvinylene	p-decoxy-phenylene	0.025	0.032
MeLPPP	ladder p-phenylene	p-decylphenylene, hexyl	0.014	0.021
MEH-PPV	phenylene-vinylene	methoxy, 2-ethylhexoxy	0.008	0.012
PPP	p-phenylene	3-methylbutoxy	0.004	0.009

As discussed in the previous section, the differences in $\Sigma\mu_{1D}$ may be ascribed more to differences in the morphology and structural backbone disorder rather than differences in the (optimum) intrinsic conductive properties of a particular polymer chain. For example, the two compounds at the top of the list are both liquid crystalline and highly ordered at room temperature.[6,30] Also, the third highest member, regioregular poly(3-hexylthiophene), is known to form well-organized lamellar domains,[31,32] and mobilities in field effect transistors using rrPHT have been determined which are even larger than the value of $\Sigma\mu_{1D}$ given here.[32,33] It should be pointed out that, because of the lamellar structure, charge migration via interchain electron transfer may play an important, or even dominant, role for this compound.

A somewhat surprising result was the finding of a relatively low mobility for the ladder polymer MeLPPP, which has a rigid, planar backbone structure. This compound is in fact one of the very few conjugated polymeric materials for which nondispersive Gaussian transport has been observed.[34] The time-of-flight mobility determined was relatively weakly dependent on temperature with a room-temperature value of ca. 1×10^{-3} cm^2/(V s), still considerably lower than the present value of 0.014 cm^2/(V s) for $\Sigma\mu_{1D}$. It is possible that this relatively low mobility is due to extensive delocalization of the charge on the MeLPPP backbone. If, as a result, the scattering frequency is comparable with or lower than the radian frequency of the microwaves used (ca. 2×10^{11} s^{-1}), then the mobility determined from the real component of the conductivity would be lower than the limiting low-frequency value. To test this possibility, adaptations to the PR-TRMC technique, which will allow the combined measurement of the real *and* the imaginary components of the conductivity, are in progress.

Discotics. Discotic materials differ essentially from conjugated polymers in that the individual molecular units are not covalently linked but rather self-assemble into columnar aggregates. Their one-dimensional conductive properties depend on the interaction between the delocalized π-orbitals of adjacent aromatic cores.[35]

Discotic materials frequently display thermotropic mesomorphism with one or more liquid crystalline phases between the crystalline solid, “K-phase”, and the isotropic liquid, “I-phase”. In the columnar mesophase (denoted here the “D-phase” but more recently by others the “Col-phase”) the aromatic cores are oriented

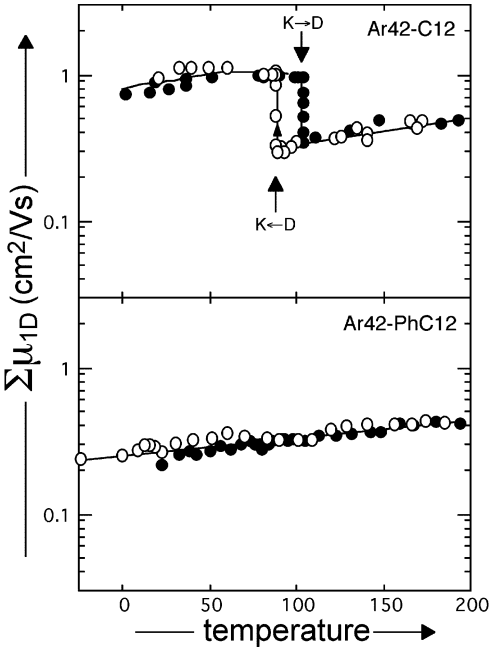

Figure 7. Temperature dependence on heating (filled circles) and cooling (open circles) of the one-dimensional mobility for hexakis-substituted hexa-*peri*-hexabenzocoronene (HBC or Ar42) derivatives with dodecyl (upper) or dodecylphenyl (lower) peripheral substituents.

orthogonal to the axis of the columnar stacks, as illustrated in Figure 2, whereas in the K-phase they are tilted.

While the majority of discotic compounds, when freshly prepared, are crystalline solids at room temperature, there are now several examples of materials for which crystallization does not occur and the characteristic liquid crystalline structural and physical properties are displayed at all temperatures below the transition to the isotropic liquid.

For all discotic compounds which display a transition from a K-phase to a D-phase, the transition has been found to be accompanied by an abrupt decrease in the mobility. The lower charge mobility in the liquid crystalline phase is attributed to increased motional freedom and hence greater structural disorder within the columnar stacks on "melting" of the peripheral hydrocarbon chains. This effect is illustrated by the results for an alkyl-substituted hexa-*peri*-hexabenzocoronene (Ar42) derivative in Figure 7.

Up to and above the transition temperature only a slight, if any, increase with temperature is observed. On cooling from the mesophase, $\Sigma\mu_{1D}$ usually returns to the initial K-phase values with a hysteresis of ca. 20°, as shown in Figure 7. There are compounds however which supercool in the D-phase and do not revert to the initial crystalline solid form at room temperature.[36] Also shown in Figure 7 are results for the dodecylphenyl derivative of Ar42, which is liquid crystalline at all temperatures and, as expected, displays no abrupt change in $\Sigma\mu_{1D}$ with temperature. Such compounds, while rare, are of considerable interest because of their ready processability and self-healing properties at room temperature.

For some of the core units studied by PR-TRMC a variety of different peripheral R substituents have been investigated. In what follows only a summary of the maximum mobility values in the K- and D-phases for a particular class of core and substituent combinations is given. More detailed information is to be found in other recent publications.[36,37]

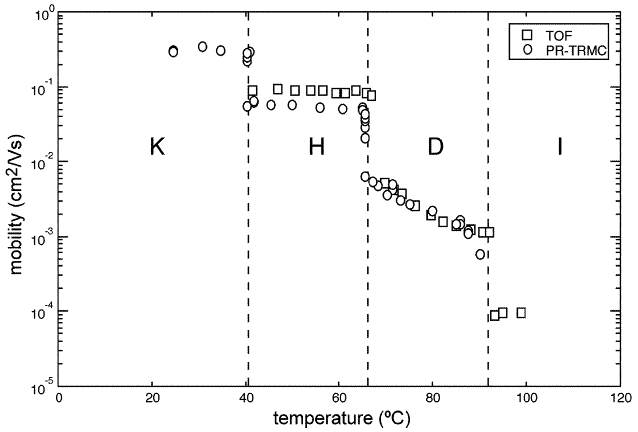

Figure 8. Temperature dependence on heating of the one-dimensional charge mobility in HHTT determined by PR-TRMC (circles) or time-of-flight (squares) measurements.

Polycyclic Hydrocarbon Cores. Of all of the aromatic hydrocarbon cores studied in the past, the triphenylene (Ar18) derivatives have been the subject of the most previous structural and charge-transport studies by others, mainly because of their low clearing points and ease of processing. This has made it possible to achieve homeotropic (orthogonal columnar) alignment between electrode surfaces and nondispersive charge transport, which is necessary for the measurement of the intracolumnar mobility by time-of-flight (TOF) methods.[38−41]

Of particular relevance are the TOF measurements of the hole mobility in the hexakis(hexylthio) derivative of triphenylene, HHTT, carried out by Haarer et al.[39] This compound displays two mesophases, a unique helical plastic phase, H, and a more fluid liquid crystalline D-phase. PR-TRMC measurements on HHTT yielded $\Sigma\mu_{1D}$ values in very good agreement with the TOF values in both mesophases, as shown in Figure 8.[42] Because of the disperse nature of charge transport in the (poly)-crystalline K-phase, only PR-TRMC measurements were possible. Conversely, only TOF measurements could be made in the isotropic liquid because of the very low mobility values pertaining to it. The combined results, however, provide a complete overview of the charge-transport properties of HHTT in all four phases of this material.

In Table 4 are given the (maximum) mobility values in the K- and D-phases for all of the aromatic cores shown in Figure 2. In both the K- and D-phases the mobility is seen to increase on going from Ar18 to Ar42, with the effect being considerably more pronounced in the liquid crystalline phase. It was on the basis of the results for Ar18 and Ar42, together with $\Sigma\mu_{1D}$ values for heterocyclic cores, given in the next section, that the empirical relationship (7) was proposed for the core size dependence in the D-phase of discotic materials.[43]

$$\sum\mu_{1D} \approx 3\ \exp[-83/m]\ [\mathrm{cm^2/(V\ s)}] \tag{7}$$

As can be seen however the values of 0.29 and 0.23 cm^2/(V s) for Ar60 and Ar96 are if anything somewhat

Table 4. Maximum Mobility Values Determined for a Given Aromatic Hydrocarbon Core and Type of Peripheral Substituent in the Crystalline Solid, K, Phase at Room Temperature and the Columnar Liquid Crystalline, D, Phase at ca. 10 °C above the K-to-D Transition Temperature

		$\Sigma\mu_{1D}$ [cm^2/(V s)]	
core	substituent	K-phase, rt	D-phase [T (°C)]
Ar18	alkoxy	0.03	0.01 [77]
Ar18	alkylthio	0.26	0.02 [70]
Ar24	alkyl	0.72	0.15 [100]
Ar42	alkyl	1.00	0.38 [105]
Ar42	alkylphenyl	*a*	0.22 [rt] 0.31 [100]
Ar60	alkyl	0.52	0.29 [108]
Ar96	alkyl	*a*	0.20 [rt] 0.23 [100]

[a] Liquid crystalline at room temperature.

smaller than for Ar42 and significantly lower than the values of 0.75 and 1.26 cm^2/(V s) predicted by (7). It is clear therefore that this expression is not of general applicability. Rather, the mobility would appear to saturate for the largest cores at values close to 1 and 0.3 cm^2/(V s) for the K- and D-phases. These values are in fact close to the mobility values which have been determined at room temperature for single crystals of aromatic molecules.[2]

In recent theoretical work, consideration has been given to the influence on the charge-transfer integral of lateral, longitudinal, and rotational fluctuations within the columnar stacks of discotic materials. One of the general conclusions reached was that "an increase in size of the conjugated core does not necessarily ensure better transport properties".[35] This can be understood simply as resulting from the counteracting effects on the overall charge-transfer integral of increasing $\pi-\pi$-overlap but decreasing average charge density as the core size increases.

The size dependence actually found for the smaller members of the Ar*m* series most probably results from a decrease in the cohesion between the molecules within a stack as *m* decreases, which allows more longitudinal and lateral disorder. This is most clearly experienced as a very much lower viscosity of the triphenylene derivatives in their liquid crystalline D-phase.

Heterocyclic Aromatic Cores. Porphyrin and phthalocyanine derivatives were the first discotic compounds to be investigated using PR-TRMC,[44,45] and a compilation of data on the large variety of substituents studied has recently appeared.[37] Energy and charge migration in these two classes of compounds is of both fundamental and practical interest, the former because of the important role played by porphyrin derivatives in natural (e.g., photosynthetic antenna) systems, the latter because of potential applications in solar energy conversion devices based on the large optical absorptions of phthalocyanines in the visible and near infrared regions.

The early PR-TRMC results on the porphyrin derivatives were of particular importance since their clearing points were well within the upper temperature range of the experiments (200 °C). It was possible therefore to demonstrate both the substantial decrease in mobility on going from the K-phase to the D-phase and the even more dramatic decrease on entering the isotropic liquid phase.[44] This provided the first direct evidence that columnar self-assembly in the liquid crystalline phase of discotic materials results in charge mobilities much larger than possible via molecular diffusion alone.

Table 5. Maximum Mobility Values Determined for a Given Heterocyclic Core and Type of Peripheral Substituent in the Crystalline Solid, K, Phase at Room Temperature and the Columnar Liquid Crystalline, D, Phase at ca. 10 °C above the K-to-D Transition Temperature

		$\Sigma\mu_{1D}$ [cm^2/(V s)]	
core	substituent	K-phase, rt	D-phase
P	alkoxyethyl	0.39	0.07
Pc	alkoxy	0.37	0.08
Pc	alkylthio	0.55	0.27
Pc	alkoxyphenyl	0.67	0.24
HATNA	alkylthio	0.59,[a] 0.13[b]	0.20

[a] Freshly prepared. [b] After cooling from the mesophase.

As can be seen from the data in Table 5, the maximum mobilities found in the crystalline solid phases of discotic porphyrins and phthalocyanines differ by less than a factor of 2 and are close to the values found for the aromatic hydrocarbon cores presented in Table 4. A substantially smaller value of $\Sigma\mu_{1D}$ in the D-phase of porphyrins is however indicated. This can be attributed to the smaller core size and reduced cohesion resulting in greater columnar disorder as suggested for the smaller core aromatic hydrocarbons in the previous section. The metal-free and nickel derivatives of octakis(alkoxyethyl)porphyrins in fact display no mesophase behavior but undergo a direct transition to the isotropic phase.[46]

The HATNA compounds, which have a highly electron-deficient central core, were recently synthesized with a view to their application as electron-transport layers in LED devices.[47] As can be seen from the results in Table 5, the values of $\Sigma\mu_{1D}$ in the pristine crystalline material and in the D-phase are very similar to the values found for phthalocyanines and for the larger aromatic hydrocarbon derivatives. On cooling back to room temperature however, recrystallization does not occur and the mobility remains at a level more characteristic of a liquid crystalline phase.

General Conclusions

The one-dimensional charge mobility values, $\Sigma\mu_{1D}$, determined for thermally polymerized or low-dose (<100 Gy) radiation-polymerized polydiacetylene single crystals using the PR-TRMC method lie within the range from 1 to 40 cm^2/(V s), similar to the majority of previous estimates using dc techniques. Fully polymerized samples prepared using radiation doses 1000 times higher display much lower mobilities, presumably due to the occurrence of chain scission or the buildup of chemical and/or physical trapping sites. The PR-TRMC results support the earlier conclusion of Bässler[20] that the realizable limit to mobilities in polydiacetylene single crystals will be close to 100 cm^2/(V s). Whether this is the limit for a hypothetical, strain-free, rigid, and perfectly planar PDA backbone is another question! The mobility value of $>2 \times 10^5$ cm^2/(V s) measured by Donovan and Wilson[19] is however considered to be unrealistially high and is most probably attributable to photoelectrons ejected into the vacuum space between the electrodes.[21,48]

In contrast to single-crystal PDAs, solution-synthesized conjugated polymers can vary dramatically in their morphology, from fibrous to flakelike, and from polycrystalline to waxy, even for highly pure materials with the same backbone structure. The fact that the PR-TRMC mobilities determined for such materials can vary by more than an order of magnitude is undoubtedly attributable to such morphological differences and the underlying structural disorder in the polymer backbones. The highest $\Sigma\mu_{1D}$ values of ca. 0.1 cm^2/(V s) are found for liquid crystalline derivatives of polyfluorene and poly(phenylenevinylene). Since even these values are probably determined by backbone disorder, considerably higher mobilities, approaching those found for PDAs, should be possible if the means can be found to improve their morphology and the planarity of the backbone structure. In this regard, the relatively low mobility found for the rigid-backbone compound MeLP-PP was unexpected.

The maximum mobility values found for the discotic materials, even in their liquid crystalline phase, are considerably larger than for the solution-synthesized conjugated polymers. The maximum values of $\Sigma\mu_{1D}$, of close to 1 cm^2/(V s), are in fact similar to those found for single crystals of aromatic molecules,[2] which might be considered to represent the ultimate attainable for noncovalently bonded materials. The higher mobilities for discotics presumably reflect their superior capability of self-organization rather than an intrinsically larger electronic coupling between the molecular units. Since mobilities significantly larger than ca. 1 cm^2/(V s) are unlikely for discotics, their successful application in molecular electronic devices will depend mainly on better control of their columnar alignment, which has been achieved recently.[11,49−51]

The relative contributions of electrons and holes to the overall charge mobility, which cannot be measured for solid samples by PR-TRMC, remains a problem. While TOF measurements on PDAs have indicated the electron to be the most mobile species,[52] all measurements on other conjugated polymers and on discotics have shown holes to be the major charge carrier. In view of the similarity of the mobilities of electrons and holes in organic single crystals,[2] this result is surprising and is usually ascribed to the much more rapid trapping of electrons. In separate PR-TRMC experiments on dilute polymer solutions, where the individual charge carrier mobilities can be determined, similar values for an electron and a hole have in fact been found,[7] indicating that electron transport should be equally efficient if the concentration of chemical and/or physical electron-trapping sites can be diminished.

Acknowledgment. We acknowledge the many international groups that have supported this research by synthesizing and making available the organic compounds investigated.

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CM049577W