Long-Lived, Mobile Charge Carriers Formed on Photoexcitation of UV-Polymerized, Spin-Coated Films of Arylimido−Spacer−Diacetylene Derivatives

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ABSTRACT: The photopolymerization of spin-coated films of diacetylene derivatives containing phthalimido or naphthaldiimido moieties has been studied by monitoring the increase in the optical absorption in the visible region on irradiation at 308 nm. The phthalimido derivatives form blue polymers with absorption maxima at ca. 630 nm, corresponding to a highly conjugated, close to planar polydiacetylene (PDA) backbone configuration. The naphthaldiimido derivative yields a red polymer with an absorption maximum at 535 nm, indicating a backbone structure with a substantially reduced degree of π-bond conjugation. The initial, "low-dose" quantum yields for monomer conversion, based on the total number of photons absorbed at 308 nm, range from 2 to 20. Monomer conversions up to ca. 50% are found. The polymerized films are found to be photoconductive using the time-resolved microwave conductivity technique (TRMC). Mobile charge carriers are suggested to be formed via the triplet state of the arylimido moieties which undergoes long-distance charge transfer to polydiacetylene chains to form the arylimido radical anion and the mobile PDA radical cation or "hole". A maximum value of 1.4×10^{-2} cm^2/(V s) for the product of the quantum yield for charge carrier formation and the hole mobility is found. The photoconductivity of the "blue" polymer is approximately an order of magnitude larger than for the "red" variety. This is attributed to a higher mobility of PDA holes in the former compound, resulting from the higher degree of backbone conjugation. The lifetime of the mobile carriers extends well into the microsecond region, which is considerably longer than previously found on direct ionization of PDA chains.

Introduction

Since the discovery of the topochemical polymerization of crystalline derivatives of diacetylene by Wegner,[1] polydiacetylenes (PDAs) have received an enormous amount of attention as potential materials for applications in photolithography, nonlinear optics, and molecular electronic devices. One of the barriers to their technological implementation, however, has proven to be the difficulty of large-scale production of PDA thin films. A considerable step forward was made with the synthesis of diacetylene derivatives which formed soluble polymeric materials on thermal or radiation treatment.[2−5] Polymer solutions could then be used to produce thin PDA layers by spin-coating,[6,7] drop-casting,[8,9] or Langmuir−Blodgett (LB) techniques.[10,11] A further advance has been the preparation of thin layers of monomeric diacetylenes by chemical vapor deposition,[12,13] LB techniques,[14,15] or, more recently, spin-coating.[16] These layers can be polymerized in situ either thermally or with ultraviolet light. This opens up the possibility of readily produced, large-area films that can be UV-patterned and incorporated into multilayer devices.

In this report we present results on spin-coated layers of the arylimido derivatives of diacetylene shown in Figure 1. These are found to be readily UV-polymerized to polydiacetylenes. The polymerized layers are furthermore shown to be photoconductive using the electrodeless, time-resolved microwave conductivity technique. The long-lived, mobile charge carriers responsible for the photoconductivity are formed via electron transfer between the triplet state of an arylimido moiety and neighboring PDA chains.

Experimental Section

The compounds studied in the present work are shown in Figure 1. Their method of synthesis and characterization and a preliminary indication of their ability to be photopolymerized have been reported in separate papers.[17] Films of the monomeric compounds were prepared by spin-coating solutions in chloroform on quartz substrates. The optical absorption of the films was measured using a Uvikon 940 (Kontron Instruments) UV/vis spectrophotometer. The wavelength dependence of the extinction coefficient, ϵ_i, for model phthalimido and naphthaldiimido compounds is shown in Figure 4. The values of ϵ_i at the wavelength maxima in the 200−250 nm region are 3.85 $\times 10^4$ (215 nm) and 3.27×10^4 M^{-1} cm^{-1} (240 nm), respectively. The extinction coefficient in the 230 nm region of the diacetylene reference compound with no arylimido group attached is only ca. 4×10^2 M^{-1} cm^{-1}. To estimate the amount of monomer present in the spin-coated layers and the layer thickness from the measured optical densities, we have made the assumption that the oscillator strengths of the imido absorptions in the 200−250 nm region are the same in the films as for the model compounds; in other words, we have corrected for the increased width of the absorptions in the solid state using the relationship

$$\epsilon_i(\text{film}) = \epsilon_i(\text{soltn})\ \Delta E(\text{soltn})/\Delta E(\text{film}) \qquad (1)$$

In eq 1 ΔE is the width at half-maximum in electronvolts of the absorption band as determined from a Gaussian fit. The resulting extinction coefficients (wavelength maxima) determined for SDA9, ADA93COOH, and NADA58 are 3.8×10^4

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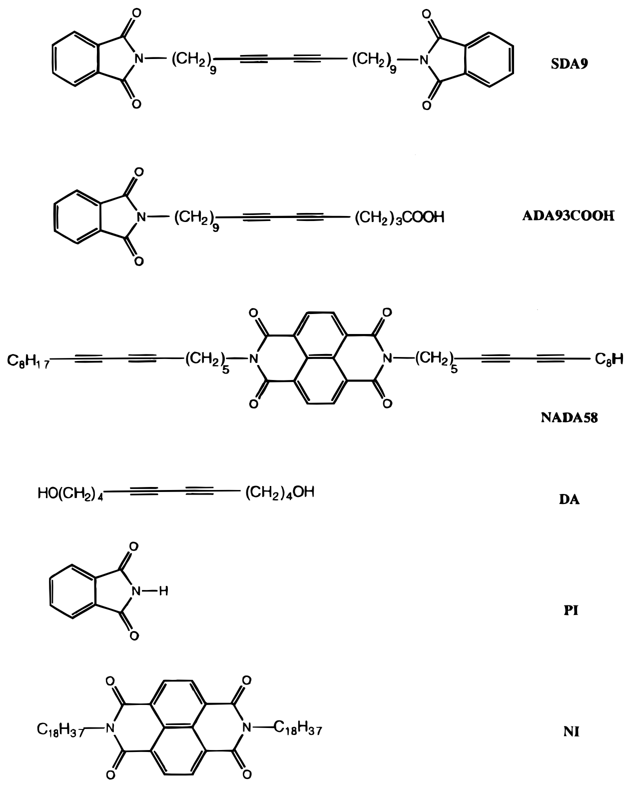

Figure 1. Molecular structures of the diacetylene derivatives studied in the present work together with the pseudonyms used in the text. Also shown are the arylimido and diacetylene reference compounds used for spectral characterization.

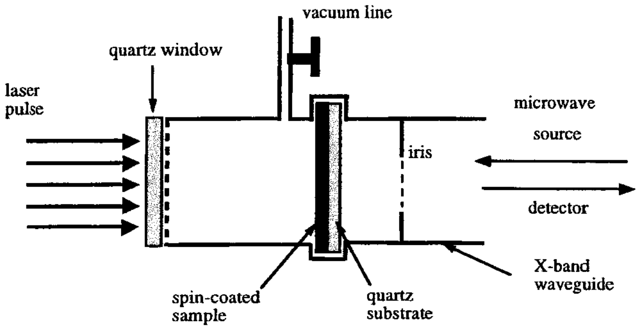

Figure 2. Schematic illustration of the microwave cell and sample configuration used in the flash photolysis TRMC measurements.

M^{-1} cm^{-1} (222 nm), 2.1 × 10^4 M^{-1} cm^{-1} (220 nm), and 2.5 × 10^4 M^{-1} cm^{-1} (244 nm), respectively. Using these values and a density of 1 g/cm^3, the thicknesses of the films corresponding to the data in parts A, B, and C of Figure 3 are estimated to be 390, 300, and 320 nm, respectively.

The optical absorption of the films was measured after exposure to a known number of 7 ns duration pulses of 308 nm light from a Lumonics HyperEX-400 laser. The intensity per pulse was measured accurately using a Scientech 365 power meter. For topological polymerization the laser intensitiy was attenuated using neutral density filters and varied between 0.1 and 2 mJ/cm^2. The range of accumulated dose studied was from 0.0001 to 1 J/cm^2.

The experimental arrangement for carrying out flash photolysis time-resolved microwave conductivity measurements (FP-TRMC) is shown in Figure 2. Prior to the measurements the air in the microwave cavity was evacuated and replaced with nitrogen. For generating charge carriers the samples were irradiated with single 7 ns, 308 nm pulses from the excimer laser or 3 ns, 544 nm photons from a Coumarin 153 dye laser which was pumped by the 308 nm line of the excimer laser.

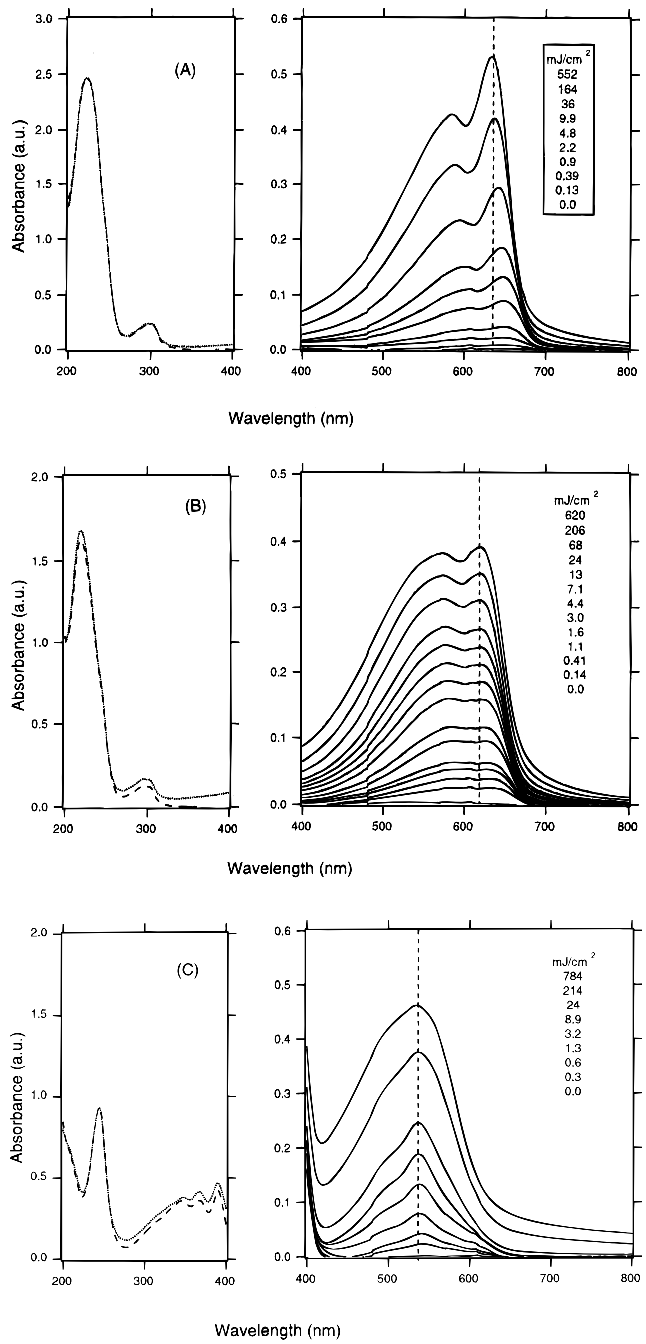

Figure 3. UV and visible absorption spectra as a function of the exposure to 308 nm radiation of a spin-coated layer of (A) SDA9, (B) ADA93COOH, and (C) NADA58. Below 400 nm only the absorptions for zero exposure (dashed line) and the maximum exposure (dotted line) are presented. A vertical dashed line is drawn through the absorption maximum in the visible region to illustrate the slight blue shift which occurs with increasing exposure.

Single-shot, FP-TRMC transients were measured at intervals after known accumulated doses of 308 nm irradiation within the same range as to those used in the optical absorption study. Details of the X-band microwave circuitry and detection equipment used have been reported previously.[18,19] The change in conductivity of the sample, $\Delta\sigma$, is monitored as a decrease in the fractional microwave power reflected by the cell, $\Delta P_R/P_R$.

$$\Delta P_R/P_R = -A\Delta\sigma \qquad (2)$$

The sensitivity factor, A, was calculated from the character-

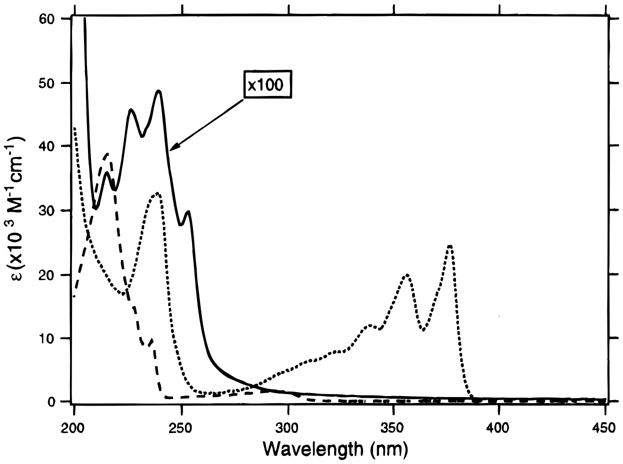

Figure 4. Wavelength dependence of the extinction coefficient of the reference compounds shown in Figure 1: DA (full line), PI (dashed line), and NI (dotted line).

istics of the microwave cavity used and the geometry of the sample. The overall time response of ca. 20 ns was determined mainly by the loaded quality factor of the cavity.[18]

Results and Discussion

Photoinduced Optical Absorption. Spin-coated films of all three of the arylimido–diacetylene compounds studied displayed a pronounced increase in optical absorption in the visible region on irradiation at 308 nm, as shown in Figure 3. The spectra are similar to those found previously on thermal or radiation-induced polymerization of other diacetylene derivatives,[15,16,20–27] indicating therefore that photoinduced polymerization has taken place in the present, spin-coated monomer layers.

For the two phthalimido derivatives the polymer absorption has a maximum at close to 630 nm, which is very similar to that attributed to an all-trans, coplanar polydiacetylene backbone.[24,28,29] The naphthalimido derivative, on the other hand, has a blue-shifted absorption with a maximum at 530 nm, indicating the formation in this case of a polymer with either a considerably smaller degree of conjugation or possibly, as suggested by some authors,[21] a polybutatriene structure of the polymer backbone. All of the visible spectra display a slight tendency to shift to the blue with increasing monomer conversion, as shown in Figure 3. This could be due to an initially higher yield of polymer in those regions of the sample in which the enyne units are more optimally geometrically juxtapositioned for polymerization to take place or to a buildup of strain within the matrix.

During the course of polymerization the absorptions below 400 nm change very little, as shown in Figure 3. This is as expected since the major contribution to the absorptions in this region arises from the arylimido moieties, as shown by the spectra for the reference compounds in Figure 4.

The fractional conversion of monomer diacetylene units to polymer, F_m, can be determined from the optical density of the polymer at its absorption maximum in the visible, OD_p, if the extinction coefficient per enyne unit, ϵ_p, is known using the following relationship.

$$F_m = OD_p\epsilon_i/OD_i\epsilon_p \tag{3}$$

In (3), OD_i and ϵ_i are the optical density of the monomer film and the calculated extinction coefficient of the arylimido moieties of the monomer at their wavelength maximum in the 200–250 nm region, as mentioned in the Experimental Section.

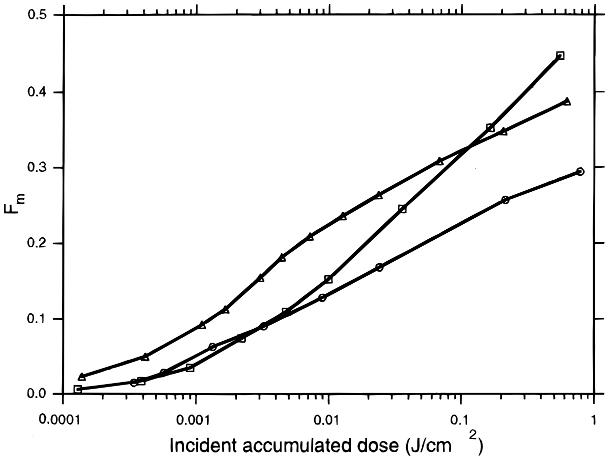

Figure 5. Dependence of the fraction of monomer units converted to polymer, F_m, on the accumulated incident radiation dose at 308 nm for SDA9 (squares), ADA93COOH (triangles), and NADA58 (circles).

The value of ϵ_p at the absorption maximum of the polymer was estimated by taking the value of 1.75×10^4 M^{-1} cm^{-1} per enyne unit previously determined for a polydiacetylene derivative[4] and assuming that the oscillator strength associated with the transition in the visible is the same for the present polymerized materials, i.e., using the relationship[30]

$$\epsilon_p \approx 1.75 \times 10^4 \times 0.59/\Delta E_p \tag{4}$$

The values of ΔE_p were determined from the visible spectra in Figure 3 from the upper and lower wavelengths at which the spectra were intersected by a horizontal line corresponding to half of the height of the maximum absorption. The value of ΔE_p tended to increase somewhat with increasing conversion, and the following values which were used are averages for low and high conversions: 0.57, 0.80, and 0.63 eV for SDA9, ADA93COOH, and NADA58, respectively, thus yielding ϵ_p values of 1.8×10^4, 1.3×10^4, and 1.6×10^4 M^{-1} cm^{-1}, respectively. Since NADA58 contains two diacetylene units, twice the value of ϵ_p was used to determine F_m for this compound.

The values of F_m determined as described above are plotted as a function of the accumulated incident radiation dose in Figure 5. As can be seen, conversion efficiencies close to 50% are attained. This demonstrates, perhaps surprisingly, that monomeric diacetylene units must be very well stacked even in these spin-coated samples.

The values of F_m determined from the optical absorption of the films were checked by carrying out solvent extraction of the residual DA monomer in the films with CH_3CN after an accumulated dose of 0.4 J/cm^2. By comparing the DA monomer optical absorptions of the solutions from irradiated films with those for identical, unirradiated films F_m values of 0.43, 0.33, and 0.25 for SDA9, ADA93COOH, and NADA58, respectively, were obtained. These values are considered to be in agreement with the values of 0.42, 0.37, and 0.27 obtained directly from the optical density of the films within the

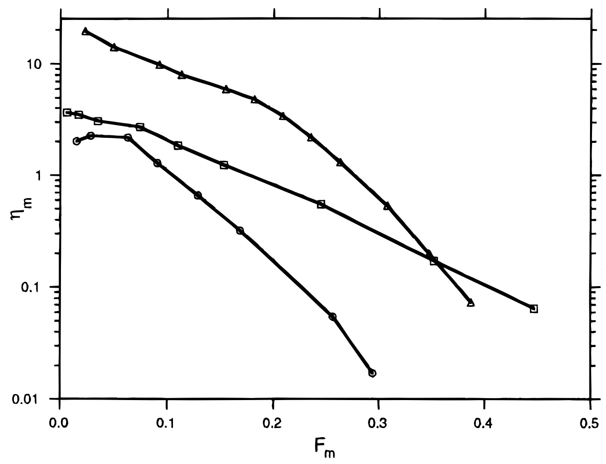

Figure 6. Quantum yield of monomer conversion based on the total number of photons absorbed at 308 nm as a function of monomer conversion for SDA9 (squares), ADA93COOH (triangles), and NADA58 (circles).

Table 1. Values of the Wavelength Maximum of the Polymer, λ_{max}, the Maximum Monomer Conversion Measured, F_m(max), the "Low-Dose" Quantum Yield for Monomer Conversion Based on the Total Number of 308 nm Photons Absorbed, η_m(tot), or Based on the Number of Photons Directly Absorbed by the Dienyne Moiety, η_m (DA), and the Maximum Value of the Product of the Quantum Yield and Mobility of Charge Carriers Formed, $\eta_c\mu$ (max)

monomer	λ_{max}[a] (nm)	F_m(max) (%)	η_m (tot)[b]	η_m (DA)	$\eta_c\mu$ (max) (10^{-3} cm^2/(V s))
SDA9	635	45	3.6	672	5.7
ADA93COOH	620	39	20	2521	14.1
NADA58	535	30	2.2	390	0.84

[a] Corresponding to the dashed vertical lines in Figure 3. [b] From extrapolation to zero of the low-dose data in Figure 6.

combined errors of the two methods of preparation and measurement.

The quantum yield for monomer conversion, η_m(tot), has been calculated on the basis of the total number of photons absorbed at the polymerization wavelength of 308 nm. These values are plotted as a function of the monomer conversion in Figure 6. The "initial" values obtained by extrapolation to zero dose are 3.6, 20, and 2.2 for SDA9, ADA93COOH, and NADA58, respectively. These values may be compared with the parameter *nq* given by Bässler[31] with *n* the number of monomer units that react per initiation event and *q* the probability that photoexcitation will lead to chain initiation. For crystalline samples of the bis(*p*-toluenesulfonate) and uracil derivatives of diacetylene, PTS and 4-BCMU, values of *nq* for irradiation at 308 nm of 0.15 and ca. 100 have been determined, respectively.[31] The present values are seen to fall within this range. This is of particular interest since (a) the present samples are not single crystals and (b) most of the photons at 308 nm are initially absorbed by the arylimido moieties which have extinction coefficients at 308 nm that are 2 orders of magnitude larger than that of the diacetylene moiety.

If no energy transfer occurs from the arylimido moieties to the diacetylene and polymerization is thus only initiated by those photons absorbed directly by the diacetylene moieties, then values of η_m(DA) ranging from 400 to 2500 are calculated (see Table 1). These values correspond to the maximum chain lengths determined for single crystals, and it is therefore likely that at least a fraction of the excitation energy initially absorbed by the arylimido groups is transferred to the diacetylene groups which leads to initiation of polymerization.

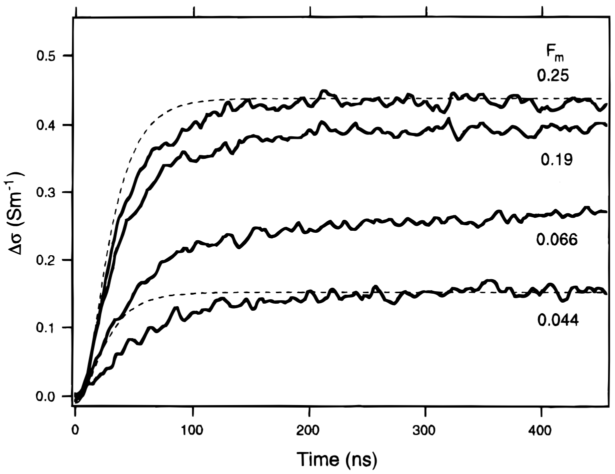

Figure 7. Transient change in conductivity measured by TRMC resulting from flash photolysis of ADA93COOH with a 7 ns, 308 nm, 0.14 mJ/cm^2 pulse for different monomer conversions. The dashed lines are calculated curves of the laser pulse convoluted with the response time of the detection equipment.

The quantum yield for monomer conversion is seen in Figure 6 to decrease with increasing conversion. This is to be expected and can be attributed to a combination of factors, i.e., the decreasing amount of monomer present, competitive absorption by the growing polymer of 308 nm photons, an increasingly less favorable orientation of the diacetylene moieties, and energy transfer to the polymer. The SDA9 compound is seen to be less sensitive to the negative effects of increasing conversion than the other two compounds. This can be explained by the smaller absorption of the SDA9 polymer at 308 nm, as can be seen in Figure 3. Because of this, less of the incident UV light is absorbed preferentially by the polymer in competition with the monomer as the polymer yield increases. The photoinitiation process, which is dependent on light being absorbed by the monomer, can therefore proceed efficiently up to higher conversions for SDA9.

Photoinduced Conductivity. The conductivity of the samples resulting on flash photolysis was measured by time-resolved microwave conductivity (TRMC) as shown in Figure 2 using single laser pulses of 308 or 544 nm after different accumulated doses. For all three compounds conductivity transients were observed on flash photolysis at 308 nm which increased in magnitude with increasing monomer conversion. Examples are shown for ADA93COOH and NADA58 in Figures 7 and 8, respectively. No photoconductivity transients could be detected on flash photolysis of high-monomer-conversion samples of SDA9 or ADA93COOH at 544 nm. A photoconductivity transient was, however, observed using this wavelength for a polymerized layer of NADA58, as shown in the inset to Figure 8.

In the present TRMC measurements only the change in the real (dielectric loss) component of the microwave conductivity of the sample is measured. This reflects the formation of mobile charges which could be either freely diffusing, separated charges with a mobility sum $\sum\mu$ or dipoles with a rotational mobility M.[18] For dipoles the

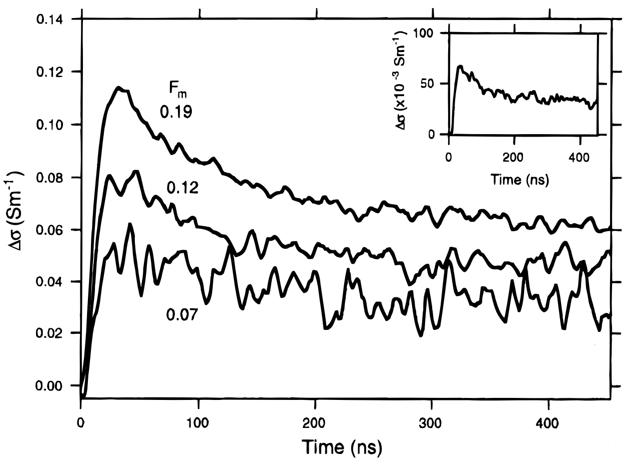

Figure 8. Transient change in conductivity measured by TRMC resulting from flash photolysis of NADA58 with a 7 ns, 308 nm, ca. 0.4 mJ/cm^2 pulse. Inset: the conductivity transient observed on flash photolysis at 544 nm for a monomer conversion of ca. 20% and a 3 ns, 0.5 mJ/cm^2 pulse.

maximum value of M is given by

$$M_{\max} = (\epsilon' + 2)^2 \mathbf{p}^2/[27ek_BT\,\tau_r] \qquad (5)$$

with ϵ' the dielectric constant of the medium, $\mathbf{p}$ the dipole moment of the dipolar species, e the elementary charge, k_B the Boltzmann constant, T the temperature, and τ_r the dipole relaxation time. For a dipole moment as high as 10 D and a relaxation time of 100 ps, which is short for a rigid, solid sample, we derive a value of $M_{\max}$ of 1×10^{-4} cm^2/(V s). This is approximately 2 orders of magnitude less than the value of the quantum yield times mobility product determined as described in a later section. Because of this we conclude that separated mobile charge carriers are responsible for the conductivity transients observed.

The transients for the phthalimido compounds differ from those for the naphthaldiimido derivative in that they are substantially larger for a given pulse intensity and accumulated dose and they decay much more slowly. In addition, the transients for SDA9 and ADA93COOH display an after-pulse growth at low conversions over a period of approximately 100 ns with the growth becoming increasingly rapid with increasing monomer conversion, as shown in Figure 7. A further significant difference between the phthalimido and naphthaldiimido compounds is the observation of a photoconductivity transient even on irradiation at 544 nm for the latter compound as mentioned above.

Photoconductivity in polydiacetylenes has been previously shown to occur on irradiation in the ultraviolet with an onset approximately 1 eV above the visible absorption band.[32,33] Direct photoionization of the PDA chains could therefore explain at least part of the conductivity observed in the present work on irradiation at 308 nm. We believe, however, that direct PDA ionization is not the major source of the photoconductivity observed for the following reasons: (i) direct photoionization of PDA chains would result in a prompt conductivity transient and cannot therefore explain the delayed growth found for SDA9 and ADA93COOH at low conversions, (ii) large photoconductivity transients are found even for low monomer conversions where the vast majority of 308 nm photons are absorbed preferentially by the arylimido moieties, and (iii) the charge carrier lifetimes are considerably longer then found for PDAs without electron-accepting moieties.

We propose the following explanation of the results: Flash photolysis at 308 nm results in photoexcitation of the arylimido moieties which is followed by rapid intersystem crossing to form the long-lived triplet state.[34,35] The triplet state subsequently undergoes long-distance electron transfer with polydiacetylene chains to form the arylimido radical anion and the PDA radical cation or “hole”. The latter species is then responsible for the photoconductivity observed.

Long-distance electron transfer between a donor molecule and the triplet state of an arylimido moiety has been previously observed in molecules consisting of a carbazole or methoxyaniline donor entity separated from an arylimido group by a saturated hydrocarbon bridge.[36,37] For the longest hydrocarbon bridge studied, consisting of seven methylene groups, electron transfer was found to occur in 200 ps.[36,38]

The time scale for long-distance electron transfer through alkane bridges has been found to be exponentially dependent on the length of the bridging unit, R, according to

$$\tau = \tau_0 \exp(-\beta R) \qquad (6)$$

with an approximate value of 0.9 Å^{-1} for β.[39] Taking the time of 200 ps given above for the 8 Å long heptamethylene bridge compound, we can estimate τ_0 to be 1.5×10^{-13} s for long-distance electron-transfer involving the triplet state of an arylimido moiety and a donor entity.

For the present phthalimido compounds the shortest distance from an arylimido group to a dienyne unit is equal to the length of the nine carbon atom long chain separating the two, i.e., ca. 10 Å. Using (6) the estimated time scale for electron transfer over this distance is estimated to be ca. 2 ns, which is shorter than the 7 ns laser pulse and the 20 ns response time of the microwave cavity. The formation of mobile charge carriers at high conversions would therefore be expected to result in a conductivity transient that follows fairly closely the integrated pulse form convoluted with the time response. This behavior is shown by the dashed lines in Figure 7. For the highest conversion shown the agreement between the form of the calculated line and the experimental conductivity transient is seen to be reasonably good although a slight delay of the conductivity does appear to be operative. For only 4% conversion a more significant delay, over the first few hundred nanoseconds after the laser flash, is apparent. Under low conversion conditions the probability that the dienyne unit adjacent to a photoexcited arylimido moiety is incorporated in a PDA chain is correspondingly low. The delayed growth of the conductivity can then be explained by the occurrence of either long-distance electron transfer between more distant arylimido and copolymerized dienyne units or by triplet migration within the stacked arylimido moieties to a position for which the adjacent dienyne unit is incorporated into a PDA backbone.

The lack of a slow growth, even at low conversions, in the case of the naphthaldiimido compound can be explained by the much shorter alkyl chains separating the arylimido moiety from the diacetylene group, i.e., five carbon atoms instead of nine. This would also explain the more rapid decay of the conductivity transient for NADA58 since charge recombination between

PDA$^+$ and the naphthaldiimido radical anion should also be much faster.

The relatively long decay times of the conductivity transients found for the present compounds provide further evidence for the long-distance, triplet-sensitized electron-transfer model proposed since the lifetimes found for conductivity transients produced by direct PDA ionization on flash photolysis[40−42] or pulse radiolysis[43,44] are only a few tens of nanoseconds. The faster decay in the case of direct PDA ionization can be ascribed to rapid intrachain charge recombination between electrons and holes. The alkyl chains in the present compounds therefore likely play an important role, not just in controlling the molecular stacking, but also by acting as an insulating layer which increases the lifetime of mobile charge carriers once formed.

The observation of a photoconductivity transient on irradiation of polymerized NADA58 even at 544 nm is not readily explained by the triplet sensitization mechanism. Thus, while the absorption spectrum of the naphthaldiimido moiety is substantially red-shifted compared with that of the phthalimido moiety, its absorption in the 544 nm region is still negligible (see Figure 4). We suggest that electron transfer can occur from an excited singlet PDA chain to the naphthaldiimido moiety. An alternative explanation is that the higher electron affinity of NADA58 and its greater proximity to the PDA chains results in the possibility of a direct optical transition to a charge transfer state; i.e., there exists a charge-transfer absorption band underlying the polymer absorption in the visible, as has been suggested previously.[9]

The sensitized photoconductivity of polydiacetylene has been observed previously for a derivative containing the carbazole moiety.[13,45,46] In thoses cases the conductivity was attributed to electron transfer involving the excited singlet state of the carbazole to the PDA chain, and singlet energy transfer for this compound has been found to be very rapid.[47] Since carbazole derivatives are also known to undergo efficient intersystem crossing to the triplet state, it is possible that the triplet-sensitized electron-transfer mechanism proposed for the present compounds is also operative in the carbazole case. A singlet-state sensitization mechanism can be ruled out in the present case since the lifetime of the singlet state of the arylimido derivatives is expected to be only a few nanoseconds at most.[36,37] This mechanism could therefore not explain the slow growth of the conductivity signal at low conversions.

A value for the product of the quantum yield for charge carrier formation, η_c, and the charge carrier mobility, μ, can be determined from the absolute value of the photoinduced conductivity using the relationship

$$\Delta\sigma = e\eta_c \mu I_0(1 - 10^{-\mathrm{OD}})/L \qquad (7)$$

where e is the elementary charge, I_0 is the incident photon flux, OD is the optical density of the layer, and L is its thickness. The values of $\eta_c \mu$ derived from the maximum conductivities found after 308 nm flash photolysis are plotted as a function of the monomer conversion in Figure 9. As can be seen, $\eta_c \mu$ increases toward a plateau value for conversions in excess of approximately 15%. We conclude that this conversion is sufficient to ensure that all arylimido triplet states formed are capable of undergoing electron transfer with polymer chains within their lifetime. The maximum values of $\eta_c \mu$ obtained are given in Table 1.

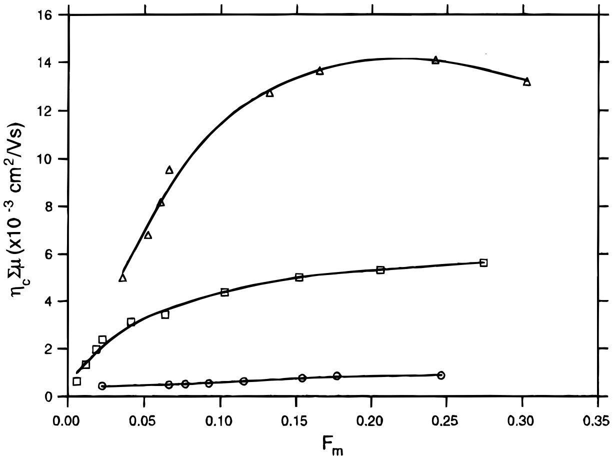

Figure 9. Product of the quantum yield for charge carrier formation on flash photolysis at 308 nm, η_c, and the charge carrier mobility, μ, as a function of the monomer conversion for SDA9 (squares), ADA93COOH (triangles), and NADA58 (circles).

The maximum value of $\eta_c \mu$ obtained is 1.4×10^{-2} cm^2/(V s) for the ADA93COOH compound. Since the majority of 308 nm photons are absorbed initially by arylimido moieties, the maximum value of η_c resulting from the triplet-sensitization mechanism proposed will be equal to the quantum yield for intersystem crossing for which values in the range 0.1−0.5 have been estimated.[36] A lower limit estimate of the mobility of ca. 3×10^{-2} cm^2/(V s) can therefore be made from the above value of $\eta_c \mu$. While this is quite large, it is still considerably less than the mobility values of 3−5 cm^2/(V s) found for charge transport along the direction of the PDA chains in polymerized single crystals.[41,42,48,49] However, according to Spannring[49] and Fischer, [50] these reported mobility values are for electrons, whereas in our films the mobile charge carriers are holes. We have been unable to find literature references for hole mobility measurements in PDAs.

We emphasize that mobilities determined using the TRMC method are microscopic values which correspond to that for charge carriers only within the polymerized regions of the film. The low maximum field strength of ca. 100 V/cm and the ultrahigh frequency (ca. 10 GHz) result in only a small pertubation of the otherwise diffusive motion of the carriers. The charge carriers are thus not transported over macroscopic distances as in DC experiments using electrodes. In addition, the short time scale of the observations ensures that effects due to charge carrier localization at impurities or domain boundaries are minimized.

The actual hole mobility could be much higher than the lower limit given above if the intersystem crossing efficiency is in fact less than 0.5 or the efficiency of triplet-state electron transfer is less than unity. A further possible reason for a low measured mobility could be the known high anisotropy of charge transport in PDAs with the mobility in the direction of the polymer backbones being orders of magnitude higher than the mobility perpendicular to the polymer chains.[42−44,51] A lower mobility would therefore be found if the polymer chains in the present materials are preferentially aligned perpendicular to the surface of the quartz substrate since the electric field vector of the microwaves is parallel to the surface. Further structural analysis of the present films should help to clarify this point.

The value of $\eta_c\mu$ for the naphthaldiimido compound is approximately an order of magnitude lower than for the phthalimido derivatives. This is most probably due to a lower charge carrier mobility resulting from a less well-conjugated backbone structure, as evidenced by the blue-shifted absorption spectrum of the NADA58 polymer.

Conclusions

Spin-coated layers of phthalimido derivatives of diacetylene can be photopolymerized using 308 nm pulses from an excimer laser to form *all-trans*-polydiacetylene (absorption maximum ca. 630 nm) with monomer conversions as high as 50%. A naphthaldiimido derivative forms a polymer that absorbs at shorter wavelengths (maximum 530 nm). The low-dose, limiting quantum yields for monomer conversion vary from 2 to 20 on the basis of the total number of photons absorbed at 308 nm.

Large photoconductivity transients are found for the polymerized layers with a quantum yield times mobility product of charge carriers, $\eta_c\mu$, as high as 1.4×10^{-2} $cm^2/(V\ s)$. The photoconductivity is attributed to polydiacetylene holes formed by electron transfer to the triplet state of the arylimido moieties. The value of $\eta_c\mu$ for the "red" polymer formed from NADA58 is an order of magnitude lower than for the "blue" polymers formed from SDA9 and ADA93COOH. A conductivity transient observed on irradiation at 544 nm for the polymerized naphthaldiimido derivative but not for the phthalimido compounds is attributed to either electron transfer involving the S_1 state of PDA or the presence of a PDA-naphthaldiimide charge-transfer band in the visible.

A particularly important aspect of the present data is the long lifetimes of the mobile charge carriers, which extend well into the microsecond time regime. The long lifetimes are attributed to the alkane chains which act as an insulating barrier separating the arylimido radical anions from the holes on the polymer backbone.

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