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Topochemical Polymerization of Naphthalenediimide-Substituted Diacetylene Suspensions

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Over the past decade, many reports have appeared on the polymerization of functionalized diacetylenes (DAs), not in the last place in view of potential application of polydiacetylenes (PDAs) in optoelectronics and photovoltaic solar cells.[1] Because of the geometric restrictions under which this topochemical polymerization can take place, the polymerization of DAs has been investigated in a variety of media: (single) crystals,[2−5] liquid crystals[6,7] and thin films,[8−11] gels,[12−15] Langmuir−Blodgett films,[16−20] self-assembled mono/multilayers,[21−23] and bilayers/vesicles.[24−26] Surface polymerization reactions from diacetylene monomer solutions onto transparent substrates have also been reported.[27]

In this communication we report the solution-phase polymerization of aggregates of naphthalenediimide-substituted diacetylenes (compounds under study in Figure 1).[28] Our studies indicate that the mechanism of formation of this polymer may involve radical cations as the primary species, formed by photoinduced electron transfer from a DA donor to a photoexcited, covalently linked naphthalenediimide electron acceptor. This proposed mechanism is different from the commonly proposed biradical mechanism for UV-induced DA polymerizations[1,29,30] and to our knowledge would be the first case in which the PDA formation is electron-transfer-initiated.

The solution-phase polymerization was observed for naphthalenediimide-substituted DAs with general structure $C_8H_{17}-C\equiv C-C\equiv C-(CH_2)_n-\mathrm{Naphth}-(CH_2)_n-C\equiv C-C\equiv C-C_8H_{17}$ (compound symbol: ***n*−8**; see Figure 1). Homogeneous solutions (~0.03 M) of ***n*−8** were prepared in chloroform. These stock solutions were then diluted in hexane (0.5% v/v) resulting in semistable dispersions, indicating formation of large aggregates similar to those obtained via the "reprecipitation" method by Nakanishi and co-workers.[31] Before and after light-induced polymerization the characterization of these solutions was performed by UV−vis absorption spectroscopy, as this reveals the characteristic absorption bands on PDA formation.[1] Typical absorption spectra of a monomeric solution of **5−8** in chloroform and of aggregates of **5−8** in hexane are shown in Figure 2. For comparison, the transmission spectrum of a spin-coated film of **5−8** on quartz, which was studied previously in our laboratories,[11] is also shown.

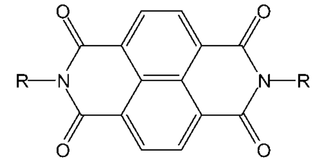

Figure 1. Compounds under study: ***n*−8** ($R = -(CH_2)_n-C\equiv C-C\equiv C-(CH_2)_7-CH_3$; $n = 4, 5, 7, 9$) and reference compound ***NA*−18** ($R = C_{18}H_{37}$).

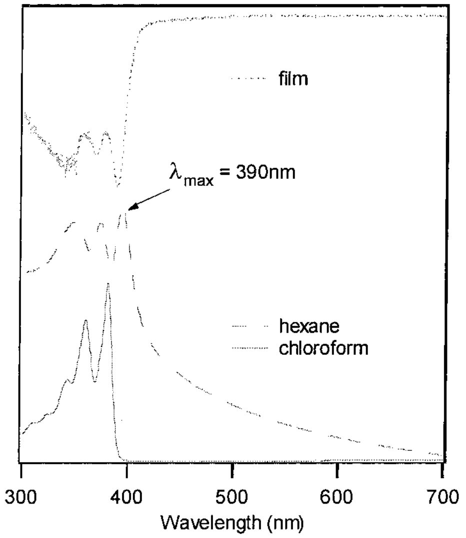

Figure 2. Optical spectra of **5−8** in chloroform and in hexane (in absorbance) and of a spin-coated film on quartz (in transmission).

Spectra of a bis-$C_{18}H_{37}$-substituted naphthalenediimide (reference compound ***NA*−18**) and of the other ***n*−8** derivatives, in both monomeric and aggregated state, are nearly identical to the corresponding spectra of **5−8** and are therefore not shown here. In the spectra of aggregates of ***n*−8** in hexane a characteristic absorption band with $\lambda_{max} = 390$ nm was observed, which is red-shifted by ~10 nm with respect to the lowest energy absorption of the monomer in chloroform. This well-resolved, red-shifted band strongly suggests the presence of ordering. According to point-dipole exciton models such as suggested by Kasha,[32] the observed red shift can be explained by parallel stacking of the aromatic naphthalenediimide rings, shifted in the aromatic plane with respect to each other, resulting in a predominant head-to-tail orientation of the transition dipole moments. Such an orientation has also been found for perylenediimide compounds[33] and is the result of the balance between attractive $\pi-\pi$ interactions between the aryl moieties and partially repulsive dipolar interactions between diimides moieties in the stack. Also, for spin-coated films of these ***n*−8** compounds an absorption band with $\lambda_{max} = 390$ nm is observed, i.e., at the same position as observed for the aggregates.

Ordering of ***n*−8** molecules is a necessity to meet the geometric requirements of topochemical polymerization. Such ordering can be achieved in single crystals and in ordered media (e.g., Langmuir−Blodgett films), but—as shown here—also via aggregation in solution. For ***n*** ≥ **5** polymerization of the aggregates of ***n*−8** derivatives

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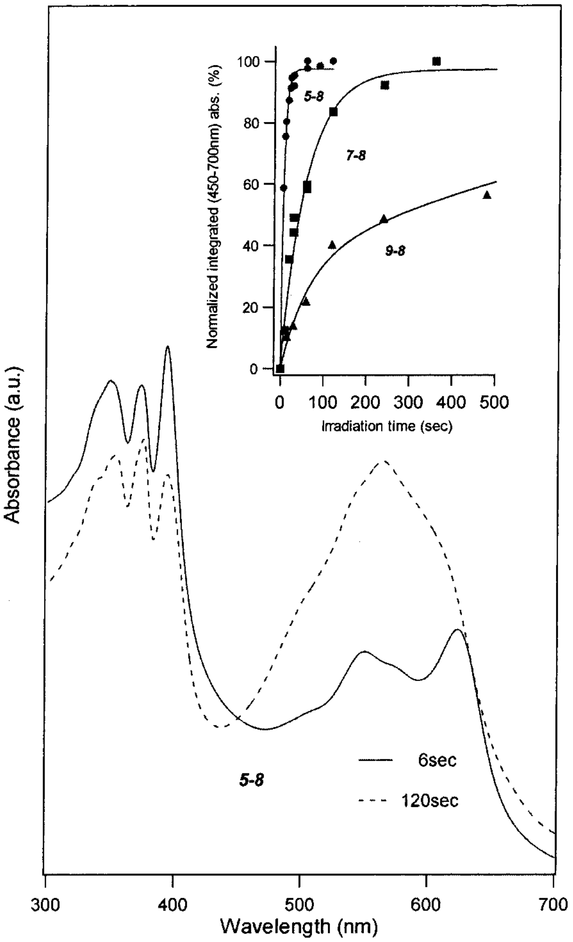

Figure 3. Absorption spectrum of aggregates of **5**−**8** in hexane at different irradiation times. The inset shows integrated intensities of the absorption spectra (450−700 nm) of the compounds **5**−**8**, **7**−**8**, and **9**−**8** plotted vs irradiation time, normalized to 100%.

takes place upon irradiation with UV light (254 nm; results not shown here), but remarkably also upon selective excitation in the low-energy absorption band (390 nm) of the naphthalenediimide moiety. At this wavelength the DA moiety does not absorb light. For aggregates of **4**−**8**, which has a relatively short spacer between both functional groups, the conformational freedom of the DA functions is probably limited to such an extent that they cannot get into the geometry required for 1,4-polymerization.[10] Extension of the spacer length overcomes this limitation.[34] Polymerization of the other compounds upon irradiation with 390 nm is visible to the eye by a rapid change of the color of the suspension to blue. Because of this polymerization, characteristic absorption bands in the region between 450 and 700 nm were observed in the absorption spectra of aggregates of ***n***−**8** ($n \geq 5$) in hexane. This has also been observed for a set of related compounds in thin films.[11,35] As an example, the absorption spectrum of aggregates of **5**−**8** in hexane is shown after 6 s and after 2 min of irradiation with 390 nm (see Figure 3).

The fact that polymerization for $n \geq 5$ proceeds well not only with UV light, but also with "monochromatic" light of 390 nm, suggests that a new mechanism lies behind this reaction, in which the DA moiety is not involved in the initiating step. Upon excitation with 390 nm light, the naphthalenediimide moiety becomes an even better electron acceptor, and sufficient driving force becomes available for electron transfer from a ground-state DA monomer to a nearby photoexcited naphthalenediimide molecule. The thus-formed DA radical cation may react with its DA neighbor, eventually resulting in PDA formation. The details of this mechanistic conjecture are currently under investigation.

By plotting the visible absorption of the ***n***−**8** suspensions, which is proportional to the PDA concentration, vs irradiation time, differences in relative reaction rates can be visualized.[19] To account for the gradual shift in the absorption maximum to shorter wavelengths ("blue" PDA → "purple" PDA) that is characteristic for this class of polymers,[1,10] the integrated absorption spectra (450−700 nm) were used (see inset in Figure 3). Considering an overall rate constant, k, of the consecutive first-order polymerization reactions monomer → blue PDA → purple PDA, we were able to fit the experimental data for **5**−**8** and **7**−**8** to the equation $A_t = A_{\mathrm{inf}}(1 - \mathrm{e}^{-kt})$.[19] Here A_t and A_{inf} represent the integrated absorbance values at times t and the time when it reaches a maximum intensity, respectively. For **9**−**8** a biexponential equation was needed to fit the data, probably because of (relatively slow) simultaneous adsorption to the quartz windows of the cuvette, which was noticed to affect the measured absorbance. Because quantification of the reaction rates is beyond the scope of this communication, we only show the fits in Figure 3 for illustrative reasons.

The difference in time behavior clearly results from differences in the length of the spacer (given by "***n***") in the monomer and thus on the conformational freedom of the DA functions. In relation to this, the blue shift of the absorption band of aggregates of **5**−**8** upon longer irradiation times may be explained by a decrease in PDA backbone conjugation.[36] Such a decrease likely results from strain induced by attractive $\pi-\pi$ interactions between naphthalenediimide moieties that have to find a new optimal $\pi-\pi$ stacking for themselves in the polymer.

Monomer conversion after **5**−**8** polymerization was determined by isolating the blue solid material from the mixture in hexane by centrifugation; the remaining clear hexane solution contained <1% of the original amount of monomer and no traces of polymer. The concentration of monomer that was coprecipitated was determined spectroscopically after mixing the solid with chloroform, in which the monomer redissolves while the polymer does not. In this way a monomer conversion of at least 80% was estimated for **5**−**8**, which is much better than the ~25% for the spin-coated films reported earlier.[11]

To conclude whether irradiation of the suspensions really results in polymer formation or in formation of oligomeric species having optical properties that are similar to polymers,[37] dynamic light scattering (DLS) measurements were performed on the polymer fractions obtained after repeated centrifugation.

Samples of poly**5**−**8** and poly**9**−**8** in chloroform (red phase), toluene (red phase), and hexane (blue phase) were characterized by means of DLS using an ALV light-scattering apparatus and an Ar ion laser (514.5 nm).[38] Diffusion coefficients for scattering angle 90° (average of 10 measurements) are presented in Table 1. For different scattering angles slightly different diffusion coefficients (not included in Table 1) were observed, which suggests that the samples were heterogeneously dispersed or that the particles are not

Table 1. Diffusion Coefficients Measured by DLS and Particle Radii Calculated Using the Stokes−Einstein Relation for Spherelike Particles

polymer	solvent	diff coeff (cm^2/s)	particle radius (nm)
pNADA58	hexane	2.04×10^{-8}	325
	chloroform	1.78×10^{-8}	210
	toluene	1.49×10^{-8}	246
pNADA98	chloroform	17.16×10^{-8}	22

spherical.[39] Nevertheless, calculated particle radii were obtained using the Stokes−Einstein relation that assumes spherelike particles, to get an estimate of the order of magnitude of the particle sizes (see Table 1). The thus-derived magnitudes evidently show the formation of substantial polymers rather than oligomer formation. The size of several hundred nanometers does not result from aggregation of nanocrystalline polymer particles to larger aggregates, as it is observed for both polar and apolar solvents. In addition, measurements at elevated temperatures (up to 50 °C) do not reveal any temperature dependence of the particle size, as would have been expected for such aggregation. The PDAs resulting from this suspension reaction are therefore true polymers and provide an interesting comparison with both “solid-state PDAs” and oligomeric analogues.

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