Design and Synthesis of Extended π-Systems: Monomers, Oligomers, Polymers

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Received 6 September 1991; revised 12 September 1991

The synthesis of unconventional extended π-systems is described in an attempt to tailor the structures of organic compounds for specific optical and electrical properties. In order to emphasize the role of the π-conjugation and to correlate chemical structure and physical function both one-dimensional arylenes and two-dimensional ribbon-type molecules are considered. In the synthesis of the former the arylnaphthalenes coupling according to Heck is of special value, the synthetic of the latter is achieved by repetitive Diels–Alder cycloadditions and by two-step processes in which carefully designed polyaryl precursors are subjected to ring closure. Key ingredients of the present approach are the interplay of synthetic organic chemistry and synthetic macromolecular chemistry and the needs outlined by materials science. Thereby, transition from monomers to oligomers and polymers defines new requirements for the selectivity of the synthetic reactions and the tractability of the products.

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1. Introduction

The search for novel electrophores and chromophores is of fundamental and practical interest. Particularly important features of electro- or photoactive materials are:

1. a small HOMO/LUMO energy difference which brings about attractive optical, electrical and photoelectrical behavior;
2. high hyperpolarizabilities and, thus, the creation of nonlinear optical effects; and
3. fast chemical processes which allow for the rapid change of these properties.

Thus, a key ingredient and a major challenge for organic synthesis is the active physical function of organic materials. To be able to tailor organic compounds for a specific physical behavior requires a detailed correlation of structure and properties.

When focusing on the materials aspect of organic compounds, however, a correlation of structure and physical properties cannot be restricted to the single molecules, but must also include supramolecular effects such as the solid-state structure and morphology.

Interest in macroscopically detectable and usable chromophoric and electrophoric properties of organic materials defines certain requirements for a rational synthesis. One approach comprises the creation of single molecules possessing extended π-conjugation with attractive electronic properties and the subsequent control of the supramolecular architecture. The other approach is based on the formation of extended π-conjugation via the regular linking of unsaturated building blocks. The latter "macromolecular" route can be pursued in two ways: On the one hand, one can synthesize oligomeric model compounds by making use of well-known coupling reactions of organic chemistry. This stepwise approach, at a first glance, appears as a straightforward extension of methods and principles which are common to low molecular weight species of organic chemistry. Transition to larger molecular entities, however, can create severe problems, e.g., with purification and structural elucidation.

The other possibility of synthesizing macromolecules with extended π-conjugation can make use of typical polymer forming reactions. In this case, one arrives at (polydisperse) mixtures of products with different molecular weights, and a separation into monodisperse oligomers is in most cases only possible for the lower homologues.

While polymerization reactions starting from unsaturated monomeric building blocks have only limited importance (a typical example is the synthesis of polyacetylene and poly(phenylenevinylene)), condensation reactions under formation of extended π-conjugation play the most important role. Several important requirements must be met, however, for a polycondensation to be suitable for the formation of conjugated polymers. The reaction must be highly selective, because any side reaction produces a structural defect of the macromolecule and cannot be "corrected" by the removal of a side product. The structural homogeneity required for the product comprises not only the constitution, but also the configuration and conformation of the
macromolecule since even subtle structural changes are known to bring about important consequences for the macroscopic physical properties.\textsuperscript{4}

A further requirement, which must be given by the applied polymer forming reaction, is a high degree of conversion since this is crucial to attain high molecular weights of the products.\textsuperscript{5}

Attempts to correlate structure and physical behavior of macromolecules meet with problems which are uncommon to the study of low molecular weight products.

First of all, one must be aware that the resulting data are always characteristic for a polydisperse mixture of different chain lengths. Closely connected with this polydispersity is the fact that many spectroscopic methods such as NMR or ESR techniques become less significant due to the occurrence of signal broadening and signal overlap. Furthermore, macromolecules differ from small molecules both in their solution properties (e.g., high viscosity, diffusion behavior) and in their solid-state properties (e.g., amorphpous or semicrystalline structures). Therefore, the physical properties of polymers often depend strongly upon the preparation procedure (orientation, annealing) of the samples investigated.

In view of these shortcomings it is generally helpful to synthesize and characterize homologous series of soluble, structurally defined monodisperse oligomers as model compounds. This approach, in addition to producing attractive molecules with extended $\pi$-conjugation, allows one to carefully follow molecular properties as a function of chain length and to extrapolate the resulting properties toward the polymer. One can therefore gain information on conjugated polymers which is not available from a study of the polymer itself.\textsuperscript{6,7} Herein, we describe synthetic methods which, starting from suitably functionalized monomers, allow the creation of oligomeric and polymeric $\pi$-systems with extended conjugation.

It will become evident that: (1) organic synthesis, if directed toward physical properties, is as challenging as, for example, natural products synthesis; (2) physical properties of the final supramolecular state can to some extent be anticipated on a molecular basis; (3) transition from smaller to larger molecules defines a completely new set of requirements for the synthetic approach.

The structure types we have chosen to investigate most fully are:

1. Oligo- and poly(arylenevinylene)s with linear $\pi$-systems;
2. Double-stranded (ribbon-type) structures with two-dimensional $\pi$-systems.

While transition from mono- to two-dimensional $\pi$-systems is rewarding from an electronic point of view, the synthesis of ribbon-type structures appears to require a higher level of subtlety.

2. Oligo- and Poly(arylenevinylene)s

Poly(arylenevinylene), especially poly(1,4-phenylenevinylene) (4, PPV), have been extensively investigated over the last few years. However, publications concerning synthetic and structural aspects are few.\textsuperscript{2,8–16} This is a serious shortcoming since the particular synthetic method selected for the formation of conjugated polymers (e.g., PPV\textsuperscript{10,12} or polyacetylene\textsuperscript{17}) drastically affects the mi-

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**Biographical Sketches**

**Klaus Müllen** obtained a Diplom-Chemiker degree at the University of Cologne in 1969 after work with Professor E. Vogel. His PhD degree was granted by the University of Basel, Switzerland, in 1971 where he undertook research with Professor F. Gerson. In 1972 he joined the group of Professor J. F. M. Oth at the Swiss Federal Institute of Technology in Zürich where he worked in the field of dynamic NMR spectroscopy and electrochemistry. He received his Habilitation from the ETH Zürich in 1977 and was appointed Privatdozent. In 1979 he became Professor in the Department of Organic Chemistry, University of Cologne, and accepted a call to the University of Mainz in 1983 where he held a chair in Organic Chemistry. In 1989 he joined the Max-Planck-Society as one of the directors of the Max-Planck-Institute for Polymer Research. His current research interests focus on synthetic macromolecular chemistry, synthetic organic chemistry and physical organic chemistry.

**Ulrich Scherf** studied chemistry at the Friedrich Schiller Universität in Jena gaining his Diplom working with Prof. Dr. H. H. Hörhold in 1983. In 1988 he finished his Ph.D. thesis on polymer analogous reactions together with structuring and carbonization experiments on polyarylenevinylenes at the Institute of Organic Chemistry at the FSU Jena (Prof. Hörhold). After working at the Institute of Animal Physiology of the FSU Jena (Prof. Penzlin) for one year, he joined the MPI for Polymer Research in Mainz as a post-doctoral fellow in April 1990. His research interest include the synthesis of polyconjugated and ladder type polymers.
crostructure and the morphology of the solid product which in turn control the material properties such as the electrical conductivity or the mechanical behavior.

The most common method for the synthesis of poly-(1,4-phenylenvinylene) is the one first described by Wessling and Zimmermann. Its key step is the polymerization of an intermediately formed substituted 1,4-bis-methylenecyclohexa-2,5-diene structure.

![Scheme 1](image)

The resulting products are insoluble and unmeltable. Processing must therefore be done for the water-soluble polyelectrolyte 3. The following thermal elimination step to the polymer 4 is accompanied by the formation of structural defects (mainly ionic in nature) whose presence has a substantial influence, for example, on the electrical dark conductivity. In addition, the insolubility of the product 4 prevents a more detailed spectroscopic characterization.

Nonetheless, oligo- and poly(arylenevinylene)s are a favored class of substances due to their outstanding physical properties such as high photocconductivity or non-linear optical activity. One possibility to overcome the synthetic drawbacks lies in the synthesis of soluble polymers. This can be accomplished, for instance, by incorporating solubilizing substituents as described by Hörhold and others. The introduction of substituents, however, can sterically inhibit the conjugative interaction between the subunits. Thus, prominent differences are seen when comparing these materials with unsubstituted PPV 4.

Another alternative in the design of poly(arylenevinylene) is a variation of the structure of the arylene building block itself which offers the additional advantage of tailoring electronic properties. Attractive subunits are anthracene – due to the extension of the \( \pi \)-system, cyclooctatetraene – due to its outstanding redox activity, or 2,2'-biphenyl – due to its conformational mobility (see Section 2.1.).

2.1. Structurally Defined Oligo(1,4-phenylenvinylene) – Valuable Model Systems for Understanding Properties of the Corresponding Polymers

In the search for new unconventional poly(arylenevinylene) structures we found it useful to first investigate structurally related oligomeric model compounds. A stepwise assembly of oligo(phenylenvinylene) through repeated Wittig- or Horner–Emmons-type olefination reaction sequences leads to oligomers with \( n \) up to 5. In contrast to their unsubstituted analogues, which are poorly soluble or even insoluble, the oligomers are sufficiently soluble in common organic solvents. This is due to the existence of tert-butyl substituents in the terminal phenyl rings. An investigation of these model substances by optical and NMR spectroscopy gives results essential for an understanding of the electronic structure of (phenylenvinylene). Apparently, with \( n = 5 \), convergence of the longest wavelength absorption maxima occurs, and the \( \lambda_{\text{max}} \) value of PPV 4 is almost reached.

Cyclic voltammetric studies of the oligomeric systems reveal the mechanism of stepwise charging of phenylenvinlenes. First of all, in contrast to the unstructured, broad reduction or oxidation waves of the polymer (PPV) 4, separated quantifiable reduction and oxidation waves are obtained for the oligomers.

When following the reduction potentials as a function of chain length, they appear to shift to more positive values and to approach a borderline value. Also, one can clearly determine the number of repeat units for which the difference of the first and second redox potential reaches a minimum. This potential difference is a measure of the Coulomb repulsion between the extra charges. Accordingly, upon extrapolation toward the polymer with a given degree of polymerization one can reliably predict how many charges can be stored without electrostatic interaction.

In addition, the ESR and ENDOR spectroscopic characterization of monocharged derivatives of 5 points out that the unpaired electron tends to be localized in the central part of the \( \pi \)-chain. This leads to the identification of an effective conjugation length. The nonlinear optical behavior of conjugated polymers such as PPV 4 has recently been under intensive study, a sound structure/property relation has not yet been obtained, however, so that an optimization of materials, for example, for an application in optoelectronic devices, is still difficult. Inclusion of structurally defined model systems is thus crucial. Measurements of the third-order optical susceptibilities \( \chi^3 \) of 5 by third harmonic generation or degenerate four-wave mixing indicate that the nonlinear components of the hyperpolarizability increase with increasing chain length and that there is a relation between \( \chi^3 \) and linear optical properties such as longest wavelengths and extinction coefficients of absorption maxima.
2.2. Oligomers and Polymers Containing the 9,10-Anthrylene Unit in
the Main Chain

The incorporation of larger aromatic π-systems as anthracene into arylenevinylene chains has proven to be valuable since the substantially lower energy difference between aromatic and quinoid resonance structures, when compared with the 1,4-phenylene unit, leads to a smaller HOMO/LUMO energy difference (corresponding to the energy gap between the valence and conduction band of the macromolecule). The incorporation of anthrylene units, however, cannot be achieved via the known synthetic methods, e.g., via the Wessling/Zimmermann or via the reductive dehalogenation route.

A newer method for the preparation of aryl olefins from aryl halides and olefins is the so called Heck reaction,\textsuperscript{32} whose synthetic possibilities have been investigated extensively by Heitz.\textsuperscript{13,14} We were able to show that a reaction of 9,10-dihaloanthracenes (bromides, iodides) with olefins (for instance ethylene, styrene) proceeds to the 9,10-alkenyl-substituted anthracene derivatives 6 in good yields (70–90%), whereby a catalyst system composed of palladium(II) acetate/tris(o-toly)phosphine/triethylamine was chosen.

![Diagram of 6](image)

The reaction between the corresponding 9,10-divinylanthracene and bromo- or iodobenzene does not lead to the expected coupling products. The reason for this failure obviously is the sterically demanding situation at the reaction center; the presence of the peri-hydrogens in the anthracene derivative (1/4, respectively, 5/8 position) prevents an addition of the organometallic intermediate to the olefinic double bond.

When reacting an equimolar amount of 1,4-divinylbenzene (7) and 9,10-dibromoanthracene (8) under Heck conditions, however, a nearly quantitative yield of oligo(arylenevinylene) 9 with alternating (1,4-phenylenevinylene) and (9,10-anthrylenevinylene) building blocks is obtained.\textsuperscript{23} Since due to the decreasing solubility with increasing chain length, the products precipitate during the reaction, only oligomers containing up to 8 repeating units were formed. NMR spectroscopic investigations prove the defect-free structure of the coupling products. Disubstitution at the olefin component, a side reaction described in the synthesis of poly(1,4-phenylenevinylene) when using Heck conditions\textsuperscript{13,14} can be ruled out.

Oligo(9,10-anthrylenevinylene-1,4-phenylenevinylene) (9):

9,10-Dibromoanthracene (1.68 g, 5 mmol) and 1,4-divinylbenzene (0.65 g, 5 mmol) were dissolved in DMF (25 mL). Then Pd(OAc)$_2$ (45 mg, 0.2 mmol), tris(o-toly)phosphine (305 mg, 1.0 mmol) and Et$_3$N (10 mL) were added. The mixture was stirred under argon atmosphere for 1 d. The resulting oligomer was precipitated in 2 M HCl, dried and redissolved in CHCl$_3$. Reprecipitation into MeOH gave 1.50 g (theoretical yield: 1.52 g) of a yellow amorphous powder.

Our attempt to synthesize poly(9,10-anthrylenevinylene) via repetitive Heck reaction is a continuation of the above finding. Unfortunately, coupling between 9,10-dibromo- or 9,10-diiodoanthracene with 9,10-divinylanthracene failed, again because of the strong steric hindrance at the reaction center.

An obvious possibility to circumvent this sterically unfavorable situation is to increase the distance between the anthracene units involved in the reaction, for instance by elongating the vinylene group to a butadienylene unit. A reaction between 9,10-dibromoanthracene (8) and 9,10-bis[1-(1,3-butadienyl)]anthracene (10) proceeds readily under the Heck conditions described above.\textsuperscript{23} A red colored product 11 is obtained whose solubility compared with poly(arylenevinylene)s is rather good due to the flexible butadienylene units incorporated. The double bonds of the product only possess a trans configuration as seen from a comparison with the NMR spectra of corresponding low-molecular weight model compounds [such as all-trans-1,4-di-9-anthryl-butadiene].

An alternative to the use of AA-/BB-type monomers (two different bifunctional monomers with the same functionality in each case) is the synthesis and reaction of an AB type (one bifunctional monomer with the two different functionalities in the same molecule) starting material. Thus, 9-bromo-10-[1-(1,3-butadienyl)]anthracene (12) is accessible in a two-step reaction sequence from 9-bromoanthracene-10-carbaldehyde. Repetitive Heck reaction of this monomer leads again to all-trans configurated oligomers 11 with an average degree of polymerization of 12.
In a similar fashion, 9,10-di-1,3,5-hexatrienylanthracene (13) can be reacted with 9,10-dibromoanthracene (8) under Heck conditions with formation of oligo(9,10-anthrylenehexatrienylene)s 14, again in all-trans configuration.23

As with the oligo(phenylenevinylene)s, the physical properties of oligomeric anthrylenevinylene can be extrapolated to the yet unknown poly(9,10-anthrylenevinylene) (15). Thus, the UV/VIS-absorption spectra of the compounds 16 show a significant bathochromic shift of the longest wavelength absorption maximum with growing chain length, proving the conjugative interaction between the subunits in spite of the sterically demanding situation. With n = 5, convergence is reached.

With the help of numerical extrapolation techniques the limit of the HOMO/LUMO energy difference in the oligomeric series can be estimated as 2.05 eV for the unknown poly(9,10-anthrylenevinylene) (15). A similar approximation is possible from the difference between the first reduction and oxidation potentials as measured by cyclic voltammetry. The approximation for the band gap of the corresponding polymer 15 leads to a value of 2.0 eV, which is in good agreement with the values obtained from the absorption spectra. In the case of the (9,10-anthrylenevinylene) oligomers with n = 2, it can be seen that the first two reductions in the cyclic voltammetric experiments occur at very similar potentials or even coincide. This points towards an independent charging of the subunits in contrast to the behavior of PPV 4.24

The electronic properties of extended π-systems sensitively depend on the way in which the active building blocks are linked. It is therefore important that we have also succeeded in synthesizing the linear poly(anthrylenealkylene) structure 17 in which 9,10-anthrylene moieties are connected via saturated 1,ω-alkylene chains and are, thus, electronically independent. The synthesis proceeds via repetitive alkylation of carbons which are produced by reduction of anthracene or deprotonation of 9,10-dihydroanthracene species. The products have a high structural homogeneity and possess number-average molecular weights $M_n$ of about 10000.33–35 It appears from chemical and electrochemical reduction experiments that each anthracene group can be reversibly charged with two electrons. In that respect 17 is similar to the oligo(anthrylenevinylene) and oligo(anthrylenebutadienylene) systems in which each repeating unit can be charged twice. Cyclic voltammetric studies reveal, however, that the charging mechanisms and the arising electrostatic effects are quite different.29,36 A comparison between oligo(phenylenevinylene) and oligo(anthrylenevinylene), on the one hand, and oligo- or poly(anthrylenealkylene), on the other hand, has proven significant for the classification of conducting polymers and redox polymers.29,37–39
2.3. Unusual Redoxactive Systems via Incorporation of 1,5-Cyclooctatetraene Units

One motivation of replacing the benzene ring of arylenevinylene chains by larger benzenoid systems such as anthracene is the higher charge-storage capacity of the products. An additional motivation comes from the expected thermo- and photochemical reactivity of anthracene\(^{40}\) which allows for a subsequent chemical modification of the extended \(\pi\)-systems. Both aspects strongly suggest the incorporation of nonbenzenoid [8]annulene cyclooctatetraene. While 1,4-disubstituted cyclooctatetraenes are available by literature-known techniques,\(^{41-43}\) the synthesis of the appropriate 1,5-difunctionalized cyclooctatetraenes needed as precursor molecules for coupling reactions, however, is by no means trivial.

**Dimethyl 3,7-Dimethylcyclooctatetraene-1,5-dicarboxylate (19):**

Dimethyl 1,5-dimethyldimethylvalene-3,7-dicarboxylate (18, 496 mg, 2.0 mmol) was pyrolyzed in vacuo (5 \(\times\) 10\(^{-4}\) Torr, turnover: 1 g/d) at 480°C. The products were condensed and chromatographed on silica gel with petroleum ether/CHCl\(_3\) (1:1). The diester 19 was formed in 70% yield as a yellow, semicrystalline material. Unreacted starting material (30%) was also recovered.

The reduction of the oligo(cyclooctatetraenevinylene)\(_n\) convincingly documents the role of these compounds as unusual redox systems. Inspite of the extended \(\pi\)-conjugation, each COT subunit is able to accept two electrons, whereby the charge is largely localized on the COT rings, as can be shown by a combination of NMR and cyclic voltammetric measurements. During the course of the charging process, however, an electronic interaction between the COT units definitely exists. The dianion formation in one COT subunit slightly influences the neighboring rings causing these to become at least partially flattened.

In the case of the oligo(arylenevinylene)\(_n\) 23 with alternating (1,5-cyclooctatetraenevinylene) and (1,4-phenylenevinylene) units, no significant charging of the phenylene units can be seen in electron-transfer experiments. Instead the negative charge is essentially localized on the COT subunits. The extra charge residing on a COT ring can be "shifted" to a neighboring, uncharged COT ring in a thermally induced process. The relevant activation energy depends on the nature of the bridging unit and, thus, the reorganization energy associated with the intramolecular electron transfer.

2.4. The 2,2'-Biphenylene Building Block – toward the Generation of Photoreactive Poly(arylenevinylene)

A major problem in the synthesis of arylenevinylene is that the solubility of the products drastically decreases with increasing chain length. As an alternative to the introduction of solubilizing alkyl or aryl substituents, one can incorporate conformationally mobile arylene units which create a kink within the \(\pi\)-chain and thus lead to a less rigid structure. An additional advantage of such subunits is that olefinic units of one and the same chain can approach each other and undergo thermally or photochemically induced reactions. A \(\pi\)-system which is
particularly attractive for this concept is the 2,2'-biphenyl moiety. Extensive investigations by Laarhooven\textsuperscript{48,49} have revealed that 2,2'-distyrylbiphenyl (24) follows two different photochemical reaction pathways depending on the wavelength of the irradiation applied.

Upon irradiation with light of a wavelength above 300 nm, an intramolecular [2 + 2]cycloaddition to the corresponding cyclobutane derivative 25 can be effected in high yields and with strictly stereoselective formation of the all-trans configuration with respect to the four membered ring.

The above cycloaddition and the possibility of a photochemical cycloreversion were an interesting starting point for tailoring the chemical and physical behavior of extended π-systems, especially for a controlled interruption or restoration of π-conjugation. The incorporation of a photoactive 2,2'-alkenyl substituted biphenyleylene unit into a polymer chain could thus allow for a rapid chemical change of the electronic properties.

Again, the Heck reaction is a promising method for the synthesis of the target molecules. Not unexpectedly, complications arise in the model reaction of 2,2'-dibromobiphenyl (26) with styrene as the olefinic component which is supposed to provide 2,2'-distyrylbiphenyl. The proximity of the bromo substituents in the 2,2'-biphenyleylene unit causes cyclization to the corresponding 9-phenyl substituted 9-fluorenylene derivative 27 through a disubstitution at the olefinic site of the 2-bromo-2'-styrlylbiphenyl intermediate. The inverse process, however, i.e., the reaction of 2,2'-divinylbiphenyl (28) with an aryl halide, is a handy alternative. Thus, in a model experiment 2,2'-distyrylbiphenyl is formed smoothly in a Heck reaction between 2,2'-divinylbiphenyl (28) and bromo- or iodo benzene. This experience can be applied in a polycondensation reaction by using the AA/BB-type monomers 2,2'-divinylbiphenyl (28) and 1,4-dibromobenzene. The oligo(2,2'-biphenylelenylene-1,4-phenylvinylene) (29)\textsuperscript{26} synthesized in this manner contain about 15 repeat units per chain. The product is free from structural defects and completely soluble in organic solvents. The reason for the latter property, which contrasts to that of the parent PPV, is the torsion about the aryl-aryl bond of the biphenyl subunits leading to a strong twist in the molecular structure.

Now the question poses itself whether or not the electronic behavior and the molecular geometry of the 2,2'-distyrylbiphenyl moieties are retained in the polymer product in a manner allowing a photocyclization.

Irradiation with light of a wavelength > 300 nm leads to the cyclobutane derivative 30. According to spectroscopic information, the distyrylbiphenyl subunits undergo the described intramolecular [2 + 2]cycloaddition in a highly regio- and stereoselective process and thus behave as isolated, noninteracting photoactive species. The unusual polymer-analogous photocyclization is accompanied by a bleaching of the color since the absorption of the originally yellow oligomers in the visible region disappears completely. Further, it must be emphasized that the photocyclization described for 29 takes place in solution as well as in the film, reflecting a high flexibility of the subunits in the solid state as well. These results offer the possibility of testing the novel polymer-analogous photo-reactions in photolithographic experiments. Thereby the “destruction” of the extended π-systems and the pronounced change in the absorption behavior during the photochemical reaction are the outstanding features.

Another relevant finding in controlling the photoactivity of a chromophor and in switching between two different molecular states comes from the photolysis of distyryl biphenyl systems 31 in the crystal. Whereas the parent system 31a is completely unreactive, the corresponding derivative with \( R = \text{tert}-	ext{butyl} \) 31b quantitatively transforms into the cyclobutane product upon irradiation. This difference and the possibility of a topochemical control\textsuperscript{50,51} can satisfactorily be rationalized by the distance and relative orientation of the vinylene units as determined from a crystal-structure analysis.

In the extended π-chains 29 a thermally induced intramolecular [2 + 2]cycloaddition is also possible, however unlike the photochemical case, the all-cis configurated system 32 is formed. This corresponds to the behavior of 24.\textsuperscript{48,52} Whereas in the case of the all-trans cyclobutane derivative 30, generated photochemically, the possibility of a photochemical ring-opening reaction (excitation wavelength < 300 nm) exists, a thermally induced cycloreversion of the thermally formed all-cis configurated cyclobutane species 32 leads to the formation of oli-
go(phenylenevinylene)s 33 with elimination of the volatile phena-threne. An advantage of this method is the possibility of carrying out the final step of the reaction sequence in the solid state.

Continued synthetic work is directed to increase the chain length of the photoreactive (arylenevinylene) polymers of type 29 and to vary the mode of linking of the (2,2'-biphenylvinylenevinylene) subunits; a reductive coupling (e.g., McMurry reaction, dehalogenation with chromium(II) salts) of appropriate starting materials is the method of choice. Since a reaction of the corresponding substituted biphenyl derivatives [2,2'-biphenylcarb-aldehyde or 2,2'-bis(dichloromethyl)biphenyl] leads preferentially to the intramolecular coupling product phena-threne, it is necessary to separate the reaction centers to prevent an intramolecular reaction. Since the McMurry reaction tends to give saturated hydrocarbons as side-products, we chose the reductive coupling of bis-geminal dichloromethyl compounds with chromium(II) acetate. A suitable extended building block for the synthesis is 2,2'-bis(4-dichloromethylstyryl)biphenyl (34), whose reductive coupling with the chromium(II) salt indeed leads to polymers 35. The structural difference to the oligomers synthesized via Heck reaction is the lengthening of the bridging unit between the 2,2'-biphenylylene moieties.

Another important aspect is that the incorporation of a π-chain into a rigid ladder avoids configurational and conformational isomerism. This is not only important for the construction of extended π-systems, but also for molecules composed of electronically “decoupled” electrophoric or chromophoric building blocks, because a defined steric and electronic interaction of the subunits is an important requirement for systematic studies of energy- and electron-transfer processes.

3. π-Systems with Ribbon- or Ladder-Type Structures

π-Systems with a ribbon- or ladder-type frame possess a two-dimensional structure and are thus intermediate between linear molecules and the three-dimensional graphite lattice. The major advantage of such double-stranded π-systems is that according to theoretical calculations they can possess small HOMO/LUMO energy gaps. Figure 1 compares the electron-absorption spectra of homologous series of (linear) oligo(phenylenevinylene) and (ribbon-type) oligorylenes. It appears that the convergence behavior is significantly different and that the band-gap energy is, indeed, much smaller in the double-stranded system.
promises a high structural homogeneity of the product. It is for this reason that repetitive Diels–Alder reactions are presently under intensive study by several groups.\textsuperscript{59-64}

The alternative possibility for constructing ribbon-type structures is the synthesis via a two-step process, that is; (1) formation of a suitably functionalized open-chain precursor, and (2) subsequent polymer-analogous ring closure.

The demands upon the second step are (nearly) quantitative conversion of the open-chain starting material and a high chemo- and regioselectivity in the reaction to minimize structural defects. These problems have raised doubts in the literature about the feasibility of this concept.\textsuperscript{64}

3.1. Ribbon-Type Structures via Repetitive Diels–Alder Reactions

The first example for the synthesis of ribbon-type structures by repetitive cycloaddition is the synthesis of molecules with o-anthracenophane subunits which have served as model compounds in charging experiments and electron-hopping studies.\textsuperscript{65} The bis-diene component for the Diels–Alder cycloaddition is in this case 1,2,5,6-tetramethylenehexaalkane (36)\textsuperscript{66} which can be prepared from 1,3-dibromomethylbutadiene in a one-step synthesis via a reductive coupling with zinc-copper couple. Depending upon the experimental conditions, reaction of 36 with 1,4-benzoquinone as bifunctional dienophile provides a 1:1-adduct 37 which, upon chromatographic purification on silica gel, rearranges to the corresponding hydroquinone derivative 38. Oxidation with iron(III) chloride affords the quinone species 39, which constitutes a suitable AB-type monomer for the repetitive cycloaddition since it possesses both a diene- and dienophile component. Quinone formation via oxidation is necessary to reach a suitable reactivity of the dienophile function.

The cycloaddition proceeds smoothly at elevated temperatures and gives rise to the desired ribbon-type structure 40. \textsuperscript{13}C-NMR spectroscopic analysis of the soluble fraction and comparison with low molecular weight model compounds fail to exhibit any structural defects. Treating solutions of 40 with oxygen allows one to achieve dehydrogenation and formation of the ribbon molecules with anthraquinone subunits 41 which comprise up to 15 repeating units. Higher molecular weight material possesses the same structure according to an IR spectroscopic comparison.

One aspect worthy of note is the first and second Diels–Alder reaction of 36. As is obvious from a crystal structure of the 1:1 adduct 37, the first cycloaddition step brings about a significant twist within the remaining butadiene subunit (\(\alpha = 102^\circ\)), which then reduces the reactivity of the 1:1-adduct in further [4 + 2]cycloadditions. It was therefore straightforward to proceed to bis-diene components with a rigid and planar structure of both diene subunits, as occurring in the bis-furan 42\textsuperscript{67} and the bicyclo[2.2.2]octane derivative 43.\textsuperscript{68} Repetitive Diels–Alder cycloaddition of 42 with different acetylene dicarboxylic esters provides ribbon-type structures 44, whose solubility can be controlled via the choice of the alcohol component of the ester.\textsuperscript{69}

\begin{align*}
\text{36} + \text{36} &\rightarrow \text{37} \\
\text{37} &\rightarrow \text{38} \\
\text{38} &\rightarrow \text{39} \\
\text{40} &\rightarrow \text{41} \\
\text{42} + \text{R} &\rightarrow \text{44} \\
\text{R} &= \text{CO}_2\text{Me}, \text{CO}_2\text{Et}, \text{CO}_2\text{C}_6\text{H}_{5-\text{H}}, \text{CO}_2\text{C}_6\text{H}_4\text{Me}, \text{CN} \\
\text{42} &\rightarrow \text{45} \\
\text{45} &\rightarrow \text{46}
\end{align*}

Another complication is encountered, however, which is quite characteristic for repetitive cycloaddition reactions. Preferentially at higher temperatures, the primary 1:1-adduct 45 transforms into the cage-type compound 46 via an intramolecular cycloaddition.\textsuperscript{69}

The major advantage of the bis-diene 43, which was first prepared by Vogel and co-workers\textsuperscript{68} is that a twofold Diels–Alder cycloaddition gives rise to a barrelene structure. On the other hand, repetitive Diels–Alder reactions of 43 with less reactive dienophiles require high-pressure conditions.
The concave shape of the barrelene subunits brings about a significantly improved solubility of the Diels–Alder adducts. Thus reaction of 43 with 1,4,5,8-tetrahydro-1,4:5,8-bisepoxyanthracene (47) produces soluble ribbon-type molecules 48,71 which can be obtained as a series of monodisperse oligomers with up to 33 six-membered rings.

\[
\begin{array}{c}
\text{43} + \text{47} \xrightarrow{\text{CICH}_2\text{Cl}_2, 40^\circ\text{C}, 2\text{h}, 75 \text{kbar}} \text{48}
\end{array}
\]

\(n = 1, 3, 5\)

Ribbon-Type Polymer 48:

2,3,5,6-Tetramethylenecyclob[2,2]oct-7-ene (400 mg, 2.6 mmol) and 1,4,5,8-tetrahydro-1,4:5,8-bisepoxyanthracene (540 mg, 2.6 mmol) were dissolved in \(\text{CICH}_2\text{Cl}_2\) (10 mL) and heated to 40°C for 2d under high-pressure conditions (7.5 kbar). The solvent was removed and the residue chromatographed on silica gel, first with hexane/EtOAc (2:1) giving 450 mg of 48a, then with CHCl₃ giving 210 mg of 48b, and finally with MeOH/CHCl₃ (1:1) giving 180 mg of 48c, as colorless powders.

Investigations of model compounds such as 49 show that the bis-diene 43 exclusively gives rise to an exo-attack relative to the oxo-bridges, as expected under the high-pressure conditions.72 The stereochemistry in relation to the ethylene bridge is not uniform, since exo- and endo-attacks of the dienophile component take place. A formation of cage-type products, however, is not observed.71 By introduction alkyl substituents into the 9- and 10-positions of 47 one can further improve on the solubility of the cyclodaddition products such that longer ladder structures with \(n \sim 20\) are formed. The formation of different diastereomers is not a major drawback within the context of the synthesis because the final target is a fully unsaturated species with a linear ribbon structure.

\[
\begin{array}{c}
\text{49}
\end{array}
\]

This aspect, however, describes the key-problem of the Diels–Alder route toward extended \(\pi\)-systems: while the repetitive formation of six-membered rings can be achieved in high structural homogeneity, the subsequent dehydrogenation reactions, eventually in polymer-analogous processes, defines new requirements.

The first step in the aromatization sequence is the removal of the oxo-bridges. Herein, the use of HCl gas as dehydrating agent in dioxane solution gives the best results. In a second step, the cyclohexadiene rings next to the barrelene moiety must be subjected to dehydrogenation (preferably with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DDQ), thus, giving rise to acene-fused barrelenes.

The synthetic approach involving the formation of barrelene subunits as intermediates is promising for obtaining oligo- and poly(acene)s, because the final formation of the extended acene \(\pi\)-system can now be achieved via a retro-Diels–Alder reaction. Recalling the instability of longer acenes,73 it is important that this latter reaction can be performed under mild conditions without additional reagents on an immobilized film of the starting material. Product formation in a film can be an advantage rather than a drawback since many physical experiments such as photoconductivity and non-linear optical measurements require good film-forming properties of the materials investigated.

The barrelene precursor offers the additional possibility of a photochemically induced formation of a cyclooctatetraene unit.74 This gives rise to a structure in which pentacene moieties are conjugatively linked by cyclooctatetraenes.

3.2. Ribbon-Type Structures via Polymer-Analogous Cyclizations of Linear Precursors

It has been pointed out that the two-step procedure to ribbon structures proceeds via chain formation followed by polymer-analogous ring closure.

In order to successfully undertake a two-step synthetic route leading to ribbon-type structures, it is much more important than in the case of the “concerted” route to optimize the structure of the starting material as well as the reaction conditions forcing the ring closure. A promising concept is as follows: the final structure must be predetermined in its precursor such that the actual intramolecular ring-closure reaction is greatly favored over all possible side reactions (formation of structural defects, intermolecular reactions).

3.2.1. Double-Stranded Poly(phenylene)s via Cyclization of Open-Chain Precursors

The synthesis of so-called oligo- or poly(arylenemethenides) 50 is attractive, especially with respect to the predicted low band-gap energy as a consequence of the degenerate electronic ground state.75,76 To this day, the synthesis of this structure has not been realized, apparently due to the extreme oxidative instability of the target molecules. The attempts described in the literature led, in spite of contrary pretentions, without exception to structurally nondefined products.77,78

\[
\begin{array}{c}
\text{50}
\end{array}
\]

Our approach to circumvent the known difficulties in the synthesis of an open-chain structure was: (1) to incorporate the arylenemethane substructure into a ribbon molecule, which provides us with the advantage of fixing a defined molecular geometry (note that the open-chain structure, in addition to being conformationally mobile, can give rise to different configurational
isomers), and (2) beyond that, to substitute the methine bridges in a manner allowing further steric and electronic stabilization.

The assembly of the underlying ribbon-type structure consisting of an alternating series of fused 6- and 5-membered rings succeeds in the following synthetic sequence: The palladium(0)-catalyzed coupling between an aromatic diboronic acid component 51 with a dibromo compound 52 leads, according to Suzuki and co-workers,79 to an oxo-substituted poly(1,4-phenylene) 53, which represents the back-bone for further polymer-analogous reaction steps. With this ary-aryl coupling method (described by Wegner and Schüler and co-workers among others)80,81 it is possible to incorporate carbonyl functionalities unchanged into the coupling product 53 (Mn = 10 000; corresponding to 25 linked aromatic rings). In addition, the electron accepting oxo substituents considerably increase the rate of the aryl-aryl coupling reaction.

Furthermore, to guarantee sufficient solubility of the polyketone 53, the incorporation of solubilizing substituents R and R' into the poly(1,4-phenylene) structure is indispensable.82 The subsequent reaction sequence involves the quantitative reduction of 53 with lithium aluminium hydride to the corresponding polyalcohol 54. Surprisingly enough, the final ring closure takes place completely and regioselectively within a few seconds. Using boron trifluoride, the 5-membered rings are closed to planar rigid poly(1,4-phenylene) ribbon-type structures 55, whose 13C-NMR spectroscopic analysis gives no indication of structural irregularities such as intermolecular cross linking or incomplete ring-closure.83 The ladder polymer 55 represents an interesting example of tacticity due to the stereochemical arrangement of the substituents at the methine bridge in the polymeric ribbon molecule.

**Polyketone 53:**
A solution of 4,4'-didecyl-2,5'-dibromoterephthalophenone (52, 0.725 g, 1 mmol) and 2,5-dihexyl-1,4-phenylenediboronic acid (51, 0.334 g, 1 mmol) in toluene (5 mL) was added to 2 N K2CO3 (5 mL). The mixture was refluxed, and tetrakis(triphenylphosphine)palladium(0) (30 g, 0.03 mmol) in toluene (5 mL) was added. After refluxing for 1 h, the mixture was poured into acetone (100 mL). The solid precipitate was filtered, washed with water, dried and redissolved in toluene. The polyketone 53 was precipitated as a colorless powder into acetone, yield: 535 mg (66%).

**Polyalcohol 54:**
The polyketone 53 (200 mg, 0.247 mmol calculated with respect to the repeating unit) was dissolved in toluene (20 mL) and added dropwise to a suspension of LiAlH4 (70 mg, 1.84 mmol) in THF (20 mL). The mixture was stirred for 30 min at r.t. and carefully quenched with EtOH, H2O, and dil. HCl. The organic layer was washed with H2O, dried and evaporated to dryness. The polyalcohol 54 was redissolved in THF and precipitated into H2O, yield: 167 mg (84%) of a colorless material.

**Ladder Polymer 55:**
A solution of the polyalcohol 54 (76 mg, 0.093 mmol) in CH2Cl2 (50 mL) was treated with BF3·OEt2 (300 mg, 2.11 mmol). After stirring for 5 min at r.t., EtoH (20 mL) was added to the mixture, followed by H2O (50 mL). The organic layer was carefully washed to remove the catalyst, dried, concentrated, and precipitated into acetone to give 55, yield: 62 mg (85%) of a yellow powder.

With respect to the reaction path outlined above, it is noteworthy that: (1) no efficient palladium(0)-catalyzed coupling reaction takes place when using the dialcohol component 56 instead of the diketone 52; and that, (2) the attempted ring closure with the polyalcohol 57 in un-
successful; the exchange of the aryl substituents against hydrogen leads to the formation of cross-linked insoluble products during treatment with BF₃.

The poly(1,4-phenylene) ribbon-type polymer 55 formed is characterized by a sharp phase-transition in the temperature range between 60 and 70 °C due to the melting of crystallized side chains. X-ray powder diffraction points to the formation of an ordered phase, characterized by staggered ribbon molecules.

A number of structural variations lend themselves in the synthetic route described above. Replacement of the 1,4-substituted dibromo component 52 by the corresponding 1,3-substituted analogue 58 and coupling in the manner described above will provide poly(phenylene) ribbon-type structures 59 containing alternating 1,4- and 1,3-linkages of the phenylene subunits. If, in addition, one replaces the 1,4-phenylendiboronic acid component 51 by the corresponding 1,3-linked compound 60, poly(phenylene) ribbon molecules of the type 61 become accessible, which are connected throughout in a 1,3-linkage.

The spectroscopic behavior of the poly(1,4-phenylene) ribbon structure 55 nicely documents the conversion of the strongly twisted open-chain poly(1,4-phenylene) precursor structure into the planar double-stranded molecule. The planarization of the conjugated polymer is accompanied by a drastic shift in the longest wavelength absorption (Figure 2). The fluorescence emission and

Figure 2. UV/VIS-absorption spectra of the polyalcohol 54 and the planarized poly(1,4-phenylene) ladder polymer 55 (solvent: CH₂Cl₂).

Meanwhile, an alternative route to the ribbon-type polymer has been worked out. If at the stage of the aryl-aryl coupling one uses 2,5-dibromoterephthalic dialdehyde 62 as the dibromo component to connect with the aromatic diboronic acid 51, one obtains the polyaldehyde 63 \( (M_w = 5000) \). Its polymer-analogous reaction with aromatic Grignard or lithium organic compounds leads to polyalcohols of structure 64, whereby a great variation in the choice of the substituent \( R \) is possible. The ring closure to ribbon-type polymers of structure 55 also takes place completely and regioselectively.

The spectroscopic behavior of the poly(1,4-phenylene) ribbon structure 55 nicely documents the conversion of the strongly twisted open-chain poly(1,4-phenylene) precursor structure into the planar double-stranded molecule. The planarization of the conjugated polymer is accompanied by a drastic shift in the longest wavelength absorption (Figure 2). The fluorescence emission and
The step still pending in the planned reaction sequence to the polymeric arylenemethanide ribbon structures is the conversion of 55 into 65, which formally is a dehydrogenation in the methine bridge. Several possibilities exist:

(a) direct chemical dehydrogenation with suitable reagents (DDQ, 7,7,8,8-tetracyano-1,4-quinodimethane (TCNQ) or tritylium-salts);
(b) oxidation of metalated (anionic) species, for instance with iodine, cadmium chloride or silver trifluoroacetate;
(c) oxidative formation of the corresponding polycation followed by deprotonation;
(d) conversion of the CH-function at the methine bridge into a CX-function \( (X = \text{halogen or OR}) \), followed by reductive elimination.

Attempts to use methods (a) and (b) have so far led to no defined reaction products. Method (c) is characterized by the formation of doped (cationic) species of 55 which, however, show little tendency to deprotonate. In contrast, the radical cationic and dicaticonic states are highly stable. For instance, the radical cations formed via oxidation of 55 with antimony pentachloride do not decompose in contact with water of dilute acids.84

\[
\begin{align*}
55 & \quad 59 \\
65 & \quad 66
\end{align*}
\]

For this reason, experiments using route (d) appear to be the most promising, whereby the search for a method to carry out a controlled dehalogenation reaction of the chloro-substituted ribbon-type polymers has special significance.

Whereas in the case of the poly(1,4-phenylene) ladder polymer 55 the transformation into the corresponding polyarylenemethanide structure is still pending, the conversion of the alternating 1,4- and 1,3-linked phenylene ladder polymer 59 into the corresponding polymer with localized 1,4-bismethylene cyclohexa-2,5-diene substructures 66 in the ribbon (nondegenerate ground state, but fully conjugated structure) has been found to take place readily by dehydrogenation with DDQ.85 The resulting stable, intensive blue colored polymer is the first structurally defined polymeric 1,4-bismethylene cyclohexa-2,5-diene. From its absorption characteristics (tailing of the UV/VIS-absorption band up into the NIR-region) interesting electronic properties of the new chromophor are expected. From a bond theoretical point of view 66 is unique in possessing an extended ribbon-type structure with a nonalternating \( \pi \)-system. As a consequence the charge distribution is different in anionic and cationic derivatives which is important for the electrical conductivity of doped material.

\[
\begin{align*}
59 & \quad 66
\end{align*}
\]

3.2.2. Oligorylene – Synthesis of Ribbon-Type Molecules with peri-Fused Naphthalene Units

The main difficulties in the formation of extended acene and arylenemethanide structures lie in the chemical instability of the products. Acenes are known to readily undergo various cycloaddition reactions,86 and arylenemethanide systems are unstable at the methine bridge against oxidation.85 It is known, on the other hand, that molecules built from double-stranded naphthalene units [e.g., oligo(peri-naphthylene)] are characterized by high chemical stability.

Oligomers from the so-called rylene series (peri-fused naphthalenes 67) have been synthesized as unsubstituted molecules up to the quaterrylene (\( n = 2 \)).87,88 However, as the molecular size increased the solubility decreased drastically; in the case of the quaterrylene, an unambiguous characterization of structure and electronic properties was no longer possible.88 Attempts to synthesize poly(peri-naphthylene) via thermolysis of

\[
\begin{align*}
67 & \quad 68
\end{align*}
\]
3,4,9,10-perylenetetracarboxylic dianhydride 68 have also been undertaken. This method, however, leads to insoluble, partially carbonized products.\(^{89–91}\)

To obtain structurally defined members of the rylene series, it is necessary: (1) to incorporate solubilizing substituents into the target molecules and, (2) to find milder methods of synthesis. The development of a "concerted" route to rylene molecules seems remote (a cycloaddition reaction of the Diels–Alder type is not possible). We therefore, again, have chosen a reaction sequence based on the cyclization of open-chain linear precursors, leading directly to the extended aromatic \(\pi\)-systems without difficult dehydrogenation steps. In order to obtain soluble material the substitution with tert-butyl groups in the terminal napthalene rings was chosen for the synthesis of the lower rylene oligomers. The 2,7-di-tert-butynaphthalene (69), which is easily accessible from napthalene by Friedel–Crafts alkylation (separation from the isomeric 2,6-di-tert-butynaphthalene via the thiourea inclusion compound), is monobrominated to 70 and then transformed into the corresponding boronic acid 71. The palladium(0)-catalyzed coupling with suitable dibromo components 72 (1,4-dibromonaphthalene, 4,4'-dibromo-1,1'-binaphthyl) leads to the desired linear terminal tert-butyl substituted oligonaphthalenes 73.\(^{92}\)

A synthetic approach for conversion into the double-stranded molecules is a reductive cyclization using alka lial metals, followed by oxidation of the resulting anionic species. Several indications point to an electron-transfer induced electrocyclic reaction at the dianion stage\(^ {93}\) followed by the elimination of hydrogen. This method, however, leads only up to perylene (\(n=0\)) and terylene (\(n=1\)) structures as largest peri-condensed naphthylene subunits in the molecules. The formation of oligorylenes 74 with \(n \geq 2\) must therefore be carried out by a subsequent cyclization reaction. A ring closure to higher condensed products is possible under rather mild oxidative conditions (aluminum trichloride/copper(II) chloride). Using this three-step reaction sequence (palladium(0)-catalyzed coupling, first reductive, then oxidative cyclization), terminally tert-butyl substituted oligorylenes 74 up to \(n=3\) have been synthesized.\(^{92}\) Furthermore, a removal of the aliphatic substituents is possible thermally or via retro-Friedel–Crafts alkylation leading to unsubstituted oligorylenes of structure 67.

3,6,3',6'-'-Tetra-tert-butyl-1,1':4,1':4',1''-quater-naphthalene (73): 3,6-Di-tert-butynaphthyl-1-boronic acid (71, 3.0 g, 10.6 mmol) and 4,4'-dibromobinaphthyl (72, \(n = 2, 340 g, 0.3\) mmol) were dissolved in toluene (10 mL) and 2 M K₂CO₃ (10 mL) and a solution of tetrakis(triphenylphosphine)palladium(0) 340 mg, 0.3 mmol) in toluene (10 mL) was added. The mixture was refluxed for 2 h under argon atmosphere. The resulting organic phase was dried, the solvent removed in vacuo and the product chromatographed on silica gel with cyclohexane/CHCl₃ (5:1). The yield of the resulting quater-naphthyl derivative 73 (\(n = 2\)) was 2.9 g (74%); mp 236–238 C.

Anionic Cyclization:

The quater-naphthyl derivative 73 (\(n = 2, 2.3 g, 3.1\) mmol) was dissolved in dry DMF (150 mL) and reacted with potassium (1.8 g, 46.0 mmol) for 7 d at r.t. in vacuo. After oxidation of the resulting anions with CdCl₂, the organic layer was separated, the solvent removed and the residue chromatographed on alumina with cyclohexane/CHCl₃ (5:1). A first fraction consisted of 1.1 g (48%) 2,2',5,5'-tetra-tert-butyl-9,9'-biperylenyl as the major product of the cyclization (mp 252–255 C). A second fraction gave 2,5,3',6-tetra-tert-butyl-11-(1'-naphthyl)birenylene (114 mg, 5%); mp 250 – 252 C.

Cationsic Cyclization:

2,2',5,5'-Tetra-tert-butyl-9,9'-biperylenyl (500 mg, 0.60 mmol) was dissolved in CS₂ (80 mL) and treated with AlCl₃ (500 mg) and CuCl₂ (500 mg). The mixture was allowed to stir for 8 d under argon atmosphere at r.t. The precipitate was formed and washed with H₂O and extracted with chlorobenzene. The organic solvent was removed and the residue chromatographed on alumina with cyclohexane/CHCl₃ (5:1) to remove the byproducts. Elution with hot CHCl₃, concentration of the solution and crystallization gave 240 mg (48%) 2,5,12,15-tetra-tert-butylquater-tert-biperylene (74, \(n = 2\)) as bluish-black crystals; mp 520–530 C.

The oligorylenes 74 possess outstanding electronic properties: in the absorption spectrum a distinct bathochromic shift in the longest wavelength absorption with increasing \(n\) is apparent. In the case of pentarylene (\(n=3\)) a value of \(\lambda_{\text{max}} = 745\) nm is determined. Since convergence of the \(\lambda_{\text{max}}\) values is not yet reached, the synthesis of the next members in this homologous series is of great interest. An extrapolation of the HOMO/LUMO energy difference (band gap) leads to about 1.0 eV for polyrylene.\(^{94}\) It should be noted that the energy gap obtained for the relatively small \(\pi\)-system pentarylene is very similar to that of the intensively studied polycylenylene. This finding, again, documents the importance of the search for novel extended \(\pi\)-systems.

As in the case of the oligo(phenylenevinylene)\(^s\) 5, NLO-measurements of the oligoarylenes 74 reveal a dependance of the non-linear components of the hyperpolarizability upon linear optical properties such as wavelength or extinction coefficient of the absorption
maxima. Remarkably enough, the absolute values of the $\chi^2$-coefficients (third harmonic generation) are by one order of magnitude smaller than those of linear conjugated systems with comparable absorption characteristics.\textsuperscript{95}

Being efficient chromophores, the oligorylenes also show interesting electrophoric properties. Depending on the size of the conjugated $\pi$-system, a number of fully reversible oxidative or reductive electron-transfer steps are observed in the cyclic voltamograms (in the case of the quaternitylene 74 ($n = 2$), for instance, seven), which in contrast to measurements on polymeric $\pi$-electron systems are fully separated and quantifiable.\textsuperscript{94}

In the case of the oligorylenes 74 with terminal tert-butyl substituents, the solubility is also limited and decreases drastically with increasing molecular size. For the synthesis of extended ribbon structures (higher oligomers and polymers containing peri-condensed naphthylene subunits), it is necessary to vary the synthetic strategy by incorporating solubilizing substituents into the central (bay) positions of theylene molecules.

One possibility is the synthesis of co-condensation products consisting of alternating 2,6-di-$n$-alkyl-substituted and unsubstituted (1,5-naphthylene) subunits as linear open-chain precursor molecules 75 for the subsequent cyclization reactions. The incorporation of the aliphatic substituents brings forth steric hindrance, but, nevertheless, the cyclization methods described, are also applicable to this route, as could be shown by the synthesis of corresponding $n$-alkyl substituted terylenes.

\[ R \quad R \]

\[ R \quad R \quad n \quad R \quad \text{n-alkyl} \]

**Scheme 8**

The next stage should be the transfer of this model reactions to more extended molecules. Investigations to this end are under way.

4. Conclusion

The synthesis of novel chromophores and electrophores and the tailoring of their physical properties involve transition from monomers to oligomers and to polymers as a straightforward process. Although significant differences emerge when comparing synthesis and structure elucidation of low and high molecular weight conjugated species, a combination of organic and polymer chemistry proves particularly fruitful. The structure-directed search for unconventional extended $\pi$-systems and the study of their capability in materials sciences thus appear as a major issue for interdisciplinary research and a real, although not yet fully appreciated, challenge for synthesis. Although this concept is motivated by the active physical function and potential applicability of the target compounds, it nevertheless is a legitimate element of basic research, since it focuses on firm correlations between molecular and supramolecular structures and physical properties.

This text would not have been possible without the skilful and dedicated work of the members of our group whose contributions are gratefully acknowledged. Our work has been financially supported by the Bundesministerium für Forschung und Technologie, the Deutsche Forschungsgemeinschaft, the Fond der Chemischen Industrie, the Volkswagen-Stiftung, the BASF AG, and the Hoechst AG. One of us (U.S.) thanks the Fond der Chemischen Industrie for a scholarship.
