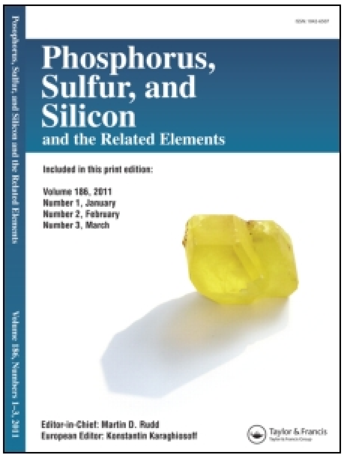

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Sulfur-Containing Conjugated Polymers

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Sulfur-Containing Conjugated Polymers

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Herein we present new synthetic approaches to sulfur containing polymers. The synthesis of poly(phenantrolinebisthiazole) (PPT), poly(phenylenesulfidephenyleneamine) (PPSA), poly(tetrathiafulvalene) (PTTF), sulfur containing [n]acenes and donor-acceptor substituted poly(phenylenevinylene) (PPV) is described. Two different strategies have been taken: The first one comprises the synthesis of suitably functionalized monomeric biulding blocks, which can be easily polymerized by common polymerization methods; the second one is based on novel methods of carbon-carbon and carbon-sulfur bond formation.

KEY WORDS sulfur containing polymers, poly(tetrathiafulvalene), poly(phenylenesulfidephenyleneamine) (PPSA), ladder polymers, carbon-carbon and carbon-sulfur bond formation, poly(phenylenevinylene) (PPV)

INTRODUCTION

It is by no means a trivial task to adopt methods of organic chemistry to the synthesis of polymers. Important criteria are the avoidance of structural defects, even for high molecular weight products, solubility, processability and the control of chemical and physical properties. Sulfur-containing conjugated polymers have played a major role in the development of temperature-stable thermoplastic materials[1] and in the search for materials being suitable as active components of opto-electronic and photonic devices[2]. Herein, we shall present a series of polymers **1** to **5** with unprecedented structures (figure 1).

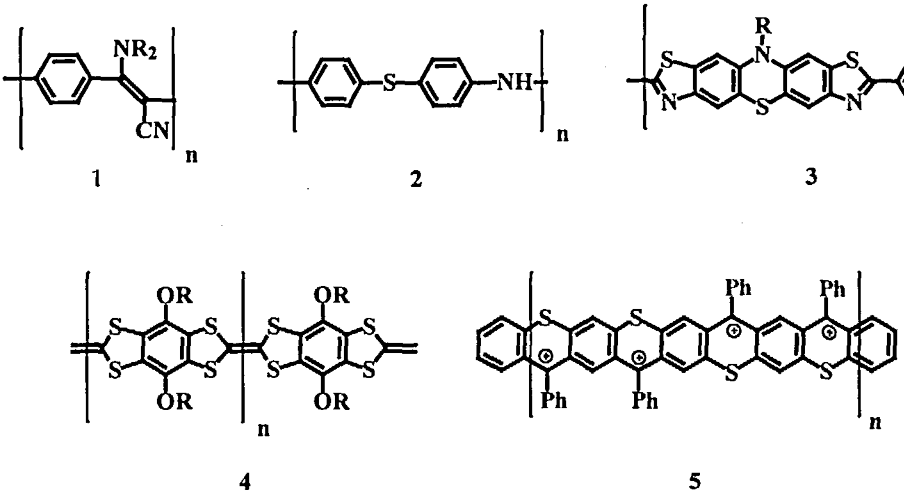


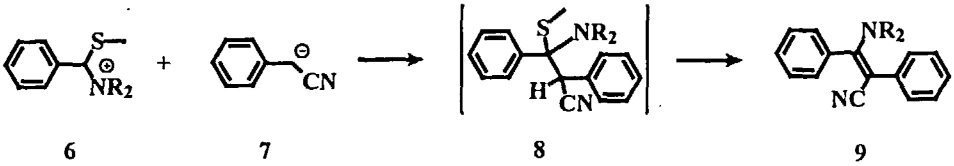
FIGURE 1 Sulfur-containing conjugated polymers 1-5, R = *n*-alkyl

The donor-acceptor substituted poly(phenylenevinylene) **1** (PPV) is intended to combine extended π-conjugation with strong dipole moments in each repeat unit, while poly(phenylenesulfidephenyleneamine) **2** can be regarded as a hybrid of two well-known polymers, namely polyaniline (PAni)[3] and poly(phenylenesulfide) (PPS)[4]. The rigid-rod polymer **3** is an example of a poly(arenebisthiazole) with phenothiazine serving as heteroaromatic component. Polymer **4** is made up of conjugated tetrathiafulvalene subunits, which are fused through benzene rings. Due to the exocyclic double bonds, it possesses an extremely rigid structure. Polymer **5** possesses a double-stranded structure and can be regarded as a ladder-type polymer. The polycation is isoelectronic to poly[n]acene.

Two different synthetic approaches will be taken: the first one proceeds via the synthesis of suitably functionalized monomeric building blocks, which can be readily subjected to polymer-forming reactions; the second on rests on novel methods of carbon-carbon and carbon-sulfur bond formation. The emphasis of this text is on synthesis. The physical properties of the target structures will be mentioned only briefly.

DONOR-ACCEPTOR SUBSTITUTED POLY(PHENYLENEVINYLENES)

Alkylation of benzoic acid thioamide creates the cation **6**, which serves as an electrophile in carbon-carbon bond formation with suitable carbanions[5], such as **7** (scheme 1). The primary product **8** undergoes thiol elimination, even at low temperatures, to afford the new stilbene **9** in 98% yield[6].



SCHEME 1 Synthesis of donor-acceptor substituted stilbene 9, R = *n*-alkyl

The solid-state structure of **9** is characterized by an appreciable torsion about the formal double bond and by a tight packing of the molecules as a result of intermolecular dipole-dipole interactions. In solution, **9** undergoes rapid E/Z-isomerization[6].

A careful control of the experimental conditions is necessary in order to suppress the attack of the nucleophile at the S-alkyl group, which would re-establish the thioamide.

A key feature of the novel stilbene synthesis is that it can be extended to the stepwise synthesis of higher oligomers. This reaction is not limited to phenylene precursors, but distinct aromatic units like biphenyl or 1,4-diphenoxybutane can be used for the oligomer synthesis, thus allowing a systematic variation of the distance between the olefin centered dipoles. These oligomeric series (figure 2) are ideal candidates for studying the cooperative effects of dipole moments and the dielectric relaxation behavior[7].

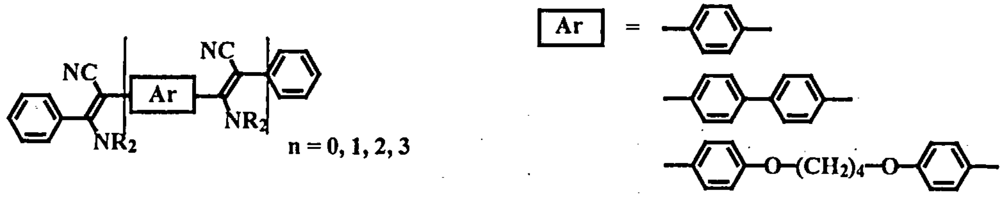
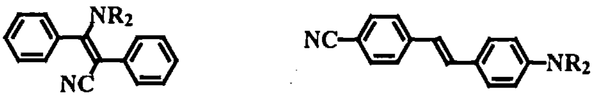


FIGURE 2: Oligomeric series with varying distances between dipoles

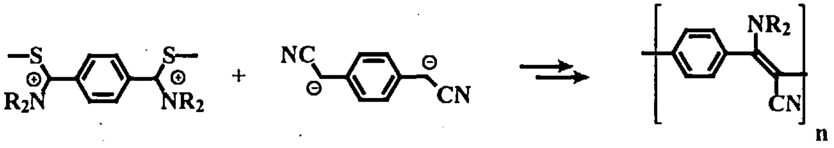
The non-centrosymmetrical structure **9** also warrants an investigation of the second order non-linear optical behavior[8], whereby it is challenging to compare the stilbenes **9** and **10** (figure 3), but only the former with unobstructed 4,4'-positions leads to the build up of a homologous series[6].



9 **10**

FIGURE 3 Donor-acceptor substituted stilbenes **9** and **10**

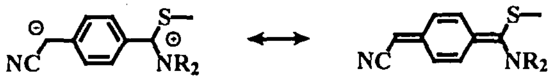
A logical extension of the synthesis of stilbene **9** and its higher oligomers is the polymer synthesis, using the bifunctional electrophile **11** and the bifunctional nucleophile **12**, in an AA/BB-type reaction (scheme 2)[9]. When dealing with the resulting polymers, it is particularly advantageous that alkyl groups attached to the amino substituents ensure sufficient solubility without creating steric inhibition of the π-conjugation along the chain. While conventional methods of molecular weight determination fail as a result of strong aggregate formation, MALDI-TOF mass spectrometric analysis reveals polymers with up to 22 stilbene units along the main-chain.



11 **12** **1**

SCHEME 2 AA/BB type polymerization to yield poly(phenylenevinylene) 1

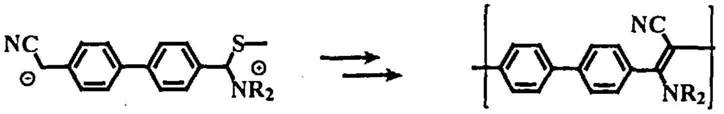
It might be challenging to proceed to an AB-type polymerization by combining nucleophilic and electrophilic functions in one molecule (scheme 3). However, species **13** does not polymerize as a result of strong donor-acceptor stabilization of the *para*-quinodimethane resonance structure (figure 4).



13

FIGURE 4 Resonance structures of **13**

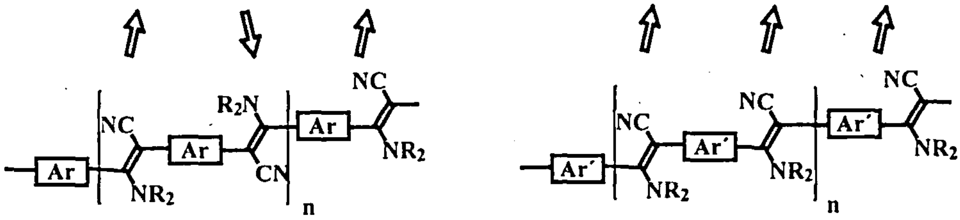
Similar stabilization does not occur in the biphenyl analog **14**, which thus readily undergoes polymerization (scheme 3).



14 **15**

SCHEME 3 AB-type polymerization to generate **15**

It should be noted that the AA/BB and AB-type syntheses yield complementary polymer structures with respect to the direction of the dipole moments in neighboring stilbene units (figure 5)[9].

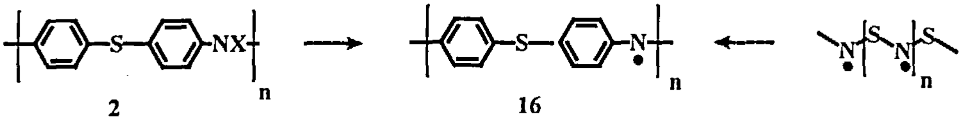


AABB-type polymerization **AB-type polymerization**

FIGURE 5 Direction of the dipole moments; Ar = -Ph-; -Biph-; -Ph-O-$(CH_2)_4$-O-Ph-; Ar′ = -Biph-; -Ph-O-$(CH_2)_4$-O-Ph-

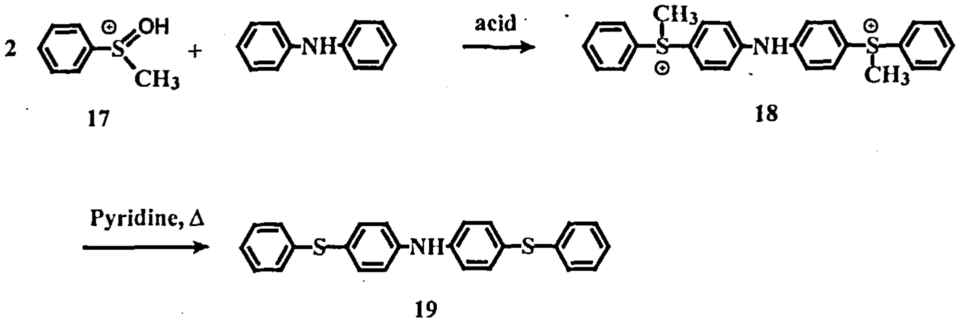
POLY(PHENYLENESULFIDEPHENYLENEAMINE)

While the classical polymer structures poly(phenylenesulfide) (PPS) and poly(aniline) (PAni) provide attractive chemical and physical properties[1,3,4] , they suffer from structural defects and limited processability. It was hoped that the hybrid structure **2** would exist as a defect-free, solution-processable, high molecular weight polymer. **2** was also designed as part of an approach, leading to new, electrically conducting polymers: **2** might transform into polyradical **16**, which constitutes an organic analog of polysulfurnitride (scheme 4)[10,14]. The latter has a high conductivity at room temperature[11] and it is a superconductor at very low temperatures[12].



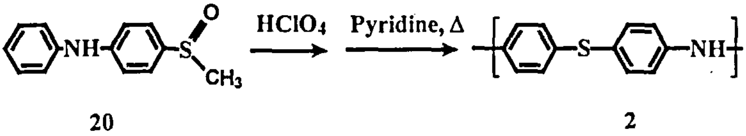
SCHEME 4 Approach to an organo analog of polysulfurnitride

According to a method proposed by Tsuchida et al.[13], the cation **17**, produced upon protonation of the corresponding sulfoxide with strong acid, constitutes a suitable electrophile for carbon-sulfur coupling with electron-rich aromatic components (scheme 5). Indeed, this method, when applied to the reaction of **17** with diphenylamine provides the dication **18**, which is transformed into the demethylated model oligomer **19** upon treatment with pyridine[14].



SCHEME 5 Model reaction for the synthesis of phenylenesulfidephenyleneamines

Here again, an AB-type approach proved successful. The bifunctional precursor **20** undergoes ready polymerization after protonation of the sulfoxide (scheme 6). The resulting polycation can be transformed into the desired target structure **2** by demethylation with pyridine[14].

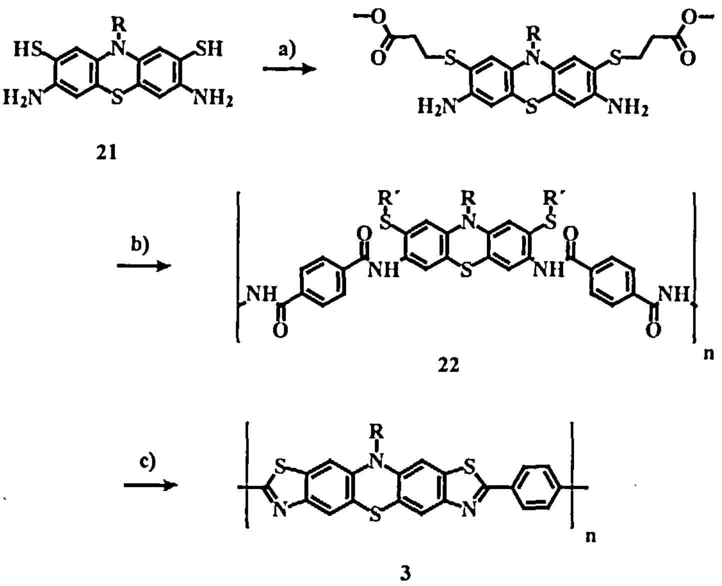


SCHEME 6 Synthesis of poly(phenylenesulfidephenyleneamine) 2

The number average molecular weight of **2** is higher than 100.000, nevertheless the material is solution-processable and forms free-standing films. The molecular weight is thus significantly higher than that of PPS and PAni. The solubility of **2** can be ascribed to the absence of cross-linking and to the amorphous character. The new polymer **2** appears as an ideal subject for studying mechanical, optical and electrical properties. In view of the electrical conductivity of PAni, doping of **2** with oxidizing agents is a particularly exciting experiment.

POLY(PHENANTROLINEBISTHIAZOLE)

The use of organic materials in photonic devices, e.g. for switching light with light, requires high values of second-order hyperpolarizability, which have not been achieved with the existing materials[10]. Measurements by the degenerate four-wave mixing have suggested that organic benzobisthiazoles are promising candidates for high χ^3-values[15]. In order to test this approach for polymers, we thought to use the electron-rich phenothiazine as an aromatic building block. Thereby, the nitrogen center should carry a long alkyl chain to improve the solubility of the polymeric target structures. The required monomeric starting compound would thus be the diaminodithiol derivative **21**, which should be subjected to a polycondensation with terephthalic acid. The synthesis of **3** required many modifications with respect to the route taken for phenantrolinebisthiazole. It was, however, finally achieved in good yields.



SCHEME 7 Synthesis of poly(phenantrolinbisthiazole) **3**, R = *n*-alkyl

a) NaOH, PTC, $BrCH_2CH_2CO_2CH_3$

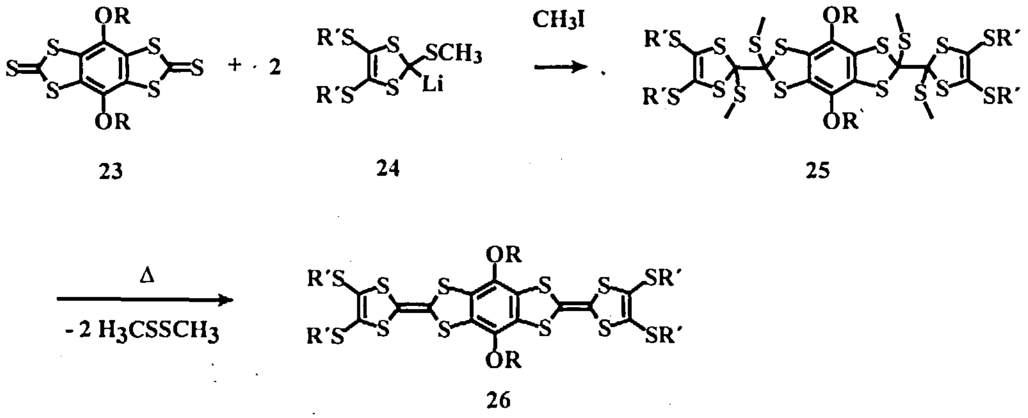
b) terephthalic acid chloride, - HCl; R′ = $-CH_2CH_2CO_2CH_3$

c) **22** as film, Δ, - $H_2C=C-CO_2CO_3$, - H_2O

It appeared, however, that alkyl substitution did not produce sufficient mobility for the target polymer, so that we had to refer to a precursor route (scheme 7)[10,16]. **21** was first protected by two-fold Michael-addition with acrylic ester, after which the polyamide **22** was formed by reaction with terephthalic acid dichloride. The resulting polyamide was sufficiently soluble and could be cast into films. The polymer films were subjected to thermal treatment, which induced extrusion of acrylic ester and subsequent polycyclization under removal of water. The corresponding weight loss could be monitored by thermogravimetric analysis, which indicated a clean formation of the target polymer **3**. In addition, the cleavage product was identified as acrylic acid methylester by pyrolysis-gaschromatographic mass spectrometry. Further support for the transformation of the polyamide **22** into the step-ladder polymer **3** could be achieved by UV/VIS spectroscopic measurements in the film. The cubic non-linearities of polymer 3 were measured by third-order harmonic generation. Polymer 3 exhibits reasonably high χ^3 values of about 10^{-11} esu. Careful comparison of the figures of merit, however, suggests that heteroaromatic polymers, such as 3, are not superior to classical hydrocarbon polymers, such as poly (phenylenevinylene)[17].

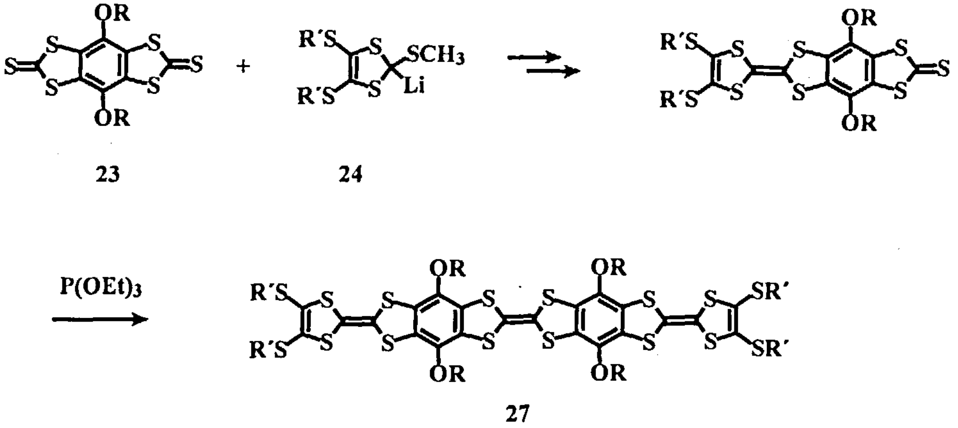
POLY(TETRATHIAFULVALENE)

Tetrathiafulvalene (TTF) is known as a donor in electrically conducting charge-transfer complexes[18]. The conductivity in the resulting solids is bound to two important structural features, namely the formation of segregated stacks of donors and acceptors and a certain degree of charge transfer between the stacks[19]. It would be tempting to incorporate tetrathiafulvalene into a polymer with extended π-conjugation, which might become electrically conducting after doping. A key advantage of this approach would be the replacement of single or microcrystalline solids by a processable and film-forming polymer. Problems associated with the one-dimensional character of the conduction process in solid TTF complexes have prompted researchers to synthesize oligomeric TTF systems[20]. Their charge-transfer complexes, if forming analogous solid-state structures as those of the parent TTF, might establish extended channels for charge transport along the stacking axes and also increase the chance for interstack interactions.



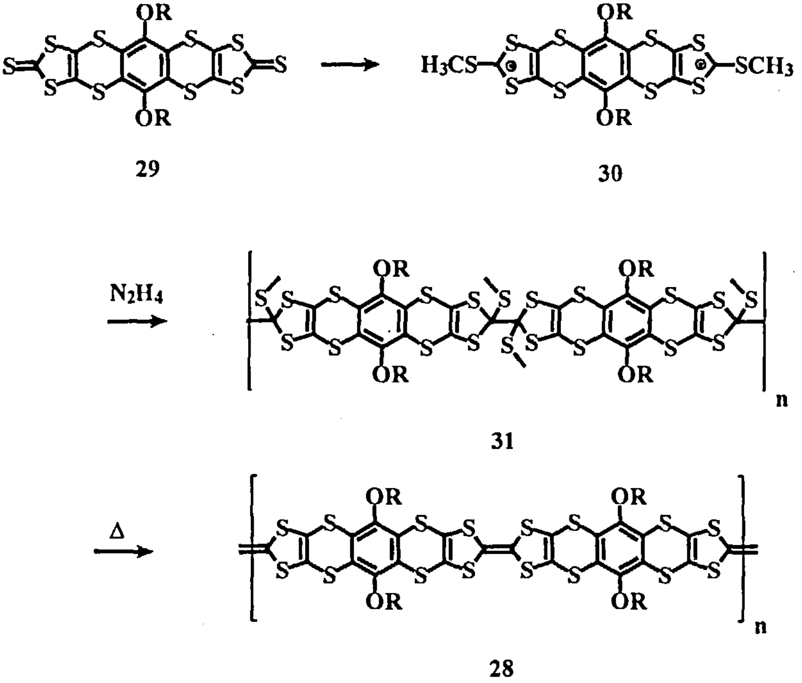
SCHEME 7 Synthesis of the bis-tetrathiafulvalene 26, R, R′ = *n*-alkyl

The synthesis of bistetrathiafulvalene **26** (scheme 7)[21] begins with a nucleophilic attack of two equivalents of **24** on the dithione **23**. This gives rise to the bishexathioorthooxalate **25** which, upon thermally induced extrusion of dimethyl disulfide, transforms into the well-defined bistetrathiafulvalene **26**. The alkyl chains attached to the central hydroquinone moiety are crucial for maintaining sufficient solubility and, indeed, electrocrystallization[21] of **26** results in radical cation salts with a semiconductor-like behavior. If one equivalent of **23** is reacted with **24** and the resulting monothione subjected to olefin formation with trisalkoxyphosphine, a homologous tris-TTF is formed (scheme 8)[22], which can be subjected to six perfectly reversible electron-transfer processes[22].



SCHEME 8 Synthetic route for the tris-tetrathiafulvalene **27**, R, R′ = *n*-alkyl

The experience accumulated in the organic chemistry of **26** and **27** paves the way for the synthesis of related polymers, such as **4** and **28**, whereby the two rigid polymer structures differ in the amount of sulfur attached to the TTF subunits. Here again, a precursor route is unavoidable in order to arrive at processable and structurally defined TTF polymers. A successful process is outlined for **28** (scheme 9)[23]: alkylation of the dithione **29** produces the dication **30**. Upon reduction with hydrazine, the latter undergoes smooth polymerization and the soluble polymer **31** is formed. Heating to about 160°C causes **31** to undergo extrusion of dimethyldisulfide to form the desired polymer **28**.

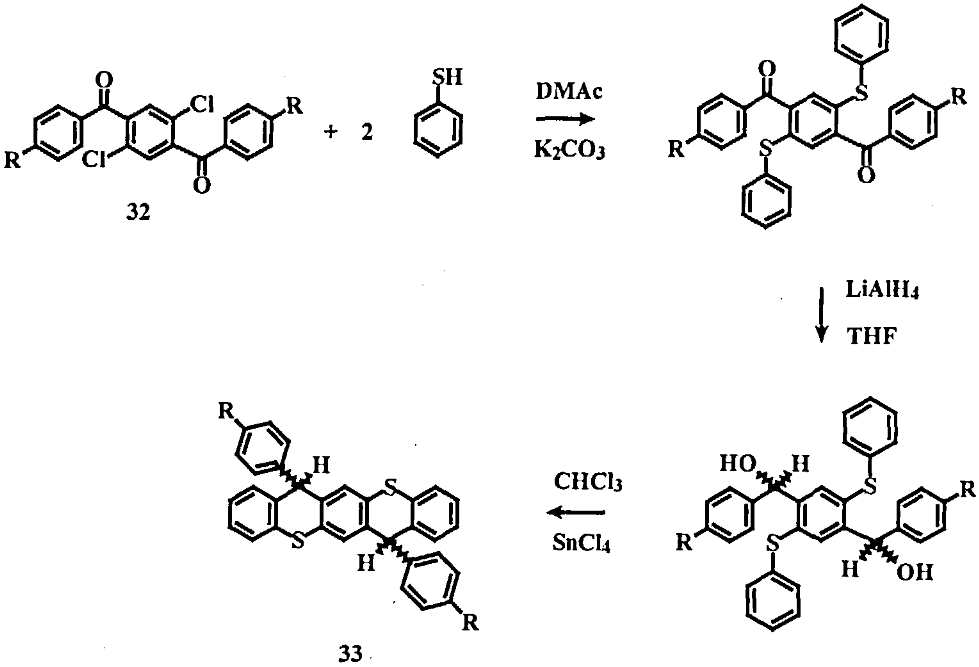


SCHEME 9 Polytetrathiafulvalene polymer **28**, R = *n*-alkyl

Here again, the process of converting a processable precursor polymer into an insoluble target structure with extended π-conjugation can be monitored by, both, thermogravimetric analysis and UV/VIS spectroscopy. **28** is the first example of a structurally defined polymer, in which TTF subunits form a rigid and extended π-conjugated system. Doping experiments appear highly promising, whereby the resulting conductivity will sensitively depend upon the morphology of the polymer, which, in turn, depends upon the conditions of film formation and thermal transformation of **31**.

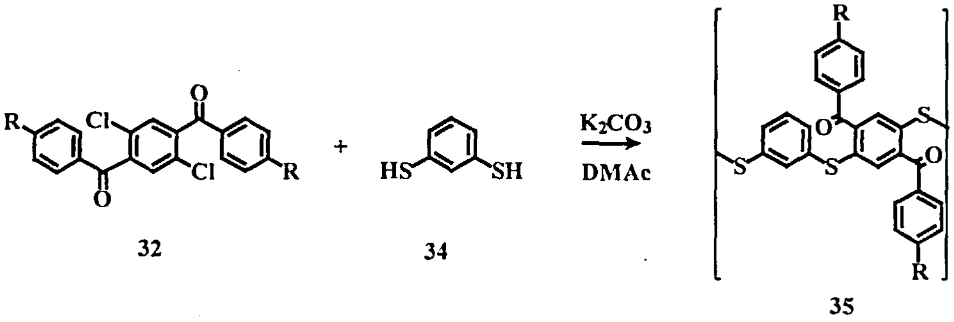
LADDER-TYPE POLYMERS WITH [N]ACENE STRUCTURE

Structurally defined ladder polymers have been a challenge of macromolecular synthesis for a long time because the resulting double-stranded structures are expected to possess unique electronic properties[24] and to exhibit significant conformational differences with respect to their linear single-stranded counterparts[25]. Herein we present an approach to xanthene based [n]acene structures, which rests upon polymer analogous Friedel-Crafts cyclization of poly(thioetherketone) precursors. The synthesis of structurally related oligomers **33**, **40** serves as an ideal test for polymer synthesis. Nucleophilic aromatic substitution of 1,3-dibenzoyl-4,6-dichlorobenzene (**32**) with thiophenol followed by reductive diol formation and Lewis acid induced twofold Friedel-Crafts cyclization affords **33** in high yields (scheme 10)[26].



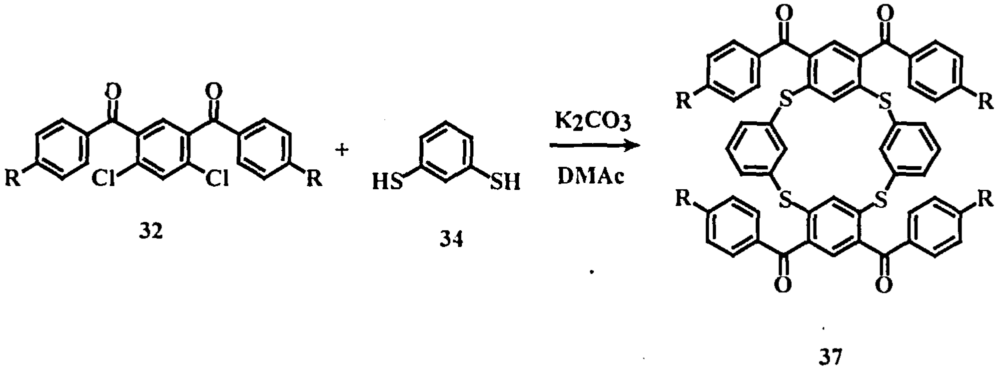
SCHEME 10 Model reaction for xanthene-synthesis **33**, R = *n*-alkyl

The analogous polymer synthesis using **32** and **34** gives benzoyl substituted poly(phenylenesulfides) **35** whose number average molecular weights can be as high as 170000 (scheme 11)[26].



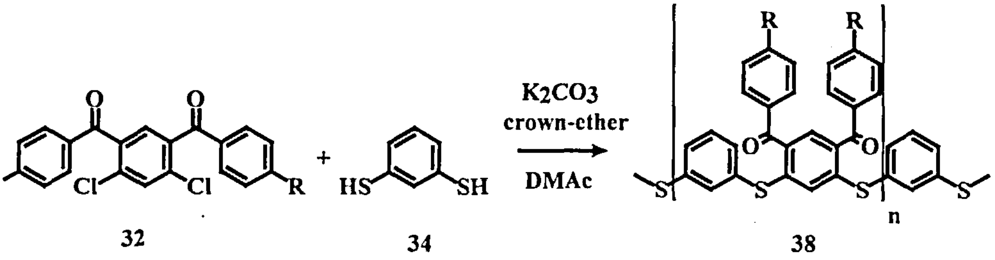
SCHEME 11 Polyxanthene synthesis, R = *n*-alkyl

A typical side reaction of the polymerization is the formation of cyclic components, which can easily be removed in a simple precipitation process. This side reaction becomes the preferred reaction if the topologically different 1,3-dibenzoyl-4,6-dichlorobenzene (**36**) is reacted with dithioresorcinol (**34**). When, both, the electrophilic and the nucleophilic component possess a meta constitution, the poly(*meta*-phenylene-sulfide) **38** is only obtained in traces whereas the cyclic phenylene sulfide **37** is formed in up to 90 % yield, even without applying high dilution conditions (scheme 12)[27].



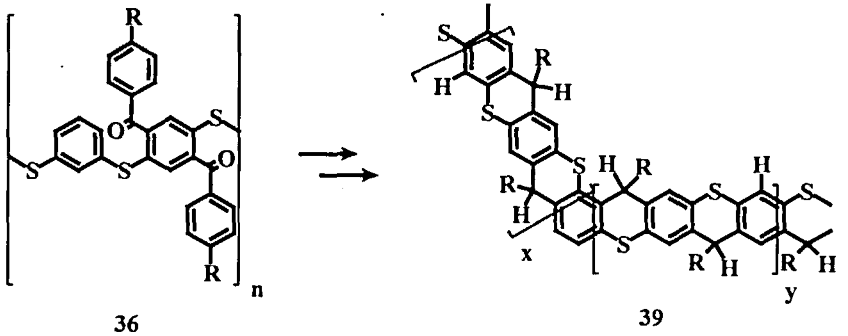
SCHEME 12 Synthesis of cyclic phenylenesulfides

The formation of the macrocyclic compounds is due to a template effect of the potassium ion. By complexation of the potassium ions with crown-ether it is possible to obtain the poly(*meta*-phenylenesulfide) **38** as the main product (scheme 13)[27,28].



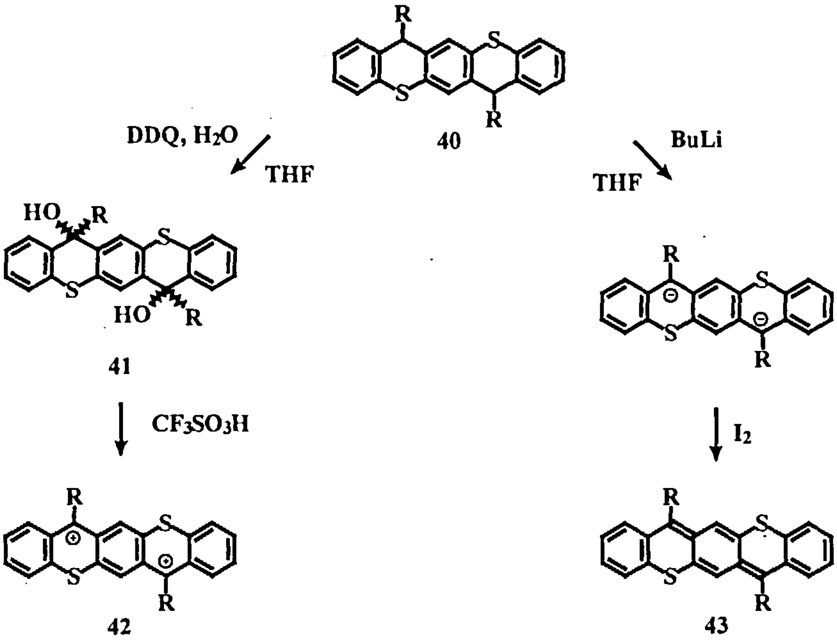
SCHEME 13 Synthesis of poly(*meta*-phenylenesulfide) 38

A surprising result is obtained when subjecting poly(phenylenesulfide) **36** to the Friedel-Crafts cyclization, because cata and angular connected structures are formed. This is, of course, an unwanted effect because the corresponding polymer will thus have kinks according to formula **39** (scheme 14)[26]. The problem of regioisomerism can be overcome and perfect poly[n]acene structures are obtained when the 2-methyl dithioresorcine is introduced into the poly(thioetherketone) synthesis[26].



SCHEME 14 Cyclization to obtain the ladder polymer 39

The resulting xanthene structures provide access to a broad spectrum of neutral and charged derivatives. Thus oxidation of **40** with *p*-dichlorodicyanobenzoquinone (DDQ) in the presence of water affords the diol **41**, which, upon treatment with acid, leads to the formation of the dication **42**, which is an isoelectronic analog of pentacene (scheme 15)[26]. Deprotonation of the dihydro system **40** with butyllithium generates the corresponding dianion, which, upon oxidation with iodine, yields the deep violet *para*-quinodimethane derivative **43** (scheme 15)[26].



SCHEME 15 Synthesis of hetero pentacene structures **42**, **43**, R = 4′-*n*-alkyl-phenyl

CONCLUSION

The above examples provide ample evidence of how new methods of polymerization and the synthesis of new, suitably functionalized monomeric building blocks lead to unprecedented macromolecules with a high degree of structural homogeneity. The problem of solubility, which is naturally associated with rigid extended π-systems, can be overcome by incorporation of alkyl substituents or by making use of precursor routes, in which soluble and processable precursor polymers are converted via a clean reaction into the desired target structures.

A key ingredient of this approach is, of course, the active physical function of the resulting products. Donor-acceptor substituted poly(phenylenevinylene)s are promising candidates for NLO applications. Poly(phenylenesulfidephenyleneamine), poly(tetrathiafulvalene) and sulfur containing aromatic ladder polymers are precursors for low band gap materials and thus are inspiring compounds for conducting polymers.

The main point of our approach is the combination of structurally well defined and soluble compounds with promising physical properties, thus allowing a broad application in material science.

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