[1] N. Rasool, A. Q. Khan, V. U. Ahmad, A. Malik, *Phytochemistry* **1991**, *30*(8), 2803–2805.

[2] Structure **1** is a member of the large and bioactivity-rich class of naturally occurring coumestans: a) W. Stadlbauer, T. Kappe, *Heterocycles* **1993**, *35*, 1425–1440; b) J. D. Hepworth in *Comprehensive Heterocyclic Chemistry, Vol. 4* (Ed.: A. R. Katritzky), Pergamon, New York, **1984**, pp. 995–998; c) F. M. Dean in *The Total Synthesis of Natural Products*, *Vol. 1* (Ed.: J. ApSimon), Wiley, New York, **1973**, pp. 485–548; d) A. Mustafa in *The Chemistry of Heterocyclic Compounds*, *Vol. 23* (Ed.: A. Weissberger), Wiley, New York, **1967**, pp. 243–255.

[3] a) V. Snieckus, *Chem. Rev.* **1990**, *90*, 879–933; b) J.-M. Fu, M. J. Sharp, V. Snieckus, *Tetrahedron Lett.* **1988**, *29*, 5459–5462; c) X. Wang, V. Snieckus, *Tetrahedron Lett.* **1991**, *32*, 4879–4882; d) J.-M. Fu, B.-P. Zhao, M. J. Sharp, V. Snieckus, *J. Org. Chem.* **1991**, *56*, 1683–1685; e) J.-M. Fu, B.-P. Zhao, M. J. Sharp, V. Snieckus, *Can. J. Chem.* **1994**, *72*, 227–236; f) W. Wang, V. Snieckus, *J. Org. Chem.* **1992**, *57*, 424–426; g) for application of this remote anionic Fries reaction to the synthesis of gilvocarcins, see C. A. James, V. Snieckus, *Tetrahedron Lett.* **1997**, *38*, 8149–8152, and for its generalization to arylfuryl and arylthiophenyl for construction of coumestans, see C. A. James, PhD thesis, University of Waterloo (Canada), **1998**.

[4] For further scope of this two-step procedure in the synthesis of 4-hydroxycoumarins, some of which are inaccessible by classical Friedel–Crafts and Lewis acid catalyzed Fries rearrangement reactions, see A. V. Kalinin, A. J. M. da Silva, C. C. Lopes, R. S. C. Lopes, V. Snieckus, *Tetrahedron Lett.* **1998**, *39*, 4995–4998; A. V. Kalinin, V. Snieckus, *Tetrahedron Lett.* **1998**, *39*, 4999–5002.

[5] B. A. Chauder, C. C. Lopes, R. S. C. Lopes, A. J. M. da Silva, V. Snieckus, *Synthesis* **1998**, 279–282, and references therein.

[6] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467–4470.

[7] Prepared according to D. E. Janssen, C. V. Wilson, *Org. Synth. Coll. Vol. IV* **1963**, 547–549.

[8] a) R. D. Stephens, C. E. Castro, *J. Org. Chem.* **1963**, *28*, 3313–3315; b) C. E. Castro, E. J. Gaughan, D. C. Owsley, *J. Org. Chem.* **1966**, *31*, 4071–4078; c) for a survey of palladium-based routes to benzofurans, see R. C. Larock, E. D. Yum, M. J. Doty, K. K. C. Sham, *J. Org. Chem.* **1995**, *60*, 3270–3271.

[9] Upon treatment with BCl_3, EtSNa, or LiCl, the corresponding methyl ether of **11** did not afford plicadin but gave product mixtures, indicating chromene and lactone ring opening.

[10] Prepared according to F. E. King, K. G. Neill, *J. Chem. Soc.* **1952**, 4752–4756; also see J. O. Amupitan, *Synthesis* **1983**, 730, and references therein.

[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101777. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] Despite numerous attempts, we were unable to obtain an authentic sample, a copy of the original ^1H NMR spectrum, and ^{13}C NMR data from the authors.

Biodegradable Polymeric Materials—Not the Origin but the Chemical Structure Determines Biodegradability

Uwe Witt,* Motonori Yamamoto, Ursula Seeliger, Rolf-Joachim Müller, and Volker Warzelhan*

Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occassion of his 60th birthday

Biodegradable polymeric materials (BPMs) are of ever increasing interest because of the many problems associated with solid wastes. As early as the end of the 1970s first attempts had been made to develop polymeric materials that combine good useage properties (such as thermoplastic processing ability for films, fibers and moulding) of conventional plastics and biodegradability by microorganisms.[1] In the meantime, such "bio-plastics" have become commercially available or are in the pre-marketing phase.[2] It is in principal possible to fall back on different sources of raw materials to produce such polymers. Thus, it is possible to distinguish between BPMs based on renewable or on petrochemical sources. Examples of such renewable sources are starch derivatives and starch blends, polyhydroxybutyrates, polylactic acid, cellophane, cellulose derivatives, caseine, and chitin polymers. BPMs produced from petrochemical resources are, for example, aliphatic polyesters such as polycaprolactone and polybutylene succinate, aromatic–aliphatic copolyesters, and polyester amides.

Whereas the biodegradability of BPMs based on renewable resources is plausible, there were doubts as to whether polymers based on petrochemical sources could also be mineralized by a natural process caused by microorganisms such as bacteria or fungi.

Aliphatic polyesters were extensively investigated as to their biodegradability.[3–5] The primary cleavage of the usually insoluble polymer chain takes place outside of the microorganisms and is catalyzed by specific enzymes that are produced in the cell and excreted by microorganisms such as bacteria or fungi. The microorganisms are then able to take up the fragments in their cells and utilize them as food.

Examinations of the biodegradability of aliphatic–aromatic copolyesters have only been known for a few years.[6–8] The chemical structure of such copolyesters examined in the literature is shown in Scheme 1. Such copolyesters are a very interesting class of substances in reference to the assessment of their biodegradation behavior because of their high aromatic component content. The introduction of the aromatic component is useful for improving physical and

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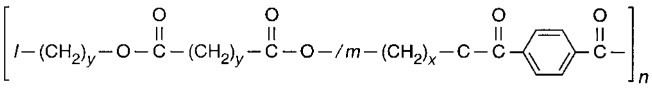


Copolyester	x	y	Abbreviation[a]
poly[(ethylenehexandioate)-co-(ethyleneterephthalate)]	2	4	ETA
poly[(trimethylenehexandioate)-co-(trimethyleneterephthalate)]	3	4	PTA
poly[(trimethylenedecandioate)-co-(trimethyleneterephthalate)]	3	8	PTS
poly[(tetramethylenehexandioate)-co-(tetramethyleneterephthalate)]	4	4	BTA

Scheme 1. Formula, nomenclature, and abbreviations of the copolyesters. [a] E: 1,2-ethanediol, P: 1,3-propanediol, B: 1,4-butanediol, A: adipic acid, S: sebacic acid, T: terephthalic acid.

mechanical properties. The amount of terephthalic acid in these copolyesters was up to about 30 wt.% (ca. 25 mol%). The first investigations for proving biodegradability concentrated on the weight losses of specimens. Sheeting was usually buried in soil or compost and the weight losses were determined after exposure to the medium (Figures 1 and 2).[9] According to Ottow both soil and compost are degradation matrices that provide a wide microbial spectrum.[10] All copolyesters investigated were attacked in soil and in compost within 12 weeks (except BTA 51:49 in soil). No significant influence of the diol components used on biodegradability of the copolyesters was observed. In all cases the content of terephthalic acid had a significant influence on the rate of degradation. Reliable statements on the mineralization of a polymer, that is, the formation of natural intermediates caused by metabolism of the microorganisms, cannot only be made by reference to weight losses.

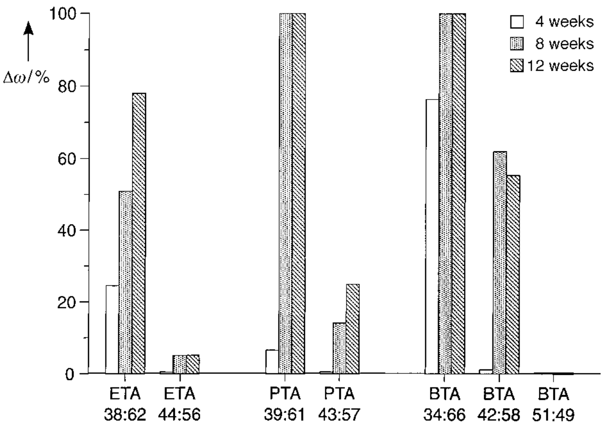


Figure 1. Weight loss (Δω) of the copolyesters during burial in soil.

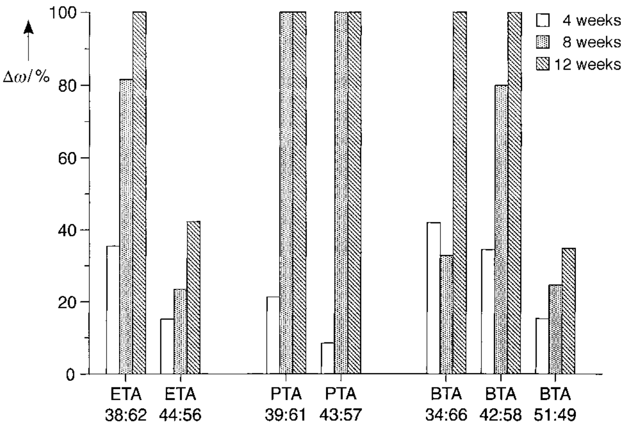


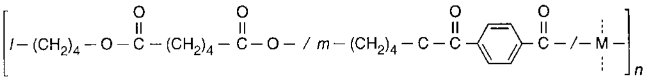
Figure 2. Weight loss (Δω) of the copolyesters during compost tests.

A technical standard, DIN V 54900, recently became available for the determination of the biodegradability of polymeric materials. The tests carried out in accordance with this standard show whether a polymeric material is biodegraded (mineralized) or disintegrated into compost components (Table 1) under the conditions of a controlled composting procedure. Different procedures are described in part 2 of the standard for the evaluation of complete biodegradability. According to the "controlled composting test" a defined quantity of polymer is mixed with compost and the amount of carbon dioxide generated by microbial conversion is measured. As a control the same amount of compost with cellulose instead of the polymeric material and a sample of the same compost without ingredients are also tested.

Table 1. DIN V 54900—Investigation of compostability of polymeric materials.

	Description
part 1	chemical test
part 2	evaluation of biodegradability of the polymeric materials in laboratory tests
part 3	testing of compostability under conditions of practical relevance including compost quality assessment

A type of copolyester marketed by BASF AG since early 1998 under the trademark Ecoflex® (Scheme 2) was examined according to the standard mentioned above.[11] The results according to part 2 of the standard are shown in Figure 3. The degradation rates (amount of CO$_2$ produced relative to the theoretical amount), were measured in three parallel reactors. After 124 days the amounts of CO$_2$ were 93% (PS1), 95% (PS2), and 96% (PS3). The mean value of the degradation curves is shown in Figure 3 and is 95% at the end of the test. The result of the compostability test according to DIN V 54900, part 3 (disintegration of the material under practical composting conditions), is shown in Figure 4. The carbon of the polymer is not necessarily converted to 100% carbon dioxide during composting, which can be explained as follows: In addition to the formation of carbon dioxide during mineralization of a substance, some parts of the carbon can be converted into biomass. Furthermore, remaining carbon could be caused by non or partial degradation of the polymer. A



Scheme 2. Formula of the copolyester Ecoflex®. M, for example, is a branching agent or a chain extender.

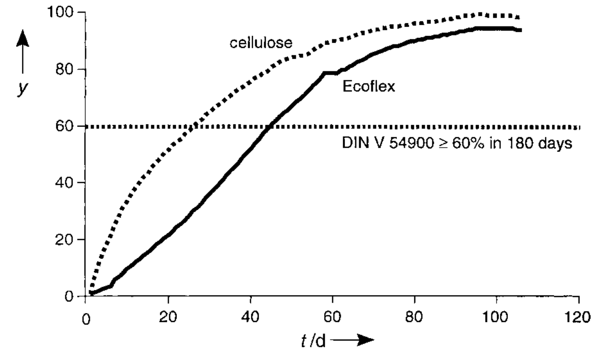
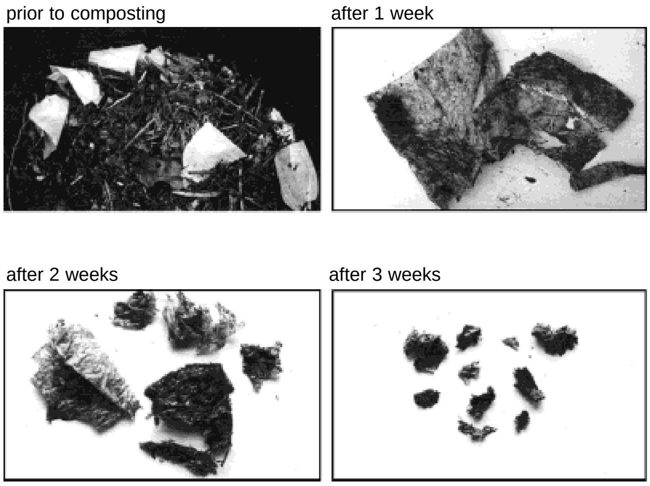


Figure 3. Biodegradability of Ecoflex according to DIN V 54900, part 2. Plastics such as Ecoflex have to be classified as fully biodegradable when at least 60 % of the total organic carbon of the polymer has been converted into carbon dioxide during a test interval of no more than 180 days. y: Amount of degradation [%] (fraction of the theoretical amount of CO_2 produced).


prior to composting

after 1 week

after 2 weeks

after 3 weeks

Figure 4. Investigation of the compostability of the copolyester Ecoflex® according to DIN V 54900, part 3.

sufficiently exact measurement of biomass in such a complex medium such as compost is not possible. By contrast, the measurement of residual polymer is different. The residual polymer can be quantified by gel permeation chromatography (GPC; Table 2) after taking aliquots from the compost and extracting with a suitable polymer solvent. After extraction the quantities of residual polymer in aliquots from the three parallel test reactors, with reference to the total amounts of inserted polymer, were 2.3, 1.3, and 3.4 %. The quantities of extracted polymer in the parallel control tests were between 0.00 and 0.02 per 100 g of polymer-compost mixture. Thus, these values were under the detection limit of identification of less than 0.1 g per 100 g. Altogether, in these tests (without determination of biomass) the average rate of recovery was about 97 %.

The stoichiometric composition of the extracted residual polymer was analyzed by ^{13}C NMR spectroscopy. A significant increase in the amount of the aromatic acid would point to a slow or nondegradation of aromatic polymer components. Within the accuracy of the method employed, no change in the stoichiometric composition was observed at the end of the test. Inhomogenities within the solid compost matrix, for example too wet, too dry or not well ventilated zones, or polymer particles that adhered to the wall of the reactor, are plausible explanations for the existence of residual polymer. The high rate of mineralization (about 95 % of the theoretical amount of CO_2 produced) shows that the material is biologically attacked and that most of it is degraded by combustion. However, no accurate conclusions can be drawn as to the degradation behavior of individual chain components.

For unequivocal proof of complete biodegradability the degradation behavior of the longer aromatic sequences in the copolyester must be proved selectively, since it is well known that high molecular weight pure polybutylene terephthalate (for example, Ultradur®) is not a biodegradable plastic. According to Cowie the following theoretical sequence distributions result from a random copolyester with an acid ratio of 50/50 (Figure 5).[12] As shown in Figure 5, from 100 M_1 and 100 M_2 sequences of the 50/50 copolyester 50 single, 25 double, 12 triple, and only 6 quadruple sequences are in the chain. If the polymer chain is cleaved by biodegradation, longer aromatic sequences might remain as nondegradable or difficult to degrade residues (Scheme 3).

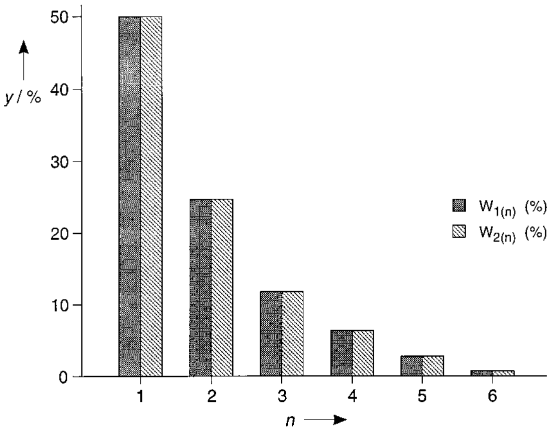


Figure 5. Sequence distributions of a copolymer. Ratio of monomers $[M_1]:[M_2] = 50:50$. $W_{1(n)}$ = Number [%] of the M_1 sequences as a function of the sequence length n; $W_{2(n)}$ = number [%] of the M_2 sequences as a function of the sequence length n.

Table 2. Analysis of residual polymer from 100 g of a dried mixture of compost and polymer for the investigation of compostability of the copolyester Ecoflex according to DIN V 54900, part 3.

Sample	Initial amount of polymer [g/100 g mixture]	Residual polymer [g/100 g mixture]			Residual polymer [%] average
		measurement 1	measurement 2	average	
PS1	15	0.39	0.30	0.35	2.3
PS2	15	0.15	0.22	0.19	1.3
PS3	15	0.57	0.44	0.51	3.4

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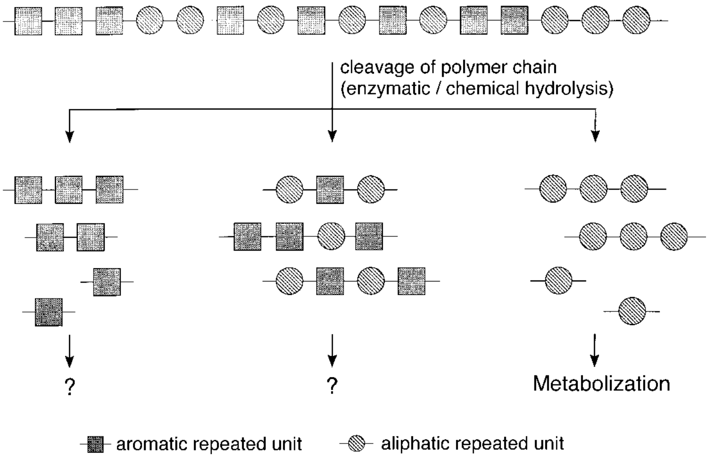


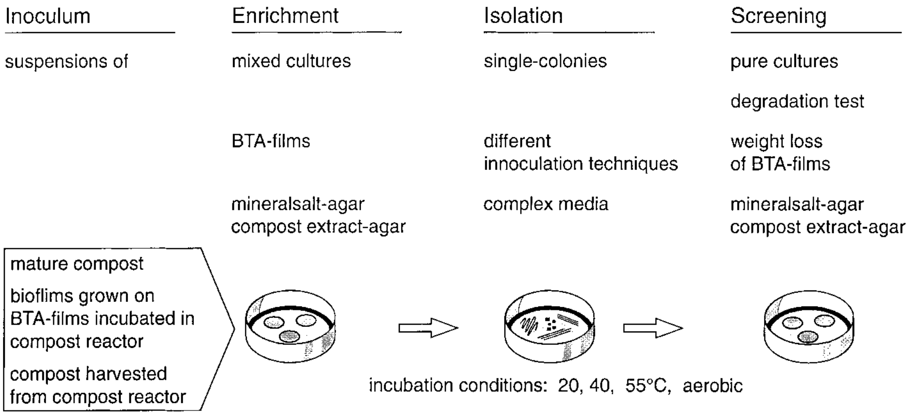
Scheme 3. Degradation of an aliphatic–aromatic copolyester with a random distribution of the monomers along the polymer chain.

Table 3. Fragments of Ecoflex after degradation with isolated pure strain (test 1–3) and with pure and mixed cultures from compost (test 4). × = detected; – = not detected.

Test[a]	Monomers[b]			Aliph. oligomers[b]		Arom. oligomers[b]	
	B	A	T	BA	ABA	BT	BTB
1	×	×	×	×	×	×	×
2	×	×	×	×	×	–	–
3	×	×	×	–	–	–	–
4	–	–	–	–	–	–	–

[a] Test 1: 1750 mg polyester in 80 mL media. Intermediates from isolated pure culture after 21 days. Enzyme activity stopped by pH shift (in situ building of high amounts of acids during degradation). Test 2–4: 350 mg polyester in 80 mL media. Intermediates from isolated pure culture after 7 days (test 2) and after 21 days (test 3). Test 4: Residues after a 7-day innoculation by isolated pure culture and a 14-day innoculation with compost eluate. [b] A: Adipinic acid, B: 1,4 butanediol, T: terephthalic acid. Intermediates from the cleavage of M (see Scheme 4) are not considered. According to test 4 no intermediates were detectable by GC analysis.

To answer the question of complete biodegradability special microorganisms that are able to degrade the copolyester were isolated from compost (Scheme 4).[13] It was possible to use these organisms in an aquatic test system, which is an excellent medium for analyzing polymeric residues. The polymer chain of the copolyester Ecoflex was cleaved with these microorganisms within a few days, and at the end of the test only water soluble intermediates were found. Although the cleavage of the copolyester chain was very fast, the microorganisms were not able to mineralize the fragments. The intermediates therefore accumulated in the aqueous media. The tests were stopped at different times and the water-soluble fragments produced were characterized by GC/MS after derivatization (Table 3) to show the course of the degradation. It could be shown that the isolated microorganisms are able to degrade the polymer chain completely into the monomers. A subsequent complete metabolization of the monomers was possible by adding a mixed culture of microorganisms, which represented the whole spectrum of ubiquitous microorganisms, from the compost to the test solution (Table 3, Test 4). In these test solutions no intermediates were detected by GC analysis.



Scheme 4. Scheme for screening and isolation of microorganisms that are able to degrade the copolyester.

The process in which individual organisms are able to perform only one degradation step, and other organisms the next, and that the microorganisms live off the metabolic products of others is called symbiosis (which means different organisms living together to their mutual benefit). It has not been proved that a symbiosis really happened in this case. It is likely that the copolyester structure "accidently" looks like the structure of natural substrates. This means that the polymer chain could be degraded by the excreted enzymes, but the microorganisms are not able to digest the soluble fragments in their cells.

It could be shown with the described degradation tests that microorganisms that are ubiquitously present in compost are able to degrade materials from petrochemical sources, for example, the aliphatic–aromatic copolyester Ecoflex®, into natural products. Consequently, what is decisive for biodegradability is only the structure and not the origin of the raw material.

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[1] R. W. Lenz, *Adv. Polym. Sci.* **1993**, *107*, 1–40.
[2] J. Schroeter, *Kunststoffe* **1998**, *88*(10), 1822–1830.
[3] Y. Tokiwa, T. Suzuki, *Agric. Biol. Chem.* **1978**, *42*, 1071–1072.
[4] Y. Yakabe, N. Kazuo, T. Hara, Y. Fujino, *Chemosphere* **1992**, *25*(12), 1879–1888.
[5] T. Walter, J. Augusta, R.-J. Müller, H. Widdecke, J. Klein, *Enzyme Microb. Technol.* **1995**, *17*, 218–224.
[6] U. Witt, R.-J. Müller, W.-D. Deckwer, *Macromol. Chem. Phys.* **1996**, *197*, 1525–1535.

[7] U. Witt, R.-J. Müller, W.-D. Deckwer, *J. Environ. Polym. Degrad.* **1997**, *5*, 81–89.
[8] E. Rantze, I. Kleeberg, U. Witt, R.-J. Müller, W.-D. Deckwer, *Macromol. Symp.* **1998**, *130*, 319–326.
[9] U. Witt, R.-J. Müller, W.-D. Deckwer, *J. Environ. Polym. Degrad.* **1995**, *3*, 215–223.
[10] J. C. G. Ottow, *Naturwissenschaften* **1978**, *65*, 413–423.
[11] U. Seeliger (BASF AG), Press release, Ecoflex®—Biologisch abbaubarer Kunststoff von BASF, **1998**.
[12] J. M. G. Cowie, *Chemie und Physik der Polymeren*, VCH, Weinheim, **1976**, p. 96.
[13] I. Kleeberg, C. Hetz, R. M. Kroppenstedt, R.-J. Müller, W.-D. Deckwer, *Appl. Environ. Microbiol.* **1998**, *64*, 1731–1735.

Radical Dimerization of 5,5′-Diphenyl-3,3′,4,4′-tetramethoxy-2,2′-bipyrrole: π Dimer in the Crystal, σ Dimer in Solution.**

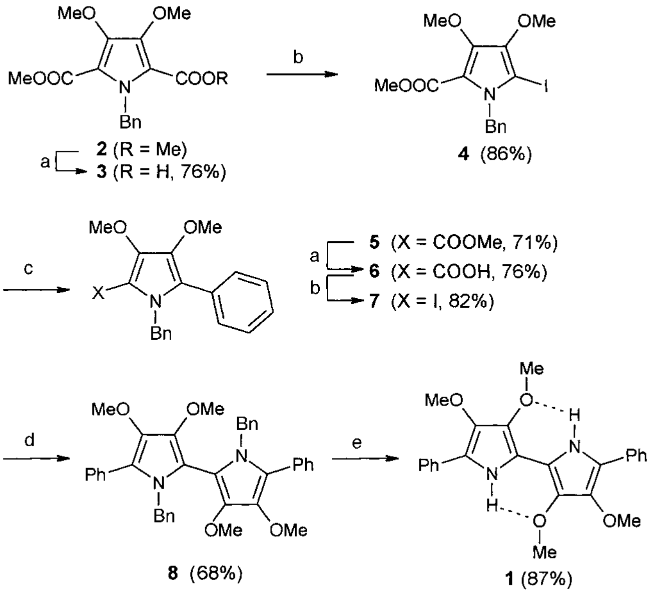
Andreas Merz*, Jürgen Kronberger, Lothar Dunsch, Andreas Neudeck, Andreas Petr, and Laszlo Parkanyi

Dedicated to Professor Gottfried Märkl
on the occasion of his 70th birthday

The highly electron-rich dimethoxypyrrole[1] (DMOP) can be electrochemically polymerized to give good conducting films with conductivities that exceed those of all other 3-, 3, 4-, or *N*-substituted pyrroles, and often even of polypyrrole itself.[2] According to ESR and spectroelectrochemical studies the conductivity of poly-DMOP might involve a transport of the charge carriers not only along the polymer chain but also across neighboring chains by "interchain hopping", similar to the situation in crystalline TTF derivatives and salts of arene cations where π stapling occurs.[3]

Spectroelectrochemical experiments with end-capped pyrrole,[4] thiophene,[5, 6] or mixed thiophene–pyrrole[7] oligomers provide evidence for equilibria between the corresponding radical cations and spinless π dimers. On the other hand a detailed investigation of certain diphenyl polyenes by cyclic voltammetry suggested that the corresponding radical cations dimerize to σ dimers and not to π dimers.[8] In the cited work[8] the existence of π dimers of pyrrole and thiophene oligomers was questioned. Recently, the radical cation of *ω*,*ω*-diphenyl-*α*-terthiophene was shown by an X-ray structure to form endless π staples in which π dimers with shorter distances can be recognized.[9] We now report on diphenyltetramethoxypyrrole **1** whose radical cation crystallizes as a spinless π dimer $(\mathbf{1}^{\bullet+}\cdot\mathrm{PF}_6)_2$ but dimerizes as a σ dimer in solution at low temperature.

The bipyrrole **1** is obtained as shown in Scheme 1 from easily accessible pyrrole **3**.[1c] The important steps are the partial hydrolysis of the of the ester **2**[10] and the iododecarboxylation of carboxylic acids **3** and **6**.[11] The introduction of the phenyl end group is achieved by a Suzuki coupling[12] and an Ullmann coupling in the melt to give **8**.[13] The benzyl group is an ideal protective group for the pyrrole nitrogen atom because a twist in the bond between the pyrrole units makes the intermediates less prone towards oxidation. The removal of the benzyl groups in **8** is achieved smoothly with Na in liquid NH_3 and quenching with aqueous $NaHCO_3$.[14] Using analogous steps higher oligopyrrole homologues with or without end caps are obtained from **2**.[15]



Scheme 1. a) *t*BuOK/H_2O (1/1), THF, 0 °C, 12 h; b) I_2/KI, Na_2CO_3, 12 h, RT, extraction with Et_2O; c) $PhB(OH)_2$, $Pd[PPh_3]_4$, 1,2-dimethoxyethane; d) Cu powder, melt, 200 °C; e) 1. Na, liquid NH_3, 2. EtOH.

The bipyrrole **1** crystallizes from a solution in CH_3OH in two different polymorphic crystals. At 90 °C the tetragonal needles **1a** turn, without melting, into the monoclinic cuboids of **1b**, which melt at 171–172 °C. Both crystal structures (Figure 1)[16] are dominated characteristically by hydrogen bonds between the NH protons of the pyrrole rings and the oxygen atoms of the inner methoxy groups. In **1b** the almost planar D_{2h} molecules are stabilized in an *anti* conformation of the pyrrole rings by H bonds. In the tetragonal modification **1a** the *syn* oriented bipyrroles are arranged with a 90° turn along a C_2 axes by intermolecular H bonds. The H bonds are also seen in the ^1H NMR spectra of **1** as a broad singlet at $\delta = 8$ ($\delta = 7$ for the corresponding signal in DMOP[1a–c]).

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