Keywords: chelates · homogeneous catalysis · multimetallic systems

[1] For a review, see M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, 1–8, and references therein.

[2] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659–663.

[3] U. Kragl, C. Dreisbach, *Angew. Chem.* **1996**, *108*, 684–685; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 642–664.

[4] a) E. C. Constable, A. M. W. Cargill Thompson, *J. Chem. Soc. Dalton Trans.* **1992**, 3467–3475; b) D. Armspach, C. Cattalini, E. C. Constable, C. E. Housecroft, D. Phillips, *Chem. Commun.* **1996**, 1823–1824; c) W. T. S. Huck, B. Snellink-Ruël, F. C. J. M. van Veggel, D. N. Reinhoudt, *Organometallics* **1997**, *16*, 4287–4291; d) W. T. S. Huck, L. J. Prins, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1998**, *120*, 6240–6246; e) J. L. Hoare, K. Lorenz, N. J. Hovestad, W. J. J. Smeets, A. L. Spek, A. J. Canty, H. Frey, G. van Koten, *Organometallics* **1997**, *16*, 4167–4173.

[5] a) M. Albrecht, R. A. Gossage, A. L. Spek, G. van Koten, *Chem. Commun.* **1998**, 1003–1004; b) D. Tzalis, Y. Tor, *Chem. Commun.* **1996**, 1043–1044.

[6] a) H. P. Dijkstra, P. Steenwinkel, J. Patel, D. M. Grove, M. Lutz, A. L. Spek, A. J. Canty, G. van Koten, unpublished results; b) The literature synthesis of **2** starts from 3,5-dimethylaniline and involves well-known organic chemistry such as diazotization, radical bromination, nucleophilic alkoxylation, Pd/Cu-catalyzed Suzuki coupling, Pd-catalyzed cyclotrimerization, and bromo-demethoxylation: K.-H. Duchêne, F. Vögtle, *Synthesis* **1986**, 659–661.

[7] Analytical data: **3**: ^{1}H NMR ($CDCl_3$, 200.13 MHz): $\delta = 6.63$ (s, 18H), 2.98 (s, 24H), 1.87 (s, 72H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 140.4$, 139.8, 136.8, 131.1, 126.8, 63.8, 45.0; elemental analysis calcd for $C_{78}H_{126}B_{12}F_{48}N_{12}$ (**3** $\cdot$ 12 HBF_4): C 41.21, H 5.59, N 7.39; found: C 41.19, H 5.55, N 7.35. **4**: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.0-7.5$ (br m, 48H), 7.40–7.18 (m, 72H), 6.32 (s, 12H), 6.04 (s, 6H), 3.72–3.48 (br s, 12H), 3.08–2.82 (br s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.4$, 138.8, 133.7 (d, ^1J(P,C) = 95 Hz), 132.3, 131.2, 131.1 (d, ^2J(P,C) = 13 Hz), 129.4 (d, ^2J(P,C) = 13 Hz), 128.8, 128.2 (d, ^2J(P,C) = 12 Hz), 36.4 (d, ^1J(P,C) = 65 Hz); ^{31}P NMR ($CDCl_3$, 122 MHz): $\delta = 29.8$ (s); elemental analysis calcd for $C_{198}H_{162}O_{12}P_{12}$: C 76.59, H 5.26, P 11.97; found: C 76.38, H 5.36, P, 11.87. **5**: ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.29-6.94$ (br m, 72H), 6.13 (s, 6H), 3.17–3.24 (br s, 24H); ^{13}C NMR (C_6D_6, 50 MHz): $\delta = 139.6$ (d, ^1J(P,C) = 11.3 Hz), 136.4, 133.5 (d, ^2J(P,C) = 12.1 Hz), 128.4, 128.3, 128.2, 127.9, 127.6, 36.3; ^{31}P NMR (C_6D_6, 54 MHz): $\delta = -7.95$ (s). **6**: ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.22-7.10$ (m, 60H), 6.96 (s, 12H), 6.64 (s, 6H), 3.67 (s, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.1$, 140.9, 139.8, 137.2, 136.0, 130.8, 128.8, 126.9, 125.9, 38.4; elemental analysis calcd for $C_{126}H_{102}S_{12}$: C 75.63, H 5.14, S 19.23; found: C 75.85, H 5.29, S 19.42. **7**: ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.60-7.28$ (br m, 60H), 6.50 (br s, 12H), 4.08 (br s, 24H). **8**: ^{1}H NMR (CD_3CN, 200 MHz): $\delta = 7.42-7.61$ (br m, 60H), 6.55 (br s, 12H), 4.41 (br s, 24H), 2.57 (br s, 18H).

[8] P. Steenwinkel, S. Kolmschot, R. A. Gossage, P. Dani, N. Veldman, A. L. Spek, G. van Koten, *Eur. J. Inorg. Chem.* **1998**, 477–483.

[9] Crystals of **7** were obtained by slow evaporation (in air) of a solution of **7** in a toluene/CH_2Cl_2 mixture. $C_{126}H_{96}Cl_6Pd_6S_{12} \cdot$ solvent, $M_r = 2845.85$, trigonal, $R3$, $a = b = 27.195(3)$, $c = 15.728(4)$ Å, $V = 10074(3)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.407$ g cm^{-3}, $T = 150(2)$ K, $(\sin\vartheta/\lambda)_{max} = 0.649$ Å^{-1}, yellow block $0.25 \times 0.38 \times 0.38$ mm^3, 9086 measured reflections, of which 8113 were unique ($R_{int} = 0.051$), R values ($I > 2\sigma(I)$): $R1 = 0.0756$, $wR2 = 0.1709$, all data: $R1 = 0.1201$, $wR2 = 0.1942$. $-0.52 < \Delta\rho < 1.06$ e Å^{-3}. Enraf-Nonius CAD4T diffractometer with rotating anode ($\lambda = 0.71073$ Å). Absorption correction based on psi scans ($\mu = 1.14$ mm^{-1}, 0.82–0.97 transmission). Structure solution with direct methods (SHELXS-97[8c]). Structure refinement with SHELXL-97[8a] against F^2. 415 parameters, 276 restraints. The SPh groups were heavily disordered and refined with isotropic parameters. All other non-hydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups. Structure graphics, checking for higher symmetry, absorption correction, and treatment of disordered solvent (CALC SQUEEZE, 830 e$^-$ per unit cell) were performed with the program PLATON.[8b] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114913. 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). a) G. M. Sheldrick SHELXL-97. Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, **1997**; b) A. L. Spek PLATON. *A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands; c) G. M. Sheldrick SHELXS-97. Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, **1997**.

[10] a) A. A. H. van der Zeijden, G. van Koten, R. Luijk, K. Vrieze, C. Slob, H. Krabbendam, A. L. Spek, *Inorg. Chem.* **1988**, *27*, 1014–1019; b) M.-C. Lagunas, R. A. Gossage, A. L. Spek, G. van Koten, *Organometallics* **1998**, *17*, 731–741.

[11] a) C. J. Moulten, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1976**, 1020–1024; b) H. Rimml, L. M. Venanzi, *J. Organomet. Chem.* **1983**, *259*, C6–C7; c) S. Nemeh, C. Jensen, E. Binamira-Soriaga, W. C. Kaska, *Organometallics* **1983**, *2*, 1442–1447; d) M. E. van der Boom, M. Gozin, Y. Ben-David, L. J. W. Shimon, F. Frolow, H.-B. Kraatz, D. Milstein, *Inorg. Chem.* **1996**, *35*, 7068–7073; e) P. Dani, T. Karlen, R. A. Gossage, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1997**, *119*, 11317–11318.

[12] a) J. Errington, W. S. McDonald, B. L. Shaw, *J. Chem Soc. Dalton Trans.* **1980**, 2312–2314; b) J. Dupont, N. Beydoun, M. Pfeffer, *J. Chem Soc. Dalton Trans.* **1989**, 1715–1720; c) S. J. Loeb, G. K. H. Shimizu, *J. Chem. Soc. Chem. Commun.* **1993**, 1395–1397.

[13] For a brief review on aryl–R bond activation, see P. Steenwinkel, R. A. Gossage, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 759–762.

[14] a) F. Gorla, A. Togni, L. M. Venanzi, A. Albinati, F. Lianza, *Organometallics* **1994**, *13*, 1607–1616; b) M. A. Stark, C. J. Richards, *Tetrahedron Lett.* **1997**, *38*, 5881–5884; c) J. M. Longmire, X. Zhang, M. Shang, *Organometallics* **1998**, *17*, 4374–4379; d) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687–11688; e) M. Gupta, C. Hagen, W. C. Kaska, R. E. Cramer, C. M. Jensen, *J. Am. Chem. Soc.* **1997**, *119*, 840–841; f) L. A. van de Kuil, D. M. Grove, R. A. Gossage, J. W. Zwikker, L. W. Jenneskens, W. Drenth, G. van Koten, *Organometallics* **1997**, *16*, 4985–4994.

Supramolecular Structure of Precipitated Nanosize β-Carotene Particles

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Jens Rieger, and Horst Weiss

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

As a consequence of the recent advances in formulation techniques lipophilic active substances can be precipitated as particles in the nanometer size range.[1–4] These particles exhibit superior properties with respect to bioavailability, dispersibility in water, and color than previous larger particles. Although several carotenoids that display these desirable

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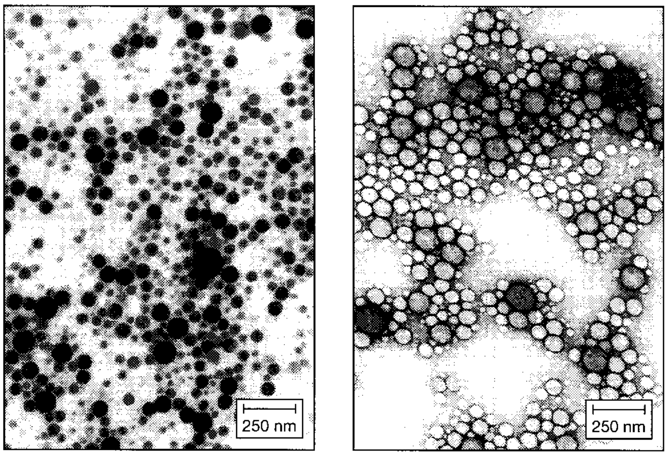
properties are formulated by precipitation techniques and are readily available as commercial products, the supramolecular structure of the nanosize particles has not yet been fully elucidated. Herein we briefly review our precipitation technique and then show how the combination of electron microscopy, light scattering, X-ray scattering, and UV/Vis absorption spectroscopy in conjunction with molecular modeling calculations yields a detailed picture of the supramolecular and the microscopic structure of precipitated β-carotene particles.

The process of mixing chamber micronization was developed for the precipitation of carotenoids.[1, 2] In this process a molecularly disperse solution of a carotenoid in a water-miscible solvent, for example, an alcohol, is mixed turbulently with an aqueous phase. The aqueous phase usually contains dissolved polymer that acts as a protective colloid. The turbulent mixing of the solvent phase with the water phase rapidly changes the character of the solvent and induces nucleation and growth of carotenoid particles. The protective polymer, for example, gelatin, plays an essential role in providing excellent colloidal stability to the nanosize particles.[5] Thus, the primarily obtained colloidally stable hydrosol can be concentrated and subsequently transformed into dry powder by techniques such as spray-drying.

The development of the precipitation technique was accomplished by the use of appropriate analytical methods. The size of nanoparticles is usually determined by quasi-elastic light scattering (QELS). Standard QELS, however, requires high dilution of the samples. Therefore, we developed fiber-optic quasi-elastic light scattering (FOQELS), which is applicable even to highly concentrated hydrosols and which can be applied on-line for the control of production processes.[6–8] The electrophoretic mobility and the ζ-potential of the particles was determined by means of microelectrophoresis.[5]

A first insight into the microscopic structure of the precipitated particles was obtained by electron microscopy. Figure 1 shows β-carotene particles obtained by precipitation in a mixing chamber. By using different staining procedures both the carotenoid and the protective colloid can be visualized separately: the carotenoid is stained with OsO_4, whereas staining with UO_2-acetate brings about the contrast of the gelatin. From Figure 1 it can be seen that the particles exhibit a core/shell structure with a β-carotene core surrounded by a gelatin shell. The average size of the particle core is about 120 nm. The thickness of the adsorbed gelatin layer in water was determined by QELS.[2, 5] We found that above the isoelectric point (IEP), that is, above about pH 5 for B-type gelatin, the thickness of a typical gelatin layer is about 40 nm. Above the IEP gelatin adsorbs onto the core through hydrophobic interactions that lead to a loose conformation with many loops and tails.[5, 9]



β-carotene stained protective colloid stained

Figure 1. Transmission electron micrographs of precipitated β-carotene particles. The core/shell structure is visualized by applying different staining techniques: the β-carotene core is contrasted with OsO_4 (left), whereas the gelatin shell is contrasted with UO_2-acetate (right).

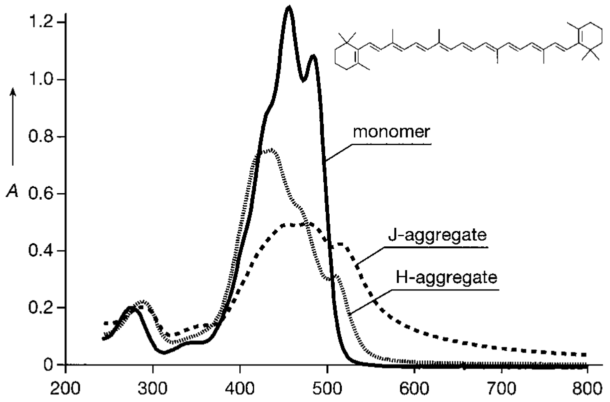


Figure 2. UV/Vis absorption spectra of a 5 ppm β-carotene solution and of 5 ppm β-carotene hydrosols. The solvent for the monomer spectrum was cyclohexane. The H-aggregated β-carotene hydrosol was precipitated under dilute conditions. The J-aggregated β-carotene hydrosol was precipitated at higher concentration and in the presence of corn oil.

Until now information on the supramolecular structure of the core of the precipitated carotenoid particles was scarce. The only information available was deduced from UV/Vis absorption spectra. Figure 2 shows the UV/Vis absorption spectrum of the β-carotene monomer molecules dissolved in cyclohexane and the spectra of two differently precipitated β-carotene hydrosols. The curve labeled "H-aggregate" was obtained from a β-carotene hydrosol that was precipitated under dilute conditions, that is, which yield a β-carotene concentration of 0.3 weight %. In this case the overall particle size, including the gelatin layer, is about 150 nm. The sample corresponding to the curve labeled "J-aggregate" was precipitated at higher concentration (1.0 weight % β-carotene) and with the solvent phase containing 40 % corn oil with respect to β-carotene. The overall particle size in this sample is about 250 nm. There are two major parameters that affect the UV/Vis spectra: particle size and type of supramolecular aggregation of the β-carotene molecules. As a consequence of the different particle sizes the trailing edge of the spectra at long wavelengths is more pronounced for the larger particles, since Mie scattering effects of larger particles contribute more to the long wavelength absorbance than they do for smaller particles. In addition to the effect of particle size, a hypsochromic shift of about 40 nm is observed for the "H-aggregate" sample and a bathochromic shift is observed for the "J-aggregate" sample. These spectral shifts can be explained by self-assembly of the β-carotene molecules during the precipitation process. It is assumed that the hypsochromic shift results from H-type aggregation ("card stack" structure), whereas the bathochromic shift has its origin in J-type aggregation, namely, "head-to-tail" or "herring bone"-type aggregation.[2] As a consequence of these spectroscopic shifts the color of the β-carotene hydrosols can be adjusted from a clear yellow to a bright orange.

The optical transitions in β-carotene crystals were investigated by Gaier et al.[10] It was not possible to locate the Davydov components because of the strong absorption and the thickness of the crystals. However, the absorption maximum, which is a $S_0(1^1A_g)\rightarrow S_2(1^1B_u)$ transition, was determined from reflectance spectra to be located at 18700 cm^{-1}, which corresponds to 535 nm. The first absorption band of β-carotene has its maximum at 20950 cm^{-1} (477 nm) in hexane or light petroleum, neither of which exhibit any solvent shift for carotenoids.[11]

Molecular modeling calculations were performed to further confirm the supposition that the observed spectral shifts are a result of molecular aggregation. The quantum mechanical CIS-method[12] in the semi-empirical INDO/1-model as implemented in the ZINDO-package[13] has been used for the calculation of both the transitions and the corresponding oscillator strengths for both the single β-carotene molecule and aggregates up to tetramers. The results are summarized in Table 1.

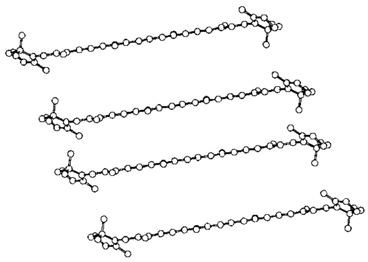
Table 1. UV/Vis transitions and corresponding oscillator strengths of β-carotene calculated with the quantum mechanical CIS-method for an isolated monomer, for an ideal, parallel oriented tetramer aggregate, and for tetramer supercells comprising two unit cells along the crystallographic *a*, *b*, and *c* axes, respectively.

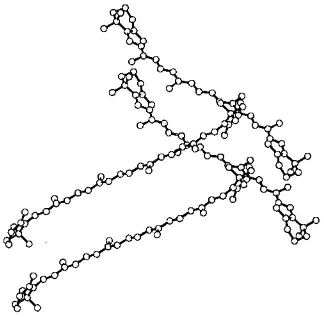
Orientation (*a*, *b*, *c*)[a]	Absorption maximum	Oscillator strength
monomer molecule	509 nm	3.9
ideal H-aggregate	465 nm	16.4
(2_1_1)-aggregate	500 nm	2.3
	469 nm	14.3
(1_2_1)-aggregate	553 nm	4.0
	502 nm	9.6
(1_1_2)-aggregate	519 nm	2.1
	487 nm	13.4

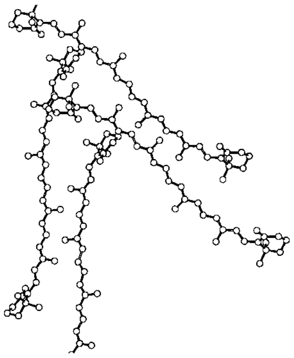
[a] The symbolism used to describe how the unit cells are joined is used to avoid any confusion with Miller indices or with the description of crystal surfaces.

The geometry for a single, isolated monomeric β-carotene molecule in the gas phase has been optimized by applying density functional theory (DFT).[14] An absorption maximum is obtained from this structure at 509 nm, which is considered to be in satisfactory agreement with the observed absorption wavelength of 477 nm. However, the amount of the relative shift that arises from molecular aggregation is much more relevant than the absolute position of the first absorption maximum.

The results of the calculations for β-carotene tetramers give a rough estimate of packing effects. First, in a model calculation, four β-carotene molecules were oriented in a parallel arrangement ("ideal" H-aggregate). For this tetramer we obtained a hypsochromic shift of 44 nm. Then, for the calculation of the optical transitions of "real" tetramers, we took four β-carotene molecules as they are oriented in two crystallographic unit cells,[15] where the unit cells are joined along the *a* axis (2_1_1), the *b* axis (1_2_1), and the *c* axis (1_1_2), respectively. The model aggregates are depicted in Figure 3. In order to ensure that the calculated shifts result from packing effects the molecules in the supercells were replaced by the DFT-optimized structure of the isolated molecule. The tetramer in the (2_1_1)-supercell resembles two H-aggregates and a strong hypsochromic shift of 40 nm


ideal H-aggregate


(2_1_1)-aggregate


(1_2_1)-aggregate

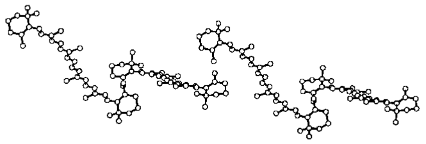

(1_1_2)-aggregate

Figure 3. Pictorial presentation of various β-carotene tetramer configurations: ideal, parallel-oriented molecules, and tetramer supercells comprising the molecules of two unit cells along the crystallographic *a*, *b*, and *c* axes, respectively.

was calculated. A bathochromic shift of 44 nm and a hypsochromic shift of 7 nm were calculated for the (1_2_1)-tetramer. Therefore, this aggregate is close to a J-aggregate and, in accordance with the simple exciton model, we find that for J-aggregates two optical transitions are allowed.[16] The (1_1_2)-tetramer yields a predominant hypsochromic shift of 22 nm and a weak transition at 519 nm. This structure, therefore, corresponds to weakly coupled H-aggregates.

The spectral features described above and the semiempirical calculations of the optical transitions give evidence for the existence of domains of regularly aggregated β-carotene molecules. However, regularly packed molecules should yield Bragg peaks in wide-angle X-ray scattering (WAXS). Therefore, a WAXS study was performed with a diffractometer (type D 5000, Siemens) operating in the reflection mode with $Cu_{K\alpha}$ radiation. The WAXS diffractograms were analyzed with respect to crystallite size by means of a line-width analysis. The width of any Bragg peak is determined by the crystallite size, by lattice distortions, and by broadening from the apparatus. By neglecting the latter two effects, for reasons which will be discussed below, one can use the Scherrer equation to determine the average crystallite size.[17]

For both samples under consideration we obtained crystallite sizes in the order of 30 nm from analysis of two pronounced peaks in the angle range $10^\circ \leq 2\Theta \leq 13^\circ$. By comparing the magnitude of the line broadening that arises from the X-ray diffractometer with the obtained line widths of our samples one can conclude that the effect of the apparatus can be neglected in the case of such small crystallite sizes. Less can be said about the existence of lattice distortions. The quality of the higher order Bragg peaks is not sufficient to decide whether lattice distortions are present or not. However, we assume that lattice distortions should only play a minor role in these small crystallites. Contrary to the case of metals or polymeric materials, it is likely that the crystallites grow without tensions.

In summary, we arrive at the following picture of the precipitated β-carotene particles (Figure 4): the particles have a core/shell structure. The shell consists of an adsorbed gelatin layer, which has a thickness of about 40 nm when the particles are dispersed in water at pH values above the IEP of the gelatin. The core of the particles consists essentially of regularly aggregated β-carotene molecules. In these aggregates either H- or J-aggregate morphologies prevail, depending on the precipitation conditions. Aggregates with small aggregation numbers do not give measurable Bragg peaks in the WAXS experiments. The larger aggregates yield an average crystallite size of about 30 nm. This crystallite size corresponds to an aggregation number of the order of 10000 molecules. The overall size of the particle core is about 120 nm. Consequently, according to our model the particle core is a composition of aggregated β-carotene molecules with a wide range of aggregation numbers.

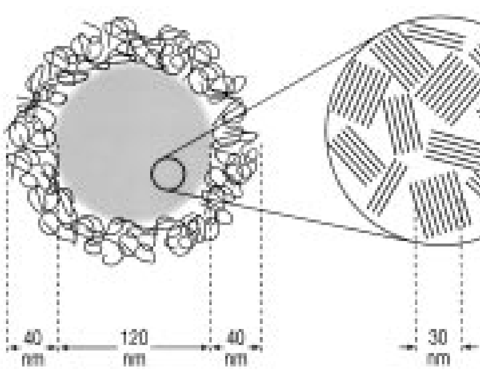


Figure 4. Core/shell structure of precipitated β-carotene particles. The particle core contains aggregated β-carotene molecules of various aggregate sizes. The largest aggregates are about 30 nm, as determined by WAXS. The particle shell consists of adsorbed gelatin which acts as a stabilizing hydrocolloid.

Received: January 5, 1999 [Z12874IE]
German version: *Angew. Chem.* **1999**, *111*, 2325–2328

Keywords: aggregation · carotenoids · nanostructures · semiempirical calculations

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[1] D. Horn, *Angew. Makromol. Chem.* **1989**, *166/167*, 139–153.
[2] "Fine Particles Science and Technology": D. Horn, E. Lüddecke, *NATO ASI Ser. 3* **1996**, *12*, 761–755.
[3] C. Köpsel, H. Auweter, H. Bettermann, J. Benade, E. Lüddecke, S. Beutner, H. D. Martin, B. Mayer, *Colorchemistry* **1998**, 1–4.
[4] H. Auweter, J. Benade, H. Bettermann, S. Beutner, C. Köpsel, E. Lüddecke, H. D. Martin, B. Mayer, *Proc. Pigm. Food Technol.* **1999**, in press.
[5] H. Auweter, V. André, D. Horn, E. Lüddecke, *J. Dispersion Sci. Technol.* **1998**, *19*, 163–184.
[6] H. Auweter, D. Horn, *J. Colloid Interface Sci.* **1985**, *105*, 399–409.
[7] H. Wiese, D. Horn, *J. Chem. Phys.* **1991**, *94*, 6429–6443.
[8] H. Wiese, D. Horn, *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1589–1597.
[9] K. A. Vaynberg, N. J. Wagner, R. Sharma, P. Martic, *J. Colloid Interface Sci.* **1998**, *205*, 131–140.
[10] K. Gaier, A. Angerhofer, H. C. Wolf, *Chem. Phys. Lett.* **1991**, *187*, 103–109.
[11] "Spectroscopy": G. Britton in *Carotenoids, Vol. 1 B* (Eds.: G. Britton, S. Liaaen-Jensen, H. Pfander), Birkhäuser, Basel, **1995**, pp. 13–62.
[12] J. Foresman, M. Head-Gordon, J. Pople, M. Frisch, *J. Phys. Chem.* **1992**, *96*, 135–149.
[13] M. C. Zerner, ZINDO program, QTP, University of Florida, Gainesville, FL; see also M. C. Zerner, G. H. Loew, R. F. Kirchner, U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **1980**, *102*, 589–599.
[14] The DFT calculations have been performed with the Karlsruhe Quantum Chemistry package TURBOMOLE (R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169.), a B-P86 (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8825) gradient-corrected density functional and a SV(P) basis set (A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835) have been used.
[15] C. Sterling, *Acta Crystallogr.* **1964**, *17*, 1224–1228.
[16] M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371–392.
[17] L. E. Alexander, *X-Ray Diffraction Methods in Polymer Science* Wiley, New York, **1969**, pp. 423–424.