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Functional Nanoparticles

Thermoresponsive and Photoluminescent Hybrid Silicon Nanoparticles by Surface-Initiated Group Transfer Polymerization of Diethyl Vinylphosphonate**

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Abstract: *We present a method to combine the functional features of poly(diethyl vinylphosphonate) (PDEVP) and photoluminescent silicon nanocrystals. The polymer–particle hybrids were synthesized in three steps through surface-initiated group transfer polymerization using $Cp_2YCH_2TMS(thf)$ as a catalyst. This pathway of particle modification renders the nanoparticle surface stable against oxidation. Although SiNC properties are known to be sensitive toward transition metals, the hybrid particles exhibit red photoluminescence in water. The temperature-dependent coiling of PDEVP results in a change of the hydrodynamic radius of the hybrid particles in water. To the best of our knowledge, this is the first example of controlled catalytic polymerization reactions on a silicon nanocrystal surface.*

In 1992, Yasuda et al. developed a new route of catalytic polymerization reactions, utilizing the rare earth metal catalyst [$Cp^*_2SmMe(THF)$] for the polymerization of methyl methacrylate to high molecular weight polymers.[1] The concept of this so-called rare earth metal-mediated group transfer polymerization (REM-GTP) was recently optimized and applied to a variety of monomers.[2] Especially dialkyl vinylphosphonates (DAVPs), which are structurally and electronically similar to acrylates, can easily be polymerized by REM catalysts yielding polymers with molecular weights in the region of 100 to 1000 kDa.[3–5] The obtained PDAVPs, for instance, poly(diethyl vinylphosphonate) (PDEVP), are water-soluble and exhibit thermoresponsivity close to the physiological range.[4] The temperature of this so-called "lower critical solution temperature (LCST) effect" is adjustable in the range of 5 °C to 92 °C by changing the comonomer composition of DEVP and di-*n*-propyl vinylphosphonate (DPVP), forming almost perfect alternating statistic copolymers.[6]

An additional important step was the development of covalently bound PDAVP brushes on flat surfaces for biomedical applications (cell growth and release surfaces). A REM catalyst, namely bis(cyclopentadienyl ytterbium methyl) [Cp_2YbMe] was immobilized on a modified silicon surface and the polymer growth occurred linearly within a few minutes. The polarity of the homogeneous surface layer can be tailored by temperature changes.[7]

The effects and strategies described before are useful for the modification of photoluminescent silicon nanocrystals (SiNCs). The application of such SiNCs requires non-agglomerating dispersions that are reasonably stable against oxidation. Such stability is readily achieved by a covalently bound organic layer that protects the particles against oxidation and renders them dispersible in various solvents.[8,9] In most cases, robust organic layers are formed through the hydrosilylation of unsaturated carbon compounds like dodecene or styrene with Si–H-terminated surfaces.[8,10,11] Instead of applying high temperatures, UV-light is often used as a mild hydrosilylation method.[11–13] Due to the size-dependent optical properties, the reactivity of SiNCs and bulk silicon surfaces often differ drastically and the mere adaption of existing protocols is likely to fail.[13] Routes to defined polymeric structures on SiNC surfaces are scarce in literature.[14,15] Hybrid particles bearing polymeric compounds on their surfaces offer the opportunity to combine the optoelectronic properties of the quantum dots with the polymer characteristics and are therefore of great interest.

Here we present a catalytic method to combine the material properties of PDEVP with the optoelectronic properties of SiNCs with a size of 3 nm. The PDEVP cover was grown using REM-GTP starting from methyl acrylic surface groups. Furthermore, we demonstrate the unique properties of both, SiNCs and PDEVP, united in one particular system.

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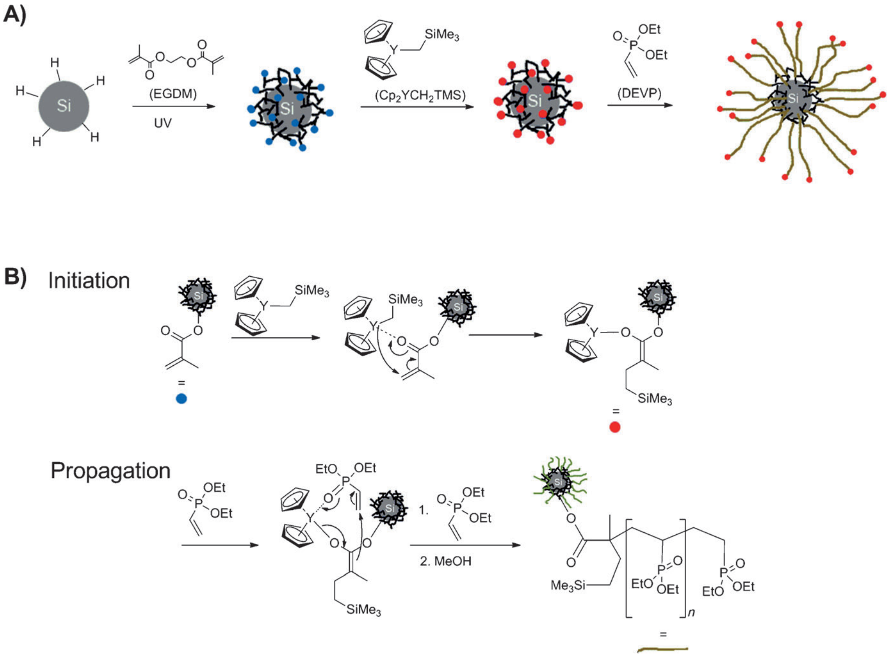

Scheme 1. A) Schematic description of the SI-GTP (grey: silicon nanocrystal, black: PEGDM network, blue: free methyl acrylate terminated binding sites, red: activated catalyst species, green: PDEVP chains). B) Insights into the mechanism of the SI-GTP achieved with methyl acrylic groups as initiating ligand and DEVP as the monomer.[16]

SiNCs with diameters of 3 nm were obtained in a silica matrix by the heating of hydrogen silsesquioxane (HSQ) for 1 h at 1100 °C under a slightly reducing atmosphere (5 % H_2/95 % Ar). SiNCs were liberated by HF etching, before the photografting of ethylene glycol dimethacrylate (EGDM).[16] UV irradiation (365 nm) of the SiNCs in an EGDM solution overnight leads to nanoparticles with free methyl acrylic surface groups (Scheme 1 A). Afterwards, the solution was diluted and centrifuged. Silicon nanocrystals-*graft*-poly(ethylene glycol dimethacrylate) (SiNCs-*g*-PEGDM) particles were sedimented by centrifugation, whereas the free homopolymer, which was formed in side reactions, was precipitated from the supernatant using pentane as an antisolvent. The particle fraction was redispersed in toluene and centrifuged to separate the residual monomer. The success of the EGDM grafting was seen in attenuated total reflectance infrared spectroscopy (ATR-IR) by a decrease of the Si−H stretch at 2109 cm^{-1} and the emergence of a C=O (1733 cm^{-1}) and C−O stretching band at 1170 cm^{-1} (Figure 1 A). Additionally, very weak C=C stretch vibrations were recorded at 1652 cm^{-1} (Figure 1 A).

The dried SiNCs-*g*-PEGDM particles were redispersed in dry toluene and impregnated with the GTP-catalyst $Cp_2YCH_2TMS(thf)$ (15.9 μmol related to 100 mg silicon–silica composite material), which coordinated to the carbonyl functionality of the residual methyl acrylic groups. This effected a covalently bound catalyst–enolate species at the surface (Scheme 1 B).[17] An aliquot of the sample was isolated and centrifuged two times under inert gas atmosphere for purification. The initiation reaction of the catalyst on the surface was followed using ATR-IR spectroscopy. ATR-IR analysis showed a decrease of the carbonyl vibration at 1733 cm^{-1}, while other bands remained constant, which is in accordance with the formation of the catalyst–enolate species (Figure 1 B).

The impregnated particles were reacted without further purification. Due to the slow initiation rate in solution,[17] an excess of catalyst was used as water scavenger to protect the catalytic species at the surface during polymerization. GTP on the particle surfaces starts immediately after the addition of DEVP. The chain propagation proceeds comparably fast to the initiation reaction, according to an eight-electron process (Scheme 1 B).[3–5,17] The polymerization was terminated after one hour by the addition of methanol and yielded linearly grown PDEVP layers, which are covalently bound to the SiNCs (SiNCs-*g*-PEGDM-*g*-PDEVP; Scheme 1 A). The purification was achieved by redispersion and subsequent centrifugation processes in toluene and methanol (see above). The PDEVP-functionalized SiNCs exhibited vinylphosphonate bands (P=O stretch at 1220 cm^{-1} and the P−O stretch at 1015 cm^{-1}) of strong intensity compared to the bands of the methyl acrylic group (C=O at 1733 cm^{-1} and C−O at 1170 cm^{-1}), which indicates the formation of a PDEVP cover (Figure 1 A). Furthermore, the appearance of the CH_2 bending vibration at 1451 cm^{-1}, which could be assigned to the polymer backbone, demonstrates the existence of poly(diethyl vinylphosphonate).

The photografting of EGDM, catalyst impregnation, and the polymerization were proven by X-ray photoelectron spectroscopy (XPS; Figure S1–3) and electron-dispersive X-ray spectroscopy (EDX; Figure S4–6). We used X-ray diffraction measurements (XRD) to confirm the presence of the SiNCs in the hybrid systems (Figure S7). Asymmetric flow-field flow fractionation (AF4) measurements confirmed the purity of SiNCs-*g*-PEGDM-*g*-PDEVP. We could show that after three centrifugation steps, the polymer was quantitatively washed out and only polymer-modified particles were collected in the pellet (Figure S12). Homopolymer, which was found in the supernatant of the first centrifugation was mixed with some of the particles to confirm the separation by AF4 (Figure S13).

To evaluate the weight proportions of PEGDM, PDEVP, and SiNCs, TGA measurements were performed (Figure S9). In the SiNCs-*g*-PEGDM system, the amount of SiNCs is dominating compared to PEGDM (Table 1). After surface-initiated group transfer polymerization (SI-GTP), a distinct quantity of PDEVP was found, whereas the SiNCs as well as PEGDM are the minor species.

The bifunctional acrylic monomer EGDM generated aggregates of both, EGDM and covalently linked silicon nanocrystals. There were no single nanocrystals detected in

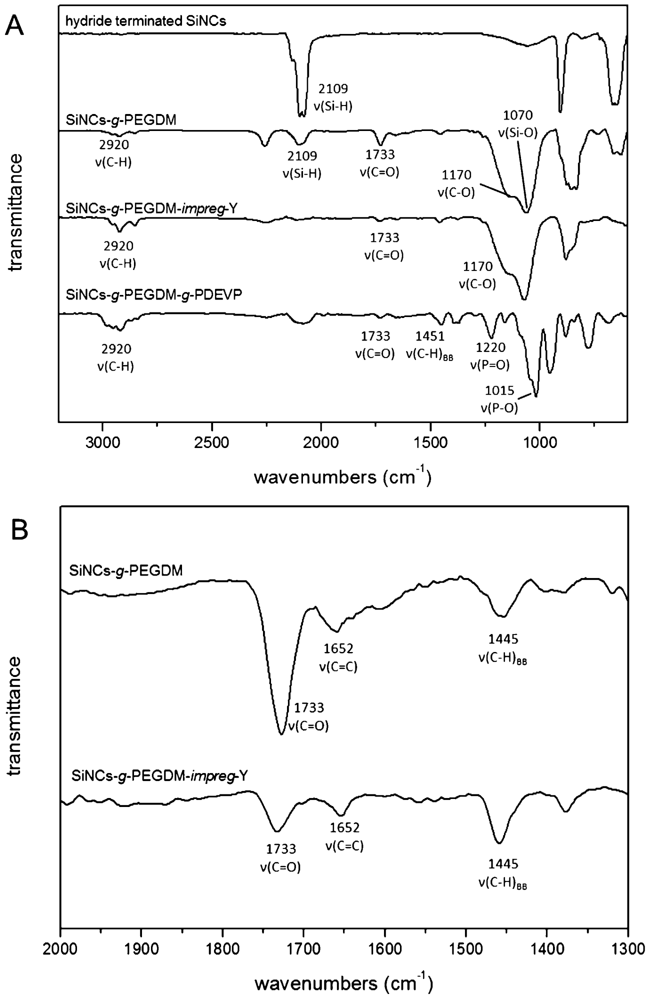

Figure 1. A) ATR-IR of hydride-terminated silicon nanocrystals, SiNCs-*g*-PEGDM, $Cp_2YCH_2TMS(thf)$-impregnated SiNCs-*g*-PEGDM (SiNCs-*g*-PEGDM-*impreg*-Y), and SiNCs-*g*-PEGDM-*g*-DEVP. B) Magnification of SiNCs-*g*-PEGDM and SiNCs-*g*-PEGDM-*impreg*-Y.

Table 1: Amounts of PEGDM, PDEVP, SiNCs, and the hydrodynamic radii (R_h) of the products.

	EGDM [wt%][a]	PDEVP [wt%][a]	SiNCs [wt%][a]	R_h [nm][b]
SiNCs-*g*-PEGDM	20	–	80	177 ± 81
SiNCs-*g*-PEGDM-*g*-PDEVP	4	81	15	441 ± 96

[a] Calculated from TGA measurements. [b] Obtained by DLS measurements using a regularization fit: SiNCs-*g*-PEGDM in ethylacetate; SiNCs-*g*-PEGDM-*g*-PDEVP in water.

transition electron microscopy (TEM) and dynamic light scattering (DLS) and the aggregates could not be redispersed by intense ultrasonication. We have shown earlier that dodecene, which is not known as a good monomer, tends to oligomerize during SiNC modification, and thus we conclude, hat EGDM tends to build up network structures.[18] We argue from the hydrodynamic radius (R_h) of 177 nm found by DLS (Table 1, Figure S10), which is much larger than the obtained radius from TEM images (Figure S8), that SiNCs-*g*-PEGDM underwent swelling while dispersed in ethyl acetate. Organic acrylates are known to be soluble in polar organic solvents like ethyl acetate, but not in water.[19] We believe that the EGDM layer collapses after SI-GTP, when a bulky PDEVP layer (Figure S11) coats the outer sphere of the SiNC-*g*-PEGDM aggregates. Particles coated with PDEVP were well dispersible in water at room temperature, whereas SiNCs-*g*-PEGDM could not be dispersed in water.

Some polymers show an LCST behavior that is caused by thermoresponsive coiling.[20] PDAVPs and their copolymers coil in a particularly narrow temperature interval and then precipitate from solution.[4,6] The temperature-dependent determination of the hydrodynamic radii of our particle–polymer combination by DLS indicated a thermoresponsive behavior of SiNCs-*g*-PEGDM-*g*-PDEVP. The hydrodynamic radius (R_h) decreased in a temperature range of 30 to 55 °C, probably due to coiling of surface polymers (Figure 2B). The smallest hydrodynamic radius, observed at temperatures above 55 °C, was 140 nm, smaller than the average radius of the swollen SiNCs-*g*-PEGDM determined in ethyl acetate. We believe that the PEGDM layer collapses in water and the PDEVP layer coils at above 55 °C. When the system was cooled to room temperature, R_h grew above the value found for freshly prepared particles. We assume that the increase in R_h after one temperature cycle is due to an elongation of the PDEVP chains on the surface to the maximum. The particles become too unpolar and slowly precipitate from water.

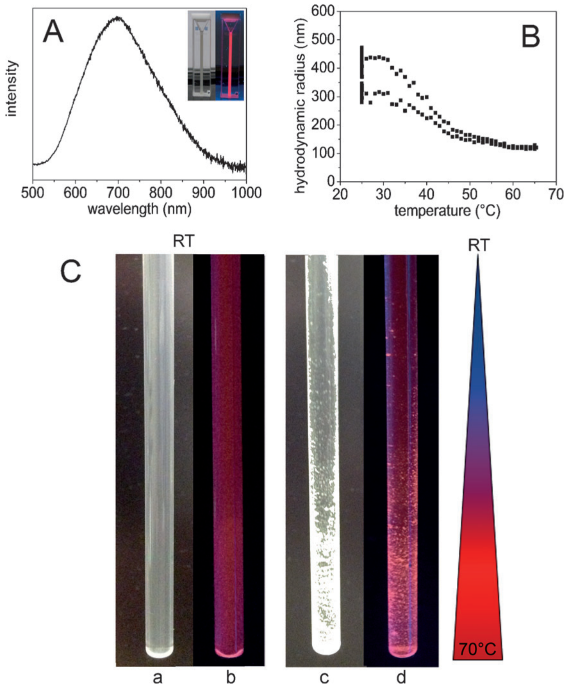

Figure 2. A) Red photoluminescence of SiNCs-*g*-PEGDM-*g*-PDEVP in water upon irradiation at 365 nm. B) LCST measurement (temperature gradient 1 °C min^{-1}, equilibration 1 min) of SiNCs-*g*-PEGDM-*g*-PDEVP in water. C) Turbid dispersion of SiNC-*g*-PEGDM-*g*-PDEVP in water at ambient conditions (a) and under UV-light (b). After heating the bottom part of the tube to 70 °C for several hours aggregates can be seen (c) and photoluminescence is focused to the aggregated part (d).

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Grafting PDEVP from SiNC surfaces leads to water-dispersible particle systems with thermoresponsive behavior and red-light photoluminescence (PL, Figure 2A,B). To achieve a visible correlation of these effects, we heated the bottom part of a glass NMR tube containing a dispersion of SiNCs-*g*-PEGDM-*g*-PDEVP to 70 °C, while the upper part was kept at room temperature. After a few hours, we obtained a precipitate at the glass wall, which showed more focused PL then the residual dispersion (Figure 2C(c),(d)). This behavior and the absence of photobleaching might allow applications as conducting membranes or flocculating agents.[5] To adapt the nanohybrid sensors to their field of application, the temperature range and haziness of the demonstrated thermoresponsive behavior can be tuned by the copolymerization of different water-soluble PDAVPs, as shown previously.[6] Efforts towards the application of this method on freestanding 3 nm silicon nanocrystals might open chances in the biomedical field, for example, in bioimaging.[15]

In summary, we have shown an unprecedented method to decorate surfaces of photoluminescent SiNCs with a size of 3 nm with hydrophilic polymers. This was achieved in a three-step synthesis route. First PEGDM was photografted on the hydride-terminated silicon nanocrystal surface under near UV conditions, whereby the methyl acrylic groups remain intact. Further steps allow the attachment of bis(cyclopentadienyl)trimethylsilylmethylyttrium(thf), forming an enolate intermediate, which is known to be an efficient catalyst for group transfer polymerization reactions. Thus, we polymerized DEVP on the silicon nanoparticle surfaces using a catalytic pathway. Thermogravimetric analysis (TGA), DLS, and TEM measurements evidence the thick PDEVP covers on the SiNC surfaces. Although the SiNCs were in contact with a transition metal center, the obtained products exhibit photoluminescence in water. In combination with the LCST effect of the stimuli-responsive polymer, which was demonstrated by temperature-dependent DLS measurements, these particles are an interesting example for the combination of the properties of SiNCs and functional polymers. Further development with regard to the application of this catalytic method to the surface of freestanding silicon nanocrystals with a size of 3 nm are currently under way.

Experimental Section

All details about the synthesis of silicon nanocrystals, SiNCs-*g*-PEGDM, and SiNCs-*g*-PEGDM-*g*-PDEVP as well as analysis details are given in the Supporting Information.

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[1] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 4908 – 4910.

[2] a) H. Yasuda, H. Tamai, *Prog. Polym. Sci.* **1993**, *18*, 1097 – 1139; b) E. Y.-X. Chen, *Chem. Rev.* **2009**, *109*, 5157 – 5214; c) N. Zhang, S. Salzinger, B. S. Soller, B. Rieger, *J. Am. Chem. Soc.* **2013**, *135*, 8810 – 8813.

[3] U. B. Seemann, J. E. Dengler, B. Rieger, *Angew. Chem. Int. Ed.* **2010**, *49*, 3489 – 3491; *Angew. Chem.* **2010**, *122*, 3567 – 3569.

[4] S. Salzinger, U. B. Seemann, A. Plikhta, B. Rieger, *Macromolecules* **2011**, *44*, 5920 – 5927.

[5] S. Salzinger, B. Rieger, *Macromol. Rapid Commun.* **2012**, *33*, 1327 – 1345.

[6] N. Zhang, S. Salzinger, B. Rieger, *Macromolecules* **2012**, *45*, 9751 – 9758.

[7] a) N. Zhang, S. Salzinger, F. Deubel, R. Jordan, B. Rieger, *J. Am. Chem. Soc.* **2012**, *134*, 7333 – 7336; b) N. Zhang, S. Salzinger, F. Deubel, B. Rieger, WO 2013/072309, **2012**;.

[8] J. G. C. Veinot, *Chem. Commun.* **2006**, 4160.

[9] M. Dasog, Z. Yang, S. Regli, T. M. Atkins, A. Faramus, M. P. Singh, E. Muthuswamy, S. M. Kauzlarich, R. D. Tilley, J. G. C. Veinot, *ACS Nano* **2013**, *7*, 2676 – 2685.

[10] a) Y. Yu, C. M. Hessel, T. D. Bogart, M. G. Panthani, M. R. Rasch, B. A. Korgel, *Langmuir* **2013**, *29*, 1533 – 1540; b) Z. Yang, M. Dasog, A. R. Dobbie, R. Lockwood, Y. Zhi, A. Meldrum, J. G. C. Veinot, *Adv. Funct. Mater.* **2014**, *24*, 1345; c) X. Cheng, S. B. Lowe, P. J. Reece, J. J. Gooding, *Chem. Soc. Rev.* **2014**, *43*, 2680.

[11] J. A. Kelly, J. G. C. Veinot, *ACS Nano* **2010**, *4*, 4645 – 4656.

[12] a) J. M. Buriak, *Chem. Rev.* **2002**, *102*, 1271 – 1308; b) R. L. Cicero, C. E. D. Chidsey, G. P. Lopinski, D. D. M. Wayner, R. A. Wolkow, *Langmuir* **2002**, *18*, 305 – 307; c) P. Stewart, J. M. Buriak, *Angew. Chem. Int. Ed.* **1998**, *37*, 3257 – 3260; *Angew. Chem.* **1998**, *110*, 3447 – 3450.

[13] J. A. Kelly, A. M. Shukaliak, M. D. Fleischauer, J. G. C. Veinot, *J. Am. Chem. Soc.* **2011**, *133*, 9564 – 9571.

[14] a) R. J. Clark, M. K. M. Dang, J. G. C. Veinot, *Langmuir* **2010**, *26*, 15657 – 15664; b) C. M. Hessel, M. R. Rasch, J. L. Hueso, B. W. Goodfellow, V. A. Akhavan, P. Puvanakrishnan, J. W. Tunnel, B. A. Korgel, *Small* **2010**, *6*, 2026 – 2034; c) F. Erogbogbo, K.-T. Yong, I. Roy, G. Xu, P. N. Prasad, M. T. Swihart, *ACS Nano* **2008**, *2*, 873 – 878; d) Y. He, Z.-H. Kang, Q.-S. Li, C. H. A. Tsang, C.-H. Fan, S.-T. Lee, *Angew. Chem. Int. Ed.* **2009**, *48*, 128 – 132; *Angew. Chem.* **2009**, *121*, 134 – 138.

[15] Z. F. Li, E. Ruckenstein, *Nano Lett.* **2004**, *4*, 1463 – 1467.

[16] C. M. Hessel, E. J. Henderson, J. G. C. Veinot, *Chem. Mater.* **2006**, *18*, 6139 – 6146.

[17] S. Salzinger, B. S. Soller, A. Plikhta, U. B. Seemann, E. Herdtweck, B. Rieger, *J. Am. Chem. Soc.* **2013**, *135*, 13030 – 13040.

[18] Z. Yang, M. Iqbal, A. R. Dobbie, J. G. C. Veinot, *J. Am. Chem. Soc.* **2013**, *135*, 17595 – 17601.

[19] M. D. Bhabhe, P. S. Galvankar, V. M. Desai, V. D. Athawale, *J. Appl. Polym. Sci.* **1995**, *56*, 485 – 494.

[20] C. de las Heras Alarcón, S. Pennadam, C. Alexander, *Chem. Soc. Rev.* **2005**, *34*, 276.

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