"Grafting From" -Living Cationic Polymerization of Poly(isobutylene) from Silica-Nanoparticle Surfaces

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Summary: This publication discusses the development of new methods for producing organic-inorganic core-shell-nanoparticles (NP's) via a combination of "grafting-from" techniques and living cationic polymerization reactions. Based on the surface initiated, quasiliving cationic polymerization of isobutylene, polymeric shells of polyisobutylene (PIB) were attached onto nanoparticles (silica NP's of different sizes, $r = 12–40$ nm) with a high degree of precision. "Grafting-from" polymerization provides an ideal method to control the number of polymer chains per particle by means of the degree of initial derivatization and the length of the polymeric chains. The resulting nanocomposite materials were analyzed using DLS, TEM, GPC, TGA, DSC.

Keywords: grafting-from polymerization; living polymerization; nanoparticles; polyisobutylene

Introduction

Nanoparticles (NP's) consisting of a hard core (for example silica) and a soft shell (like polyisobutylene, polystyrene) have advantageous chemical and physical properties with respect to the corresponding pure polymeric materials. Silica-NP's modified with different chain-lengths of polyisobutylene (PIB) show different rheological (solid, rubber-like material), thermal (decomposition temperature much higher than unbound polyisobutylene) and chemical characteristics when compared to unmodified PIB. The quasiliving cationic "grafting-from" polymerization is a useful tool to bind polymeric chains onto NP's[1–5] with a controlled chain length and grafting density of the attached polymer brushes. The present account investigates the grafting-from polymerization of isobutylene from silica-NP's.

Methods

Commercially available nanopowders (Degussa, Sigma-Aldrich) were used to produce hybrid core-shell particles consisting of a silica core and a covalently bound polymeric shell. The thickness of these polymeric shells is adjustable in a very wide range. By using "grafting-from living cationic polymerization"[1,2] it is possible to ensure that all polymer chains attached onto the particles are of almost the same length. The size distributions of the resulting NP's remains within a small range (±1–5% of the projected radius) (Figure 1).

In order to obtain modified NP's in a reproducible manner every step of the synthetic process was optimized. The optimized approach is illustrated in Figure 2. After careful drying, the NP's were modified with the reactive chlorosilane (CECE = I), thus affixing the initiator-moiety onto the NP-surface (steps a and b). Subsequently the living polymerization of isobutylene

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Table 1.
Different commercially available nanopowders.

	radius [nm]	BET-surface [m^2/g]	number of OH-groups/NP on the surface (calculated)
Sigma-Aldrich nanopowder	7,5	200	1500
Degusa Aerosil 200	6	200 ± 25	900
Degusa OX 50	20	50 ± 15	10 000

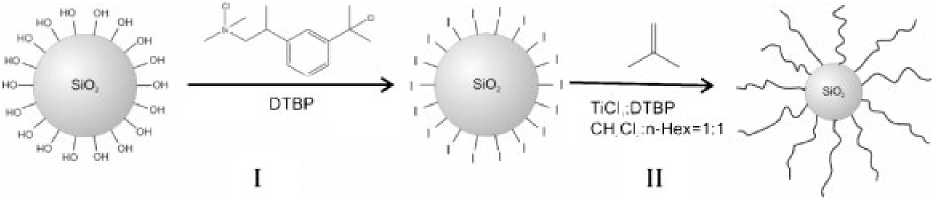

Figure 1.
Procedure of core-shell-NP-synthesis: In step I the hydroxyl-groups at the surface of the commercially available NP's (Sigma-Aldrich nanopowder 15 nm; Degussa Aerosil 200; Degussa OX 50) were modified with the initiator (I = CECE = chloro(2-(3-(2-chloropropane-2-yl)phenyl)propyl)dimethylsilane) for the carbocationic polymerization. The polymerization with isobutylene (step II) using different solvent-mixtures (dichloromethane/n-hexane) was catalyzed by the use of titaniumtetrachloride and di-tert-butylpyridine (DTBP).

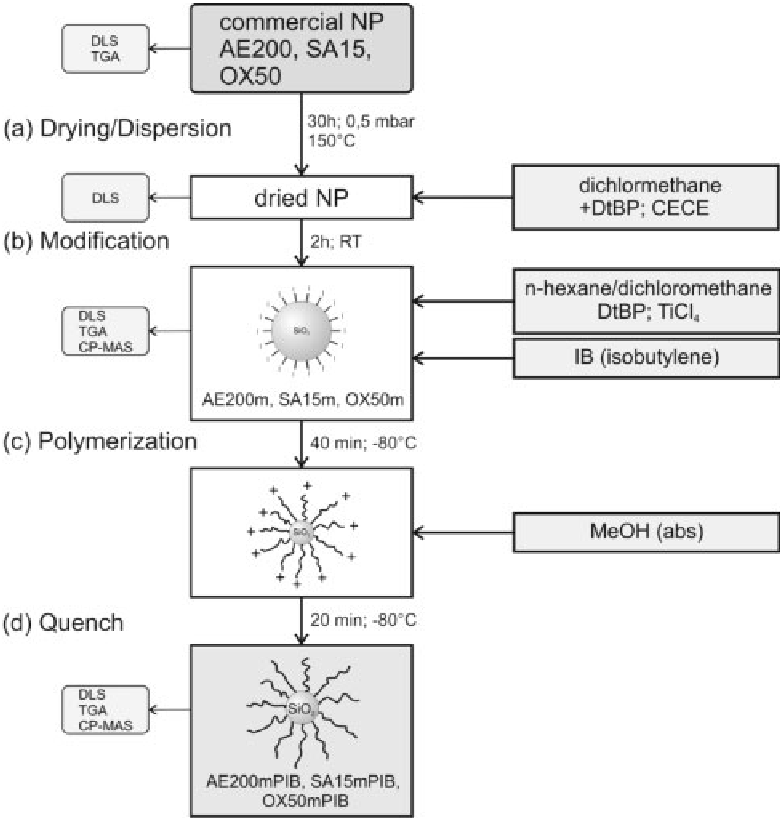

Figure 2.
Synthetic strategy to produce modified NP's.

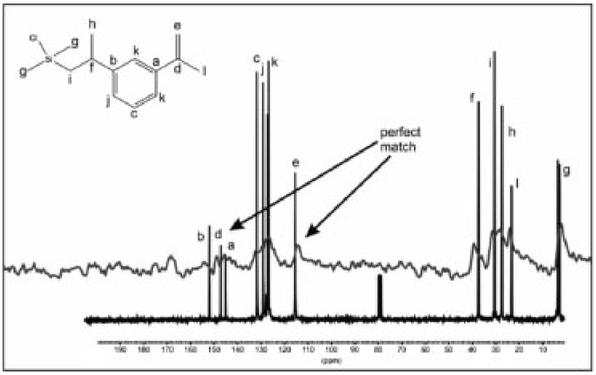

Figure 3.
^{13}C-CPMAS-NMR of NP's modified with an inactivated (destroyed) initiator.

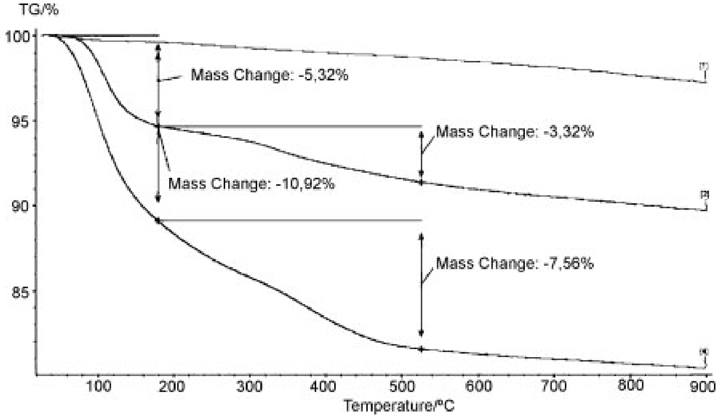

Figure 4.
TGA-curves for a selected hybrid-material ([1]: unmodified Degussa-nanopowder (AE200); [2]: chlorosilane-initiator modified AE200; [4]: Hybrid-NP's.

was initiated (step c) and quenched (step d), resulting in crude grafted SiO_2-NP. Table 1 shows the theoretical amount of silanol-sites in dependence on the size of the nanoparticles.

Drying or storing of the modified, highly reactive NP's (AE200m, SA15m, OX50m) caused a complete destruction of the reactive sites. ^{13}C-CPMAS-NMR measurements demonstrated this effect as shown in Figure 3. The initially to the surface bound initiator sites are completely destroyed during the drying process. Polymerization is therefore directly performed immediately after modification by addition of the solvents, the organic base, the catalyst and the isobutylene (step c).

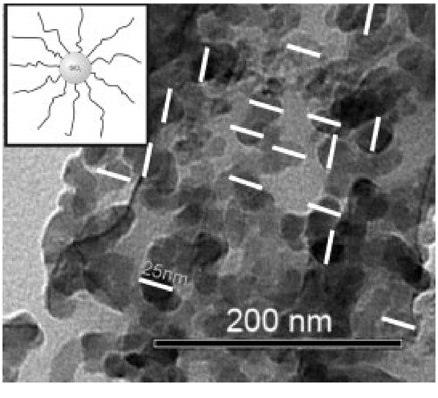

Figure 5.
Cryo-TEM picture of Degussa AE200 nanopowder (12 nm size) modified with polymeric shells (about 10 000 g mol^{-1} chain length).

TGA measurements (Figure 4) allowed the exact determination of the total amount of bound organic material. It could be shown (see Figure 4) that increasing the chain length of the polymeric shell lead to a proportionally increased total amount of organic material. Using cryo-TEM techniques (Figure 5) it could be shown that the modified hybrid-NP's correspond to the theoretically calculated size.

Conclusion

It has been shown that it is possible to modify commercially available nanopowder with a well defined, widely adjustable PIB-polymeric shell in a highly reproducible manner. By using ‘‘grafting-from’’ living-cationic polymerization methods it is possible to ensure that the thickness of the polymeric shell can be adjusted reproducibly and within a large size range. This approach opens a wide field of synthetic strategies for the surface modification of different nanoparticles with well defined polymeric shells.

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