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Recent Developments in the Surface Modification of Polymers

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Summary. Selected trends and scientific achievements in the surface modification of polymers are reported. In this context, both UV-light triggered free radical polymerization-based techniques relevant to industrial processes and ring-opening metathesis polymerization-based chemistry, relevant for the manufacture of specialty materials, are addressed.

Keywords. Photochemistry; Surface; Polymerization; Catalysts; Separation science.

Introduction

Surfaces and interfaces play an important role in daily life and routine applications. On the one hand, many biological and biochemical processes take place at interfaces. On the other hand separation processes and heterogeneous catalysis are intrinsically related to surfaces and surface-based processes. Finally, from a technical point of view, surfaces are designed to fulfill certain (multiple) functions such as (non-) wettability, hardness, abrasion resistance, roughness, smoothness, haze, degree of matting, *etc*. This article provides a brief overview over selected state of the art techniques for the non-thermal, chemical modification of surfaces. In this context, VUV-based surface modifications for technical, high speed manufacturing processes reaching 400 m/min will be presented. In addition, recent progress made in the transition metal (*i.e.* ring-opening metathesis) polymerization-based surface modification and applications both in catalysis and life science will be reported [1–13].

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Results and Discussion

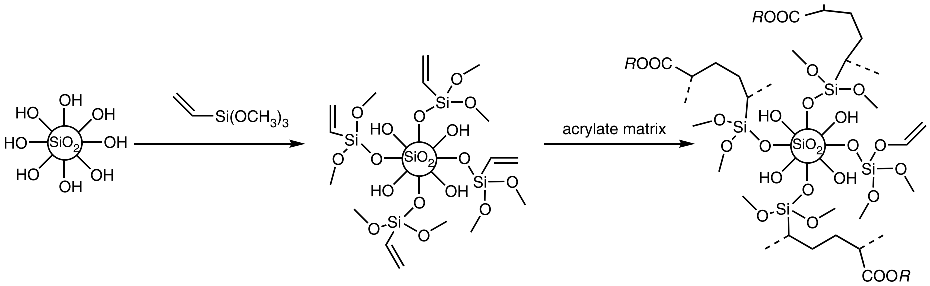
Recent Progress in Radiation-Curable Coatings

Tailor-Made Top Coatings for Photoelectrical Devices

In times of continuously increasing demands for energy and obvious limitations in fossil resources, solar energy is one of the alternative energy-producing techniques that can be expected to provide substantial amounts of energy in the near future. Consequently, significant effort and substantial amounts of money have been put into the development of devices that are capable of converting UV and visual light into energy. However, one of the major drawbacks associated with solar cells is their inherent sensitivity towards traces of oxygen and, even more important, moisture. The same applies to organic light-emitting devices (OLEDS). To realize long-time stable systems, highly transparent, abrasion and scratch resistant yet flexible and particularly cheap coatings with high gas barriers particularly for H_2O are therefore required.

This can be accomplished by two different approaches. One entails the deposition of thin, transparent coatings, *e.g.* SiO_x, usually applied by plasma deposition techniques. This is the preferred approach in case high gas barriers are required, however, production proceeds in a batch-wise manner. Alternatively, acrylate-based systems are of particular interest for low gas barrier applications, since they may easily be cured by UV irradiation, thus allowing for rapid and continuous manufacturing processes. Such acrylate-based formulations with increased hardness, improved abrasive behavior, and suitable gas barriers may be realized by an *in situ* process that entails a simultaneous particle surface derivatization of preformed silica nanoparticles in the 50–80 nm range *via* condensation with vinyltrimethoxysilane under milling conditions. As a result, silica nanoparticles with vinyl-modified surfaces are generated and covalently bound to the acrylate matrix in course of the curing process (Scheme 1) [14].

Usually, silica nanoparticles with specific surface areas >200 m^2/g, *e.g.* Aerosil® 200 or Aerosil® 380 are used for these purposes. Mills with pre-dispersing facilities are required in order to provide homogeneous, transparent dispersions that lack any agglomerates [15]. After addition of suitable photoinitiators, *e.g.* $C_6H_5COCH(OH)(CH_3)$, polymerization of the liquid coating (*i.e.* curing), which can be generated *via* regular coating techniques, is accomplished *via* UV-irradiation,



Scheme 1

e.g. using standard low pressure (LP) Hg-UV lamps. This technique can be realized in form of continuous production facilities, reaching 400 m/min.

Top Coatings for Car Industry

Among the most demanding applications for coatings, those in car industry certainly hold a top position. Coatings (and particularly top coats) must fulfill the criteria of hardness, abrasion resistance, low haze, UV and light resistance. In addition, the surfaces should possess pronounced easy-to-clean properties. While hardness is comparably easy achieved by incorporation of silica (*vide supra*) or corundum, high abrasion resistance in combination with low haze and easy-to-clean properties requires the silica and corundum particles, respectively, to be present in close proximity to the surface of the coating. All this may be realized by modifying silica particles with fluorinated acrylates. Such fluoroalkanes have some intrinsic properties that make them highly useful. Thus, they are highly apolar, giving raise to large contact angles with both water and methylene iodide when incorporated into coatings. In addition, they possess a high tendency towards phase separation and therefore enrich at the surface of such coating, thus carrying the nanoparticle with it. In summary, this provides UV-curable, scratch and abrasion resistive systems with good haze and easy-to-clean effects. Contact angles (water) up to 110° may be realized. Figure 1 gives an example of the surface of such a coating (left) and the actual degree of filling of the underlying "bulk" of the coating, visible after plasma etching (right).

Surface Matting of Acrylate Coatings via 172 nm Irradiation

It is a well-known fact that polymers suffer from volume reduction during polymerization due to shrinkage. This effect stems from the reduction of the monomer-monomer distance during polymerization, which cannot be compensated by the elongation of the former (usually vinylic) double bonds). In case thin polymeric layers are UV-cured using energy-rich irradiation, only the top layer of the coating is converted to the corresponding polymer due to insufficient penetration of the entire coating by the UV light. As a consequence, a polymer film forms, floating at

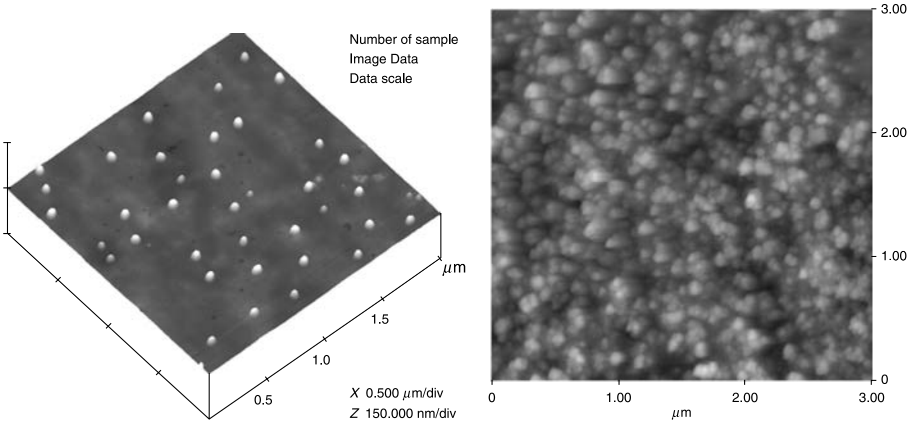
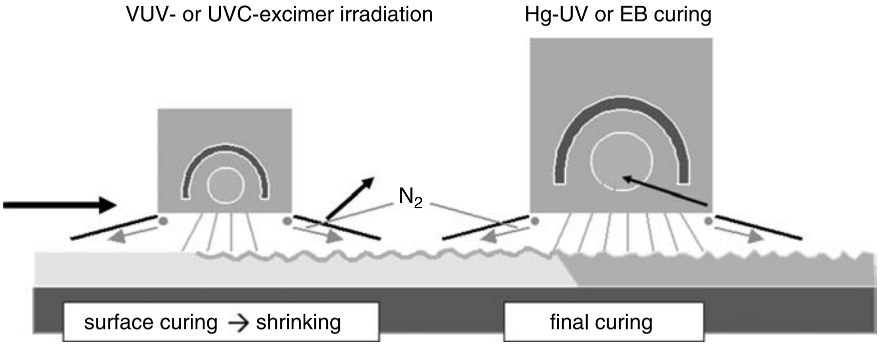


Fig. 1. Silica-filled acrylates, surface (left), bulk (right)



Scheme 2

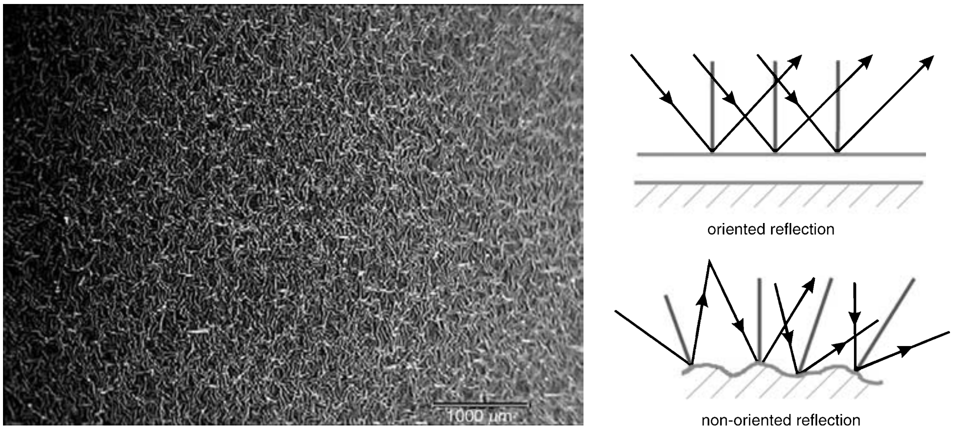


Fig. 2. Electron micrograph of a surface-matted systems (left) and the physical reason for the matt appearance (right)

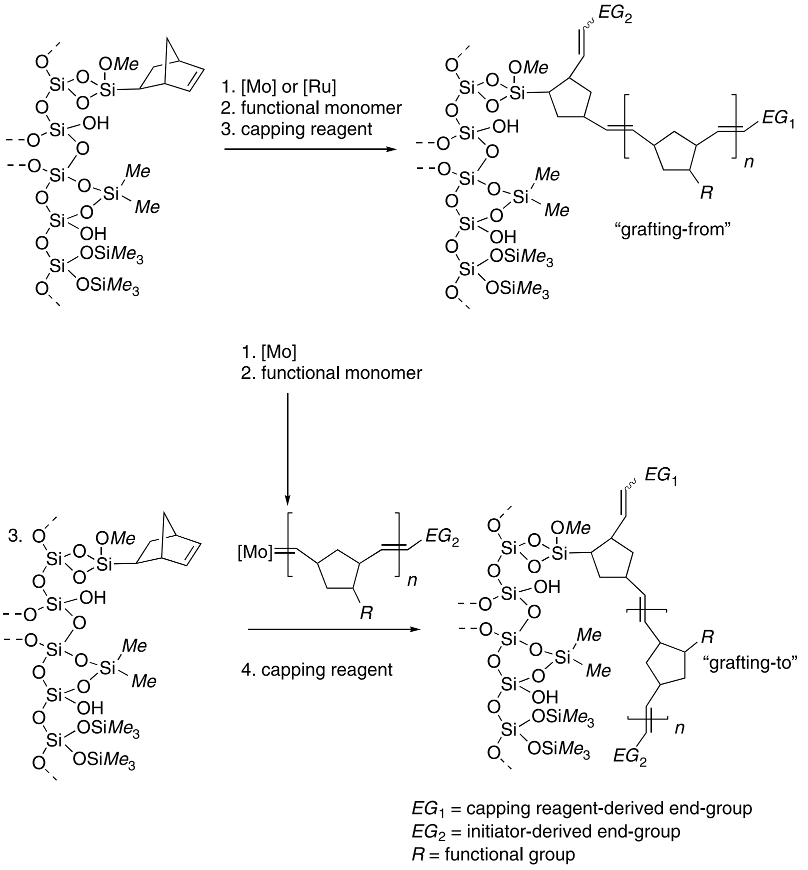
the surface of the underlying liquid coating. Similar to a polypeptide layer on hot milk, this layer shrinks. As a consequence, light is no longer reflected in an oriented (parallel) way – the surface appears matted (Scheme 2, Fig. 2). In a second step, the entire film is cured using standard Hg-UV lamps or, in case of highly colored or thick coatings, using electron beam (EB) irradiation.

Intense research has carried this technology to a point, where the degree of matting may now be adjusted in a reproducible way. In addition, continuous production techniques with integrated coating, matting, and curing at speeds up to 200 m in combination with curing widths up to 3 m have been realized [16]. A typical electron micrograph is shown in Fig. 2.

Functional Materials via Ring-Opening Metathesis Polymerization (ROMP)-Based Surface Grafting

Grafted Inorganic Surfaces for Separation Science

Our group was the first to develop ROMP-based synthetic protocols for both a "grafting-from" and "grafting-to" approach for the modification of both organic and



EG$_1$ = capping reagent-derived end-group
EG$_2$ = initiator-derived end-group
R = functional group

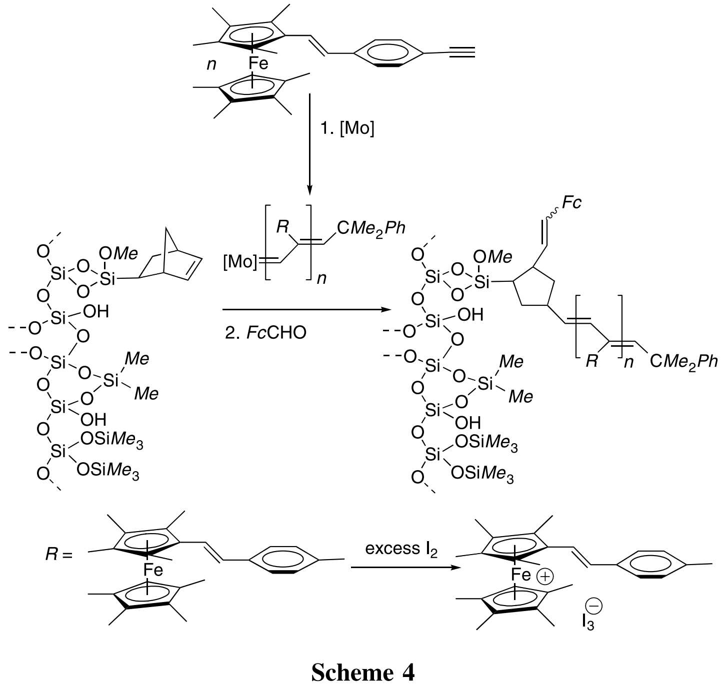
Scheme 3

inorganic micrometer-sized particles, *e.g.* silica or poly(strene-*co*-divinylbenzene) (Scheme 3) [17–19].

Surface-immobilized norborn-5-ene-2-yl-groups were used as suitable anchoring groups for the preparation of ROMP-graft-copolymers. These can easily be introduced in the case of silica materials using trichloro-norborn-5-ene-2-ylsilane, chlorodimethylnorborn-5-ene-2-ylsilane, or trialkoxynorborn-2-ene-5-ylsilanes. Subsequent "endcapping" with a mixture of chlorotrimethylsilane and dichlorodimethylsilane followed by addition of absolute methanol leads to a sufficient derivatization of a major part of the surface silanol groups (approximately 90%). For the "grafting-to" approach, the monomer has to be transformed into a living polymer *via* ROMP and subsequently attached to the support by reaction with the surface norborn-2-ene groups. This approach requires at least class-IV living systems [20] and consequently leads to the formation of tentacle type stationary phases with the linear polymer chains attached to the support. Alternatively, the initiator can first be reacted with the support to become heterogenized. Monomer is added consecutively and grafted onto the surface ("grafting-from" approach). While the first generation *Grubbs*-type initiator RuCl$_2$(PCy_3)$_2$(CHPh) is preferably used for "grafting-from" experiments, *Schrock*-type initiators are applicable to both methods.

With these methods in hand, various monomers were surface grafted on different supports. Using silica-derived Nucleosil 300-5, 60 μmol of *N*-(norborn-5-ene-2-carboxyl)phenylalanine ethylester were immobilized on the surface using a "grafting-from" approach and $RuCl_2(PCy_3)_2(CH\text{-}p\text{-}F\text{-}C_6H_4)$ as initiator [17]. With $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$, 40 μmol of this monomer could be grafted to the surface using either a "grafting-from" or "grafting-to" approach. The resulting chiral stationary phase was successfully used as HPLC support in the separation of racemic dinitrobenzoyl-protected phenylalanine ethylester [17]. The broad applicability of this concept was demonstrated by immobilizing a series of β-cyclodextrin (β-*CD*) derivatives, *i.e.* 6-*O*-(norborn-2-ene-5-carboxyl)-β-*CD*, tetrakis(6-*O*-norborn-2-ene-5-carboxyl)-β-*CD*, 6-*O*-(7-oxanorborn-2-ene-5-carboxyl)-β-*CD*, 6-*O*-(6-(norborn-2-ene-5-carbonylaminohexoyl)-β-*CD*, 6-*O*-(norborn-2-ene-5-ylmethoxymethylsilyl)-β-*CD*, tris(6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-*CD*, tetrakis(6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-*CD*, and hexakis(6-*O*-norborn-2-ene-5-ylmethoxymethylsilyl)-β-*CD*, on Nucleosil 300-5 [21]. A "grafting-from" approach using $RuCl_2(PCy_3)_2(CHPh)$ as initiator was used throughout resulting in grafting densities of 11–34 μmol/g. The chiral stationary phases (CSPs) could be prepared with high reproducibility and used within a *pH* range of 2–10. With these stationary phases in hand, a series of β-blockers, *DNS*-or *Fmoc*-protected amino acids, and planar chiral ferrocene derivatives could successfully be separated [21, 22].

Based on our studies on metallocenylalkynes [23–26], poly(ethynylferricinium)-based anionic exchangers were prepared applying the "grafting-to" concept described above [27]. Thus, metathesis polymerization of 4-ethynyl-1-(octamethylferrocenylethenyl)benzene using the *Schrock*-type catalyst $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ and subsequent grafting of the living polymer onto



Scheme 4

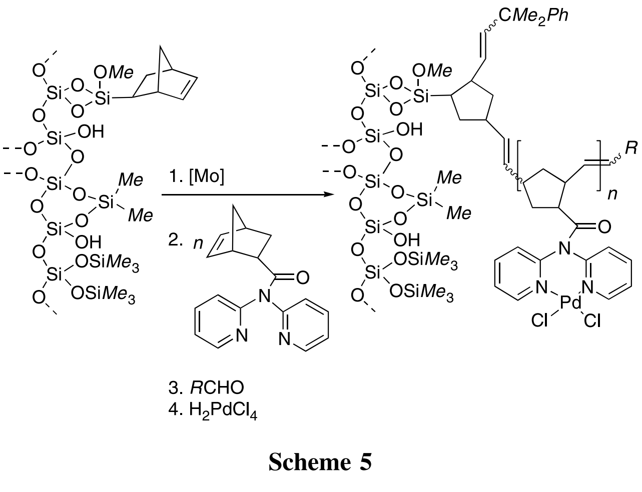
a (norborn-5-ene-2-yl)-derivatized silica support resulted in the desired octamethylferrocene-grafted stationary phase (Scheme 4). Both porous, *i.e.* Nucleosil 300-5, and nonporous, *i.e.* Micra, silica was used.

Oxidation with iodine resulted in an octamethylferricinium-based anion-exchanger that was successfully used for the separation of oligonucleotides (dT_{12}–dT_{18}). Here, it is worth mentioning that the careful endcapping of silica with a mixture of $ClSiMe_3$ and Cl_2SiMe_2 eliminates any initiator deterioration potentially caused by the interaction with the silanol groups. In addition, complete reaction of the initiator with the support as evidenced by the absence of any soluble polymer, was observed [17].

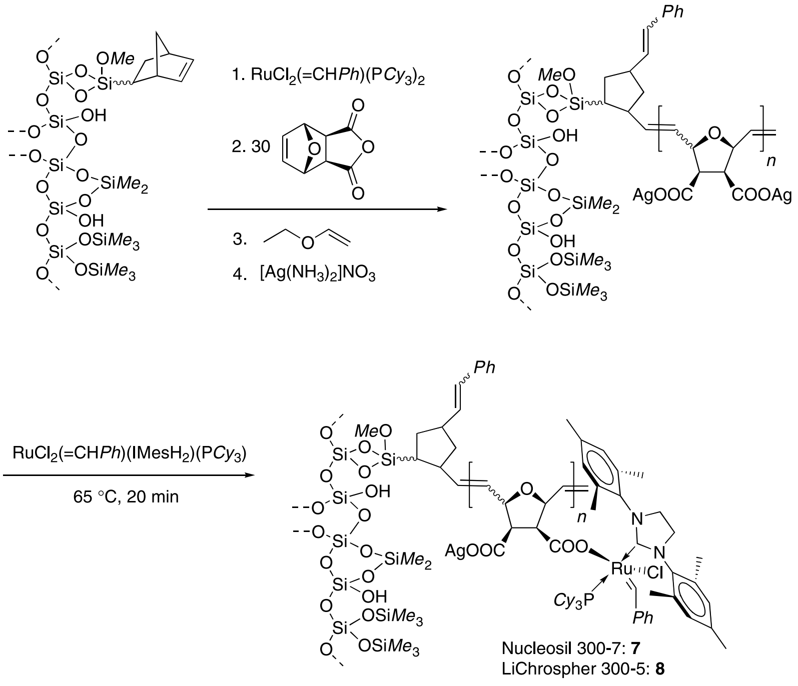
Grafted Supports for Catalysis

As shown in previous work [28], *N*,*N*-dipyrid-2-ylnorborn-2-en-5-ylcarbamide can be polymerized in a living manner using well-defined *Schrock* initiators. A class VI living system [20] can be accomplished with $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(CMe(CF_3)_2)_2$. This monomer was grafted on norborn-2-ene surface functionalized silica, using a "grafting-from" approach to generate tentacles of poly-(*N*,*N*-dipyrid-2-ylnorborn-2-en-5-ylcarbamide) with a controlled degree of polymerization (DP), typically <50 (Scheme 5) [29].

Palladium-loading of the supports was simply accomplished by reaction with H_2PdCl_4. Within a few hours, a quantitative reaction was observed resulting in palladium loadings of 0.28 mmol and 0.08 mmol Pd/g, respectively. The palladium-loaded silica materials were successfully used in various *Heck* reactions including slurry reactions under standard as well as under microwave conditions. Removal of the support was simply accomplished by filtration. In particular the use of microwave lead to a drastic reduction of reaction times, which is of particular interest for applications in high-throughput screening (HTS). Turn-over frequencies (TOFs) were typically in the range of 0.1–0.3 s^{-1}. Alternatively, palladium-loaded silica was packed into stainless steel columns, which were subsequently loaded with *Heck* monomers and used as reaction columns as employed in HTS machines. Alternatively, flow-through reactors were realized with surface-derivatized silica-packed



Scheme 5



Nucleosil 300-7: **7**
LiChrospher 300-5: **8**

Scheme 6

stainless steel columns. With these columns, a constant conversion of iodobenzene with styrene (70–80%) was observed over several hours. TOFs were in the range of 0.06–0.07 s^{-1}. In all these experiments, irrespective of the application, only minor leaching of Pd into the reaction mixture was observed, typically less than 2.5% of the original amount [29].

Finally, norborn-2-ene-5-yltrichlorosilane or norborn-2-ene-5-yl-triethoxysilane (both *exo*/*endo*-mixtures) surface-derivatized silica was consecutively reacted with $RuCl_2(PCy_3)_2(CHPh)$ and *exo,exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride, respectively 7-oxanorborn-2-ene-5-carboxylic acid. By this "grafting-from" approach, satisfactory amounts of both monomers were grafted onto the support. Thus, anhydride loadings of 0.22 mmol/g (LiChrospher 300-5) and 1.2 mmol/g (Nucleosil 300-7) were achieved. Conversion into the corresponding di- and mono-silver salts and reaction with $RuCl_2(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)(CH*Ph*) gave the desired supported catalysts (Scheme 6). Depending on the silica used, catalyst-loadings were in a range of 42 mg (Nucleosil 300-7) to 63 mg catalyst/g (Lichrospher®). RCM reactions carried out with these two silica-supported catalyst versions allowed TONs up to 90 for a series of simple α,ω-dienes [30].

Conclusions

Both free radical polymerization and transition metal-based surface modifications hold strong places within the increasing number of techniques. While free radical polymerization is nowadays conveniently accomplished by various irradiation techniques, only few, less effective and selective light-triggered controlled polymerizations, whether based on "quasi-living" radical polymerizations or transition metal initiated processes such as ROMP, exist. Future efforts will certainly focus on these topics and hopefully further enrich the existing armor of surface modification techniques.

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