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Graft-polymerization of phosphine functionalized monomers onto silica particles

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Summary

Triphenylphosphine (PPh_3), a well-known reagent and catalyst, was successfully grafted onto silica particles in a functionalized polymer form using 4-(diphenylphosphinyl)styrene as a monomer. 4-(Diisopropylphosphinyl)styrene and 4-(ditertbutylphosphinyl)styrene were also grafted onto silica in the form of a functionalized polymer and oligomer, respectively. Two methods were used: A) Copolymerization of phosphine-functionalized monomers with a vinyl compound previously attached to silica; and B) Polymerization of phosphine-functionalized monomers using a radical initiator previously attached to silica. The resulting materials were characterized by FTIR, DTA-TGA, specific surface area (S_{BET}) and XPS. The best results in grafting percent and molecular weight of the grafts were obtained by method B.

Introduction

Triphenylphosphine (PPh_3) is a chemical compound with a variety of interesting applications: it is a reagent for several chemical transformations [1-4], it is also used as polymerization initiator or promotor [5] and as ligand for many metal-catalysts in several applications [6]. Trialkylphosphines are expected to show higher reactivity due to their greater basicity and nucleophilicity [7], and they are also more easily oxidized than PPh_3, which allow them to be used as reducing agents in organic chemistry [8].

The advantages of using a polymer-supported reagent or catalyst rather than a non-macromolecular one are well addressed in the literature [9], the most exploited being the easiness of work-up procedures and the reutilization of these functionalized polymers. The potential disadvantages of using a polymeric reagent or catalyst are: diffusion limitation of substrate or product resulting in lower reaction rates and catalytic activity, low mechanical strength resulting in pulverization of the resin beads and lower stability at high temperatures and pressures than the non-polymeric heterogeneous catalysts counterparts. To avoid these problems, Challa *et al.* [10]

suggested a rationale for phosphite modified rhodium catalysts: attaching the catalyst (or reagent) to a soluble linear polymer chain, to avoid diffusion limitations, and grafting the polymer-chain onto the surface of an inert support, which gives mechanical and thermal stability.
Following the former rationale, the aim of this work was to generate both PPh_3- and dialkylphenylphosphine-functionalized materials, capable of working as improved reagents and also as improved catalysts, combining the intrinsic advantages of the polymers and silica as supporting materials. Since we have experience in producing functionalized polymers [4,11], we focused on suitable procedures for grafting the reactive polymers onto silica particles. Known methods for grafting polymer chains to particle surfaces entails the reaction of end-functionalized polymers with appropriate surface-sites [12] ("grafting to"-technique), grafting a polymer chain through a monomer covalently linked to the surface [13], or grafting a polymer chain from a surface modified with polymerization-initiators [14-16] ("grafting from"-technique). The latter two approaches usually lead to higher grafting densities because monomers more easily diffuse to reactive sites [15]. In recent years, several research-groups are reporting the use of living free-radical polymerization techniques for grafting from flat [17-19] and porous [20, 21] surfaces, with good structural control of the grafts prepared. However, the application of these techniques for surface grafting is not well advanced for non-protected functionalized monomers and still not trivial for conventional monomers. Issues like, the need of addition of deactivator [17, 18] or sacrificial initiator [19] in solution, low percent-grafting yields [20] and relative failure to control the molecular weight distribution of the grafts [21], are reported. Traditional (non-living) free-radical polymerization is still very useful for grafting from surfaces because it allows the use of a wide variety of monomers including polar and unprotected functional groups in their structure [13, 14-16]. Accordingly, we decided to test two methods: -Copolymerization of phosphine-functionalized monomers with monomer-functionalized silica, and -Polymerization of phosphine-functionalized monomers with initiator-functionalized silica by non-living free radical polymerization techniques.

Experimental

Materials

Silica Gel: Davisil-Grade 644, 100-200 mesh, 150 Å (Aldrich), was dried in a muffle oven at 800 °C for 30 min before use. Toluene and Tetrahydrofurane (Aldrich) were distilled before use. All other chemicals were used as received and were provided by Aldrich with the exception of 2,2'-Azobis(2-methylpropionitrile) (AIBN) provided by Jannsen Chimica and Magnesium turnings provided by Productos Químicos Monterrey. The phosphine-functionalized monomers were synthesized via Grignard-reactions, starting from 4-chlorostyrene and the corresponding chlorophosphine reagent by a methodology described previously [4, 11].

Characterization methods

The chemical modification of the silica in every reaction step was monitored by FTIR-Spectroscopy using a FTIR-1605 from Perkin-Elmer. Silica samples were mixed with dry KBr and conventional wafers were obtained using a laboratory press. The degree of functionalization of the silica was evaluated by simultaneous differential thermal analysis and thermogravimetry (DTA-TGA, Stanton-Redcroft, STA-780). Specific surface areas were determined with a Gemini 2060 from Micrometrics by nitrogen adsorption at –196 °C using the BET isotherm. X-ray photoelectron spectroscopy (XPS) measurements were obtained in a Riber-instrument, model Cameca 3, using non-monochromated $AlK\alpha_{1,2}$ radiation as excitation source. Grafted (cleaved) and non-grafted polymers formed during the polymerization and copolymerization grafting-experiments were characterized by gel permeation chromatography (GPC with refractive index-Detector, Varian 9002 with RI-4) using a mixed bead column (Phenogel 5 Linear) and Polystyrene-standards in THF (HPLC-Grade).

Copolymerization with monomer functionalized silica (Method A)

In order to perform the graft-polymerizations or –copolymerizations onto silica, it is necessary to functionalize the silica surface previously. The silica functionalized with 3-(trimethoxysilyl)propylmethacrylate (TMPS-Silica) was obtained by the method reported by Carlier *et al.* [22]. The copolymerization experiments were conducted varying the monomer, either 4-(diphenylphosphinyl)styrene (DPPS) or 4-(diisopropylphosphinyl)styrene (DIPS), and varying the amount of solvent used. The following is an example of the methodology by higher amount of solvent (lower concentration): in a Schlenk-flask, DPPS (4.44 g , 15.41 mmol) was dissolved in 12.5 mL of dry toluene; then monomer-functionalized-silica (TMPS-Silica) (0.3216 g, 0.4792 mmol g^{-1}) and AIBN (0.0253 g, 0.15 mmol) were added while shaking. The Schlenk-flask was degassed at least three times at – 40 °C and finally filled with argon prior to sealing. The copolymerizations were carried out with stirring at 60 °C for 48 h. The content of the Schlenk-flask was filtered-off, fresh toluene was added, stirred for 30 min and filtered-off again. The grafted-silica-samples were then extracted with dichloromethane using a Soxhlet-apparatus for 12 h. Finally the grafted-silica-samples were dried *in vacuo* at 40 °C for 12 h. On the other hand the collected toluene filtrates were evaporated, THF was added to redissolve and hexane (or diethyl ether in the case of the polymerization with DIPS) was added to precipitate the non-grafted polymer formed. After filtration this polymer was also dried *in vacuo* at 25 °C for 12 h.

Polymerization with initiator-functionalized silica (Method B)

The initiator-functionalized silica (AZO-silica) was obtained by the method reported by Carlier *et al.* [22] (see Figure 1). The polymerization experiments were conducted varying the monomer: DPPS, DIPS or 4-(ditertbutylphosphinyl)-styrene (DTBPS) and the amount of silica-bound initiator. The polymerization method was the same as Method A, with two exceptions: the polymerization temperature was 80 °C and no AIBN was added, Two products were obtained by this method as well: polymer-grafted silica and non-grafted polymer.

The polymer grafted onto silica particles by both methods (A and B) was detached using hydrofluoric acid following the procedure applied by Von Werne *et al.* [23].

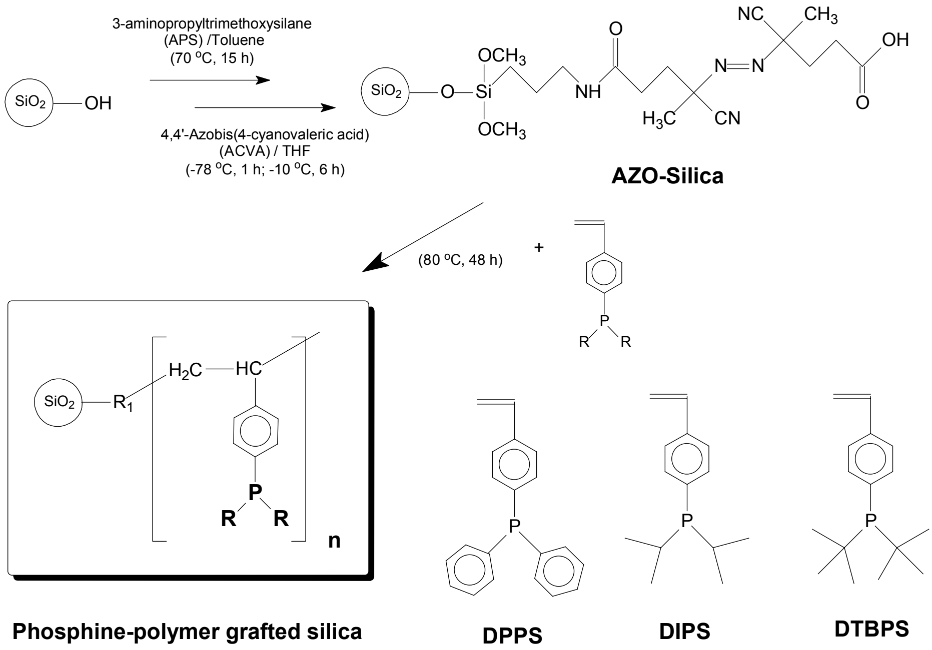

Figure 1. Methodology for the synthesis of silica-grafted polymers using AZO-initiator-functionalized silica (method B).

Results and Discussion

Drying and functionalization of silica

The specific surface area of the silica dried at 800 °C was found to be 243 m^2 g^{-1}; thermogravimetric analysis showed no adsorbed water. The surface area of the TMPS-silica decreased to 204 m^2 g^{-1}, having 10.4 wt% of monomer (TMPS) attached as determined by DTA-TGA. In its infrared spectrum this silica shows characteristic absorbance bands at 3454 cm^{-1} (O-H silica), 2928 cm^{-1} (C-H aliphatic), 1733 cm^{-1} (C=O), 1638 cm^{-1} (C=C), 1110, 809 and 467 cm^{-1} (Si-O-Si silica). The APS-silica has a specific surface area of 211 m^2 g^{-1}, with 5 wt% of APS on its surface according to DTA-TGA analysis. Its FTIR spectrum has these characteristic absorbance bands in addition to those related to silica: at 2937 cm^{-1} (C-H aliphatic) and 1624 cm^{-1} (N-H amine) (Fig. 2,a). The specific surface area of the AZO-silica was not estimated because the initiator anchored onto the silica is sensitive to light and temperature, but the thermogravimetric analysis yielded a value of 7 wt% of ACVA attached, and the infrared spectrum of this sample (Fig. 2,b) showed the following absorbance bands, in addition to the bands corresponding to silica: at 1700 cm^{-1} (C=O from carboxylic acid), 1653 cm^{-1} (C=O from amide), 1543 cm^{-1} (N-H amide), and a slight increase of the band at 2937 cm^{-1} (C-H aliphatic).

Table 1 Main characterization parameters of silica-grafted polymers

SILICA	C_{MON} (mol L^{-1})	C_{INIC} (mol L^{-1})	Graft (%)	Mon. conv. (%)	Surface Area (m^2g^{-1})	Grafted polymer		Non-grafted polymer	
						M_n (g mol^{-1})	PDI	M_n (g mol^{-1})	PDI
DPPS-A1	1.25	0.01	25	80	80	15 600	1.8	24 400	2.1
DPPS-A2	1.24	0.01	18	58	-	12 000	1.6	18 500	1.8
DPPS-B1	1.16	0.04	24	64	35	17 000	2.0	27 800	4.6
DPPS-B2	0.90	0.04	36	28	30	37 200	6.1	-*	-
DIPS-A	1.10	0.01	11	26	-	14 400	1.8	20 400	3.2
DIPS-B1	1.06	0.03	13	7	161	6 800	3.1	-*	-
DIPS-B2	1.19	0.01	23	22	69	42 800	2.5	54 400	1.4
DIPS-B3	0.98	0.005	11	27	71	23 500	1.6	35 100	2.0
DTBPS-B1	0.87	0.04	7	4	164	2711	1.5	-*	-
DTBPS-B2	0.83	0.02	10	4	158	782	1.0	1181	1.1

* No non-grafted polymer recovered

Graft polymerizations

Table 1 shows the results of the different graft polymerizations and copolymerizations. The percentage of grafting refers to the amount of polymer grafted per gram of silica. The monomer conversion was calculated considering the mass of grafted and non-grafted polymer divided by the mass of monomer in the feed.

Method A

The monomers DPPS and DIPS were tested by method A for grafting copolymerization onto TMPS-silica. The best result of grafting obtained was 25 graft% using DPPS. The surface area of this sample is 80 m^2 g^{-1}, which is 61 % lower than the area of TMPS-silica. This suggests that the pores of silica are partially covered by polymer chains. The infrared spectrum of this sample show the following characteristic bands: 3062 cm^{-1} (C-H aromatic), 2928 cm^{-1} (C-H aliphatic), 1600 and 1480 cm^{-1} (C=C aromatic), 1440 cm^{-1} (P-C aromatic), 1406 cm^{-1} (C-H aliphatic), 745 and 700 cm^{-1} (C-H aromatic). The bands corresponding to the silica and TMPS were also found. The graft-copolymerization experiments using DIPS resulted in lower monomer conversions and grafting percentages but only slightly lower molecular weights of the grafts (see Table 1, A entries). The infrared spectrum of this sample showed the same absorbance bands as discussed above for DPPS-A1 with a noticeable increase in the intensity of the band at 2956 cm^{-1} (C-H aliphatic).

Method B

In the case of the monomer DPPS, the grafting polymerization using AZO-silica gave initially similar results of grafting percentage and molecular weight of the grafts as method A. However, adjusting the polymerization conditions, grafting percentages as high as 36 % with molecular weights of 37 200 g/mol could be achieved (Table 1). This sample has a surface area of 30 m^2 g^{-1} (DPPS-B2). Since the surface area decreased by 86 %, this means that the polymer chains of DPPS would be covering much of the surface of the AZO-silica. In the case of monomer DIPS the grafting experiments showed clearly better results as by method A. Not only the grafting percentage doubled to 23 % with a decrease of surface area of 70 %, more noticeably the molecular weight of the grafts increased significantly. This gives a picture of more and longer polymer grafts in the silica by method B as by method A. In contrast, attempts to graft-polymerize DTBPS using AZO-silica yielded a maximum grafting percentage of only 10 % accompanied with high surface area values 158 and 164 m^2 g^{-1}. Thus indicating a poor coverage of silica surface. Not surprising, the molecular weight of the grafts obtained showed that only oligomers were grafted (Table 1 last 2 rows). The infrared spectra of these two types of silica grafted-polymers are similar to those of the corresponding to DIPS by method A, varying only in the bands belonging to the AZO initiator (Figure 2, c).

In general, method B, although with lower monomer conversions, yielded higher values of grafting percentage and higher molecular weight of the grafts than method A. This difference may arise from the fact that in method A, the initiating radical produced in solution need to diffuse to the silica surface to activate the grafted monomer followed by diffusion of the phosphine monomers and finally polymer-radical diffusion for termination, while in method B the initiator is already grafted to the surface and only the phosphine monomer diffusion is needed to grow polymer chains.

Surface analysis

The XPS survey spectra of the polymer-grafted silicas show the peaks corresponding to the different elements expected to be found in the silica surface: C, O, P, Si and N. The carbon peaks could be deconvoluted by curve fitting into different C1s single core level bonding states, depending on the method of functionalization of the silica and the polymer grafted onto its surface. In the case of polymer-grafted silica by method A, the C1s peaks were fitted with six components, corresponding to different carbon functionalities present at the surface: at 284.0 eV (C-P species), at 284.6 eV (aromatic C-C), at 285.0 eV (aliphatic C-C), at 287.1 eV (C-O), at 288.7 eV (C=O), and at 291.6 eV, which corresponds to the $\pi \rightarrow \pi^*$ bonding band (shake-up satellite). The C1s spectra of polymer-grafted silica (method B) were deconvoluted in seven components, the first six being the same as in method A, and the seventh at 286.2 eV the C-N species. The positions of the binding energies correspond approximately to the reported values for different polymers in the database compiled by Beamson and Briggs [24], with the exception of the C-P functionality, taken from that reported by Yamamoto *et al.* [25]. The integrated areas under each contributing peak were calculated and the relative amounts of the carbon atoms having different chemical environments could be estimated (see Table 2). In this way, the samples of silica grafted with DPPS show a ratio of C-P, aromatic C-C and aliphatic C-C species of approximately 3:18:2 (See Figure 3). DIPS-grafted silica and the DTBPS-modified silica show the corresponding approximate ratios of 3:6:8, and 3:6:10. These ratios agree reasonably well with the structure of the repeating unit of the corresponding polymeric chains grafted onto the surface of silica, and the slight differences may be due to the monomer (TMPS) or AZO-initiator-rest (depending on the method used) remaining unreacted on the surface.

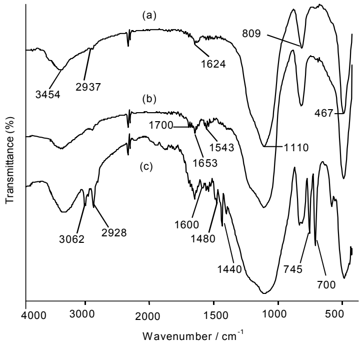

Figure 2. FTIR spectra of silica: a) Modified with APS, b) Modified with AZO and c) Grafted with poly-DPPS.

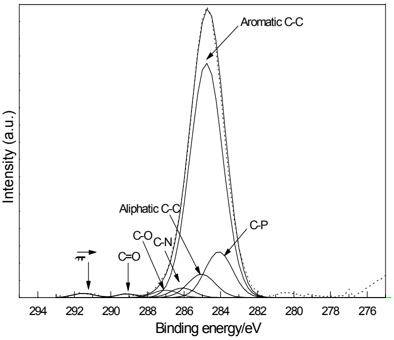

Figure 3. XPS core-level spectrum of silica grafted with DPPS (Method B).

Table 2 Relative areas of the contributing peaks in the XPS C1s spectra of modified silicas.

SILICA	ATOMIC RATIO	RELATIVE AREAS					
	C/Si	C-P	Vinyl C=C	Aromatic C-C	Aliphatic C-C	C-N	C-O / C=O
TMPS-Silica	2	-	27.64	-	41.54	-	30.82
DPPS-A2	5	13.88	-	69.92	5.97	-	7.93
DIPS-A	6	13.48	-	33.27	44.22	-	6.5
APS-Silica	1	-	-	-	72	16	12
DPPS-B2	7	12.37	-	75.83	6.31	2.23	2.4
DIPS-B1	5	15.66	-	31.78	42.12	3.48	6.7
DTBPS-B1	4	12.99	-	24.08	40.23	6.87	13.35

We also calculated from XPS-spectra the atomic ratios C/Si, which give us additional information about the amount of polymer grafted onto the surface. All polymer-grafted samples showed 3 to 6 times higher carbon/silica ratios than the monomer (TMPS-silica) or initiator (AZO-silica) grafted silica in their surface, confirming a good surface coverage by the grafted polymers.

Conclusions

The graft polymerization of three different phosphine-functionalized monomers (DPPS, DIPS and DTBPS) on monomer-modified silica or initiator-modified silica was accomplished; the use of the latter silica yielded better percent grafting. The results of the characterization methods applied proved that the grafting on the different silica surfaces was effectively carried out. As expected, there is an inverse relation between the surface areas of polymer-grafted silica and the quantity of polymer grafted. The deconvolutions and curve-fitting proposed for the XPS C1s spectra of the polymer-grafted silica showed good agreement with the structure and quantity of the polymer chains attached to silica. The molecular weights of the cleaved polymers indicate that the grafted polymer chains have a moderate size ($12 – 42 \times 10^3$ g mol^{-1}) with the exception of DTBPS which formed only oligomers. In almost all the samples the molecular weights and polydispersities of the cleaved polymers were smaller than those of the free polymers. The decrease of surface area and the high atomic C/Si ratios, suggest a good covering of the surface of the silica by the phosphine-functionalized polymers. The poor results of DTBPS, may be explained by steric-effects from the tert-butyl groups affecting polymerization. By the methods described, a series of DPPS and DIPS functionalized polymer-grafted silica materials were obtained which can be appropriate for packing reactive or catalytic columns for several applications.

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References

1. Ford WT (1986) ACS Symp Ser 308:155
2. Tunoori AR, Dutta D, Georg GI (1998) Tetrah Lett 39:8751
3. Caputo R, Cassano E, Longobardo L, Mastroianni D, Palumbo G (1995) Synthesis 141
4. Licea-Claveríe A, Rivero IA, García BL (1996) Polym Bull 37:415
5. Bajpai UDN, Otsu T (1993) Eur Polym J 29:971
6. Real J, Pagès M, Polo A, Piniella JF Alvarez-Larena A (1999) J Chem Soc, Chem Comm 3:277
7. Kosolapoff GM, Maier L (1972) Organic Phosphorous Compounds. Wiley-Interscience, New York London Sydney Toronto
8. Quin LD, Quin GS (2000) A Guide to Organophosphorous Chemistry. Wiley-Interscience, New York Chichester Weinheim Brisbane
9. Sherrington DC, Hodge P (1998) Synthesis and Separations using Functional Polymers. John Wiley & Sons, Chichester New York Brisbane Toronto Singapore
10. Jongsma T, Van Aert H, Fossen M, Challa G (1993) J Mol Cat 83:37
11. Licea-Claveríe A, Rivero IA, Morales MS, Moreno MG (1997) Polym Bull 39:551
12. Zhao W, Krausch G., Rafailovich MH, Sokolov J (1994) Macromol 27:2923
13. Nguyen V, Yoshida W, Jou JD, Cohen Y (2002) J Polym Sci, Polym Chem 40:26
14. Guo X, Ballauff M (2000) Langmuir 16:8719
15. Huang W, Skanth G, Baker GL, Bruening ML (2001) Langmuir 17:1731
16. Meyer T, Rehak P, Jäger C, Voigt I, Simon F, Spange S (2001) Macromol Symp 163:87
17. Matyjaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelman A, Luokala BB, Siclovan TM, Kickelbick G, Vallant T, Hoffmann H, Pakula T (1999) Macromol 32:8716
18. Huseman M, Morrison M, Benoit D, Frommer J, Mate CM, Hinsberg WD, Hedrick JL, Hawker CJ (2000) J Amer Chem Soc 122:1844
19. Ejaz M, Ohno K, Tsujii Y, Fukuda T (2000) Macromol 33:2870
20. Ejaz M, Tsujii Y, Fukuda T (2001) Polymer 42:6811
21. Tsujii Y, Ejaz M, Sato K, Goto A, Fukuda T (2001) Macromol 34:8872
22. Carlier E, Guyot A, Revillon A, Llauro-Darricades MF, Petiaud R (1991/1992) React Polym 16:41
23. Von Werne T, Patten TE (1999) J Am Chem Soc 32:7409
24. Beamson G, Briggs D (1992) High Resolution XPS of Organic Polymers. John Wiley & Sons, Chichester New York Brisbane Toronto Singapore
25. Yamamoto Y, Konno H (1986) Bull Chem Soc Jpn 59:1327