Polymer Bulletin 44, 223–229 (2000)

Polymer Bulletin

ATRP grafting from silica surface to create first and second generation of grafts

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Received: 17 July 1999/Revised version: 12 December 1999/Accepted: 10 January 2000

Summary

(11'-Chlorodimethylsilylundecyl)-2-chloro-2-phenylacetate **2** as an atom transfer radical polymerisation (ATRP) initiator was bound covalently to the surface of silica. ATRP grafting of styrene monomer from the silica surface was achieved and the grafts were detached from the solid particles for analysis. It is shown that after polymerisation of a first generation of grafts and work-up of the thus grafted silica the chain ends of the grafts are still active to initiate a second monomer feed to further chain growth.

Introduction

In recent time quite a few reports have been published upon initiation of graft polymerisation *from* the surface of a solid by using either the so-called stable free radical polymerisation (SFRP) mediated by 2,2',6,6'-tetramethylpiperidin-1-oyxl free radical or the atom transfer radical polymerisation (ATRP) route for "living"/controlled radical polymerisation (1-4). This technique opens an alternative to the classical free radical graft polymerisation which was very well developed especially by Rühe et al. (5,6). In order to bind polymer chains covalently to the surface of a solid, four important parameters have to be considered for *grafting from* techniques, which are first to minimize the formation of ungrafted free polymer chains, second to control the chain length of the grafts, third to control graft density on the surface, and fourth to provide a route for the formation of grafted block copolymers.

Rühe et al. (5,6) used azo initiators attached to a silica surface via a chlorodimethylsilyl anchor group. A short spacer link included an ester group to act as a weak link to detach the grafted polymer chains quantitatively in order to make them available for standard analytical techniques. A disadvantage of classical free radical polymerisation is that the once grafted chain ends are dead chain ends not allowing for the formation of tailored block copolymer grafts.

The so-called "living"/controlled radical polymerisation either by the TEMPO or the ATRP route allows for the synthesis of block copolymers (7-10) or graft copolymers (11) because the specific chain ends make possible re-initiation of a given monomer 2 after monomer 1 has been removed from the reaction mixture.

Here we wish to report the synthesis of a first and a second generation of poly(styrene) *grafted from* silica applying the ATRP technique.

Experimental part

The silica gel (Ultrasil 3370, Degussa) used in this study has a specific surface area of 165 m^2/g and a mean particle diameter of 14 nm. It was kept at 120°C in vacuo for 36 h

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prior to use. Styrene was vacuum distilled over CaH_2 and stored under nitrogen at -20°C. 2,2'-Bipyridyl (Fluka) was recrystallized from petrolether (Kp = 35-65°C). CuCl (Aldrich) was purified according to literature procedure (12). 2-Chloro-2-phenylacetyl chloride, 10-decen-1-ol , chlorodimethylsilane (Fluka), $H_2PtCl_6 \cdot 6\ H_2O$ (Merck) and anhydrous (±) propylenecarbonate (Aldrich) were used as received.

Undec-10'-enyl 2-chloro-2-phenylacetat **1**: A solution of 2-chloro-2-phenylacetyl chloride (4.8 mL, 33 mmol) in dry dichloromethane (50 mL) was added to a stirred solution of 10-decen-1-ol (6 mL, 30 mmol) and triethylamine (4.6 mL, 33 mmol) in dry dichloromethane (150 mL). After stirring at 0°C under argon for 1 h, the cooling bath was removed and stirring continued for 6 h. Triethylamine hydrochloride was separated by filtration and the solution was washed with aqueous $NaHCO_3$ (saturated), NaCl (saturated) and H_2O. The organic phase was dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel with petrolether/ethylacetate (15:1) to give the alkene **1** as a colourless oil. Yield: 65 %. ^{1}H-NMR ($CDCl_3$) δ [ppm]: 1.19 - 1.44 (b, 12H, $C\mathit{H}_2$), 1.61 (quintet, 2H, $C\mathit{H}_2$), 2.05 (q, 2H, $C\mathit{H}_2$), 4.17 (t, 2H, $OC\mathit{H}_2$), 4.93 - 5.03 (m 2H, alkene $=C\mathit{H}_2$), 5.35 (s, 1H, benzylic), 5.77 - 5.86 (m, 1H, alkene $=C\mathit{H}$), 7.38 (m, 3H, arom.), 7.52 (m, 2H, arom); ^{13}C-NMR ($CDCl_3$) δ [ppm]: 25.59, 28.32, 28.87, 29.02, 29.04, 29.29, 29.33, 33.75, 59.17, 66.50, 114.16, 127.88, 128.76, 129.18, 135.92, 139.13, 168.37; IR (film) [cm^{-1}]: 3072, 3033, 2926, 2854, 1755, 1640, 1496, 1455, 1280, 1161, 993, 910, 725, 695.

(11'-Chlorodimethylsilylundecyl) 2-chloro-2-phenylacetate **2**: To a solution of the alkene **1** (5 g, 15,5 mmol) in chlorodimethylsilane (40 mL, 370 mmol) was added a 1:1 ethanol/dimethoxyethan solution (0.5 mL) of $H_2PtCl_6 \cdot 6\ H_2O$ (30 mg), and the reaction mixture was stirred at room temperature under argon in the dark for 12 h. Excess chlorodimethylsilane was removed under reduced pressure. Dry dichloromethane (20 mL) was added and the solution was passed through s short column of dry Na_2SO_4, the column was washed with dry dichloromethane (50 mL) and the solvent was removed in vacuo. The crude product **2** was used without further purification. Yield: 95 %. ^{1}H-NMR ($CDCl_3$) δ [ppm]: 0.41 (s, 6H, $Si(C\mathit{H}_3)_2$), 0.82 (m, 2H, $SiC\mathit{H}_2$), 1.20 - 1.46 (b, 16H, $C\mathit{H}_2$), 1.61 (quintet, 2H, $C\mathit{H}_2$), 4.17 (t, 2H, $OC\mathit{H}_2$), 5.36 (s, 1H, benzylic), 7.38 (m, 3H, arom.), 7.52 (m, 2H, arom); ^{13}C-NMR ($CDCl_3$) δ [ppm]: 1.64, 18.96, 22.94, 25.60, 28.32, 29.04, 29.18, 29.37, 29.41, 29.46, 32.91, 59.17, 66.51, 127.88, 128.76, 129.18, 135.91, 168.37;IR (film) [cm^{-1}]: 3071, 3032, 2926, 2855, 1756, 1496, 1455, 1279, 1254, 1162, 856, 808, 725, 695.

Graft reactions were carried out in Schlenk flasks equipped with a magnetical stirring bar. In a typical graft polymerisation a 25 mL Schlenk flask was charged with 1.1 g silica modified with **2** (0.33 mmol surface bounded initiator), 562 mg (3.6 mmol) 2,2'-bipyridyl, 8 mL (70 mmol) styrene and 8 mL propylenecarbonate. The suspension was purged with nitrogen for 10 min. To this suspension was added 178 mg (1.8 mmol) CuCl. The mixture was degassed again by purging with nitrogen. The flask was sealed with a septum and the polymerisation was carried out at 120°C for 24 h under mechanical stirring. The viscous mixture was diluted with toluene and the polymer grafted silica was separated by centrifugation. Several washings of the poly(styrene) modified silica with toluene were done to remove ungrafted poly(styrene). Remaining Cu-salts were extracted by destilled water from a toluene suspension of the polymer-grafted silica. The product was isolated by precipitation in methanol. The solid material was collected and dried at 50°C and 10 mbar to constant weight. Yield: 2.25 g of poly(styrene) grafted silica.

For the synthesis of a second generation of grafts, the first generation grafted silica was reactivated. Therefore it was redispersed in propylenecarbonate and appropriate amounts of CuCl and the ligand were added. The grafting was carried out with calculated amounts of styrene monomer as described above. After extensive extraction of the grafted silica in a Soxhlet apparatus, no ungrafted polymer was found.

The grafts of the first as well as of the first+second generation were detached from the silica surface via transesterfication as described in (6).

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Spectra Physics SP 8100 liquid chromatograph with 2 mixed B columns from Polymer Laboratories equipped with a Water Associates differential refractometer and a Labomatic UV-detector. Measurements were performed in THF as eluent and the equipment was calibrated with narrow molecular weight poly(styrene) standards. TGA thermograms were taken from a TA Instruments TGA HiRes 2950 analyser at a heating range of 20 K/min under nitrogen atmosphere between 20°C and 550°C and in the temperature range from 550°C to 700°C under air atmosphere. NMR spectroscopy was performed on a Bruker AM 400 spectrometer using deuterated solvents with the solvent peak as a reference. FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer. Samples were prepared as KBr-pellets, films between NaCl-plates or in the case of polymer-grafted silica thin films were prepared from dilute toluene suspensions by evaporating off the solvent.

Results and discussion

Recently Hawker et al. reported ATRP grafting of methyl methacrylate from a silicon wafer surface (4). The system they used to anchor the initiating site onto the silicon wafer surface was (5'-trichlorosilylpentyl)-2-bromo-2-methylpropionate which contains a trichlorosilyl anchor group and a 2-bromo-2-methylpropionate moiety which initiates ATRP.

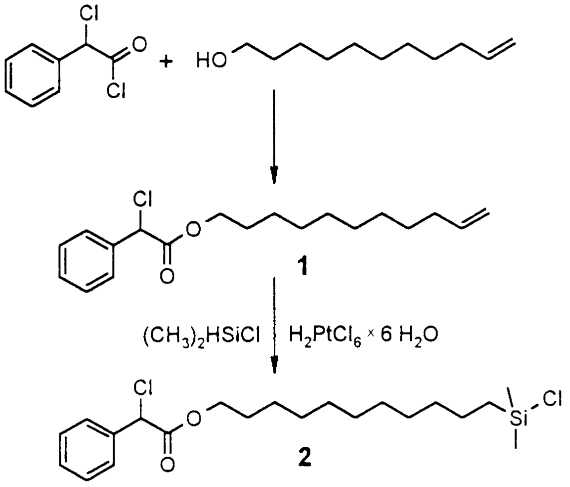

Fig. 1: Synthesis of (11'-chlorodimethylsilylundecyl)-2-chloro-2-phenylacetate **2**

According to Fig. 1, we have synthesized (11'-chlorodimethylsilylundecyl)-2-chloro-2-phenylacetate **2** as surface active initiation system by initial reaction of 10-decen-1-ol with 2-chloro-2-phenylacetyl chloride in the presence of triethylamine to give the undecenylic ester **1**. Hydrosilylation of **1** with chlorodimethylsilane in the presence of a patinum catalyst afford the chlorosilyl derivative **2** which could then attached to a variety of silanol surfaces. From such modified surfaces it is possible to initiat an ATR graft-polymerisation, see Fig.2. The initiator **2** also provides an ester link which makes it possible to detach organic molecules from the solid surface for further analyses, and we have made use of this unique possibility.

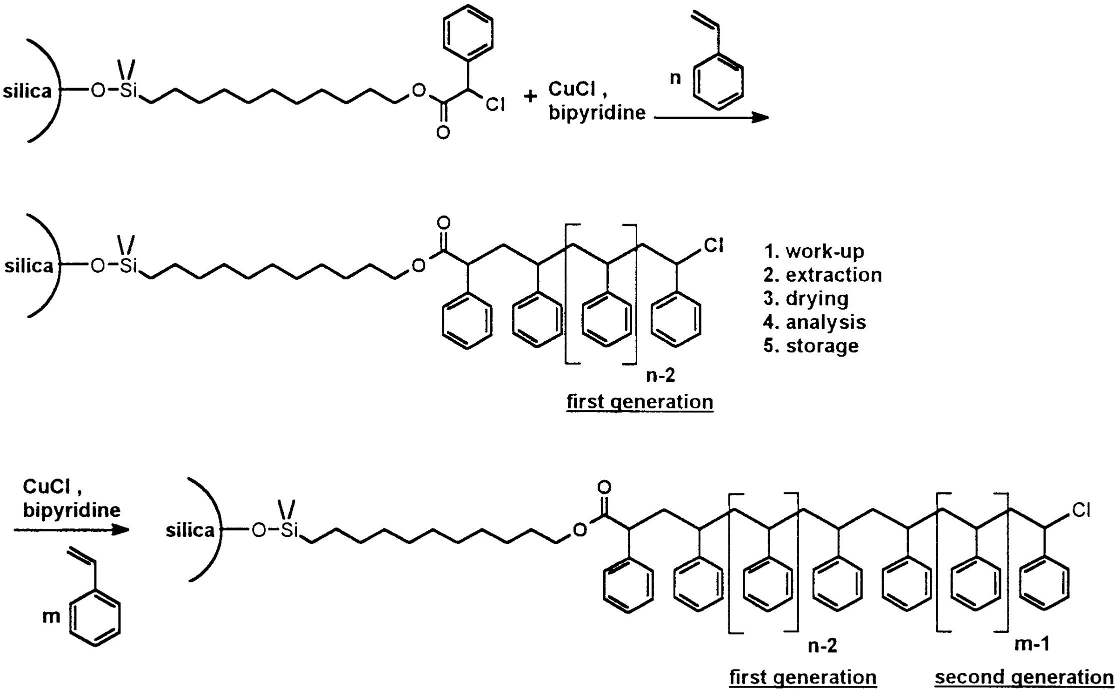

Fig.2: Scheme for ATR graft polymerisation from silica

The initiator **2** was bound to the silica surface by reacting the silica in dry toluene with **2** for 24 h in the presence of triethylamine at ambient temperature. The density of initiating sites on the silica surface was controlled by the concentration of **2** in the toluene solution that means by the **2**/silica ratio and was determined quantitatively by TGA, see Table 1.

Tab.1: Modification of silica with different amounts of **2**

entry	**2**/silica (mmol/g) a)	weight loss (%) b)	[**2**] (μmol/g) c)	[**2**] (μmol/m^2) c)
1	0.27	4.9	146	0.88
2	0.73	9.9	310	1.88
3	1.78	10.5	330	2.00

a) initial ratio of the immobilisation reaction , b) determined by TGA in the temperature range 200-650°C, c) calculated amount of bounded initiator **2** at the silica surface per g SiO_2

Under these conditions the immobilisation of **2** on the silica surface seems to reach maximum around 330 µmol **2**/g SiO_2.

A typical TGA diagram is shown in Fig.3. Although the silica was dried in a vaccum-oven for 72 h at 50°C, a considerable loss of volatile material is detected in the temperature range between 30°C and 200°C due to adsorption of humidity during storage as described by Zettlemoyer et al. (13) This is followed by the loss of organic material in the temperature range of 200°C to 650°C from which the weight loss can be derived quantitatively and the density of initiating sites on the silica surface can be calculated.

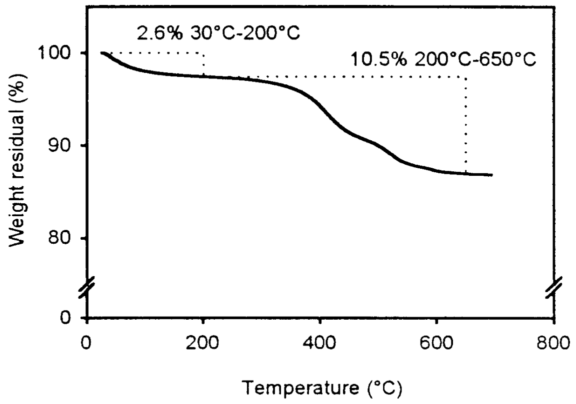

Fig.3: TGA analysis of silica decorated with **2**

ATR graftpolymerisation from silica functionalised with **2** of styrene monomer was carried out in propylenecarbonate as solvent (monomer/solvent 1/1 v/v) at 120°C in the presence of CuCl and 2,2'-bipyridyl to act as the copper complexing agent. After 24 h of polymerisation the reaction was stopped by cooling down the reaction in an ice-bath. The solidified reaction mixture was redispersed in toluene. After separation of poly(styrene)-grafted silica by centrifugation the silica was transferred into a Soxhlet apparatus for complete extraction of non-grafted poly(styrene) which might be formed due to thermal initiation.

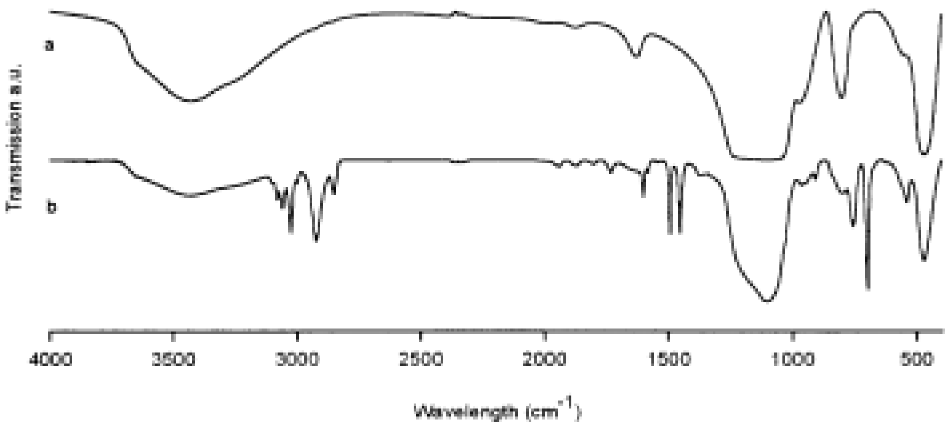

Fig.4: FT-IR spectra of a) unmodified silica and b) poly(styrene) grafted silica

The graft density of surface attached poly(styrene) chains is approximately 1.2 g poly-(styrene)/g SiO_2. The FT-IR spectrum of poly(styrene) grafted silica shows the aspected signals for poly(styrene). The broad band around 1100 cm^{-1} results from Si-O streching of silica.

A small fraction of the thus grafted silica was removed and the grafts were cleaved from the silica surface by transesterfication and molar mass and molar mass distribution, respectively, of this *first generation of poly(styrene) grafts* was determined by GPC, see Fig. 5.

From the values for initial initiator graft density, graft density of poly(styrene) and the molecular weight (M_n) of detached chains, it is possible to calculate the initiator efficiency. About 17% of the initial initiator was able to initiate a polymerisation.

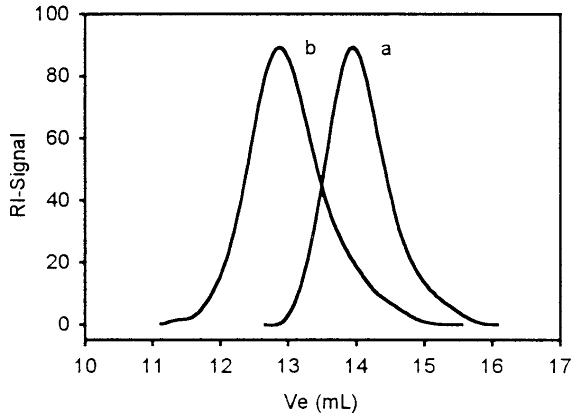

Fig.5: GPC traces of a) *first generation of poly(styrene)* and b) *first+second generation of poly(styrene)* after separation from the silica-surface

This *first generation of poly(styrene) grafts* still contains the active site for ATRP initiation and propagation at the chain ends of the grafts which means that even after work-up and storage of the polymer grafted silica, the chain ends remain active to reinitiate ATR polymerisation.

This was proven by using the thus grafted and isolated silica as a multifunctional ATRP initiator for a second feed of styrene monomer at the same conditions for polymerisation and work-up. The graft density of attached poly(styrene) increases up to 3.8 g poly(styrene)/g SiO_2. After cleavage of the grafts of this *first+second generation of poly(styrene) grafts,* in Fig.5, GPC analysis shows a considerable increase in molar mass. This GPC trace displays a small shoulder in the range of molar mass of the *first generation of poly(styrene) grafts* thus indicating that approximately 10 to 15 % of these *first generation of grafts* have not been active for re-initiation of the second monomer feed.

Tab.2: Graft density of attached poly(styrene), molecular weights and molecular weight distribution of detached poly(styrene)

	g PS / g SiO_2	M_w (g/mol) $^{a)}$	M_n (g/mol)$^{a)}$	PD$^{a)}$
first gen. poly(styrene)	1.2	31000	21000	1.47
first+second gen. of poly(styrene)	3.8	122000	70000	1.75

a) determined by GPC

From the data compiled in Table 2 it becomes obvious that the polydispersity of the grafts both of the first and of the first+second generation is slightly broader than reported in the literature for solution ATR polymerisation of linear poly(styrene) (14).
This may be caused by interference of densely propagating "living" radical chains from the heterophase solid surface. This observation is currently under further investigation.

Acknowledgement

This work was supported by a grant from the Ministry of Education and Science of Lower Saxony and by Fonds der Chemischen Industrie. We are grateful to *Georg Körner, Deutsches Institut für Kautschuktechnologie e.V. Hannover,* for carrying out the TGA experiments. We also thank *Dr B Freund, Degussa AG,* for the donation of samples of silica.

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