Anionic grafting of polystyrene and poly(styrene-*block*-isoprene) onto microparticulate silica and glass slides

Michiel L. C. M. Oosterling, Arjen Sein and Arend Jan Schouten*
Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

(Received 18 September 1991; revised 16 December 1991; accepted 6 February 1992)

Polystyrene and poly(styrene-*block*-isoprene) were grafted onto microparticulate silica by initiating immobilized double bonds at the silica surface with t-butyllithium, and subsequently adding monomer to the reaction suspension. Grafted block copolymers could be synthesized by adding a second monomer after the first monomer had reacted completely. The obtained molecular-weight distributions were somewhat broader than those for comparable anionic homopolymerizations.

(Keywords: anionic graft polymerization; microparticulate silica; polystyrene; block copolymerization; immobilized double bond)

INTRODUCTION

Grafting polymers onto solid surfaces can lead to many interesting applications. The materials can be used for enzyme immobilization[1], colloid stabilization[2–4], adhesion in composite materials[5–13], catalysis[14] and separation studies[15]. There are three ways to graft a polymer onto a surface[2–16].

The first, and most used, method is the copolymerization of a monomer with an immobilized double bond at the surface. This method leads to a grafted polymer, which might be attached to the surface at several places, and to an excess of non-grafted polymer. The main disadvantage of this system is that it is not very well defined. The structure of the grafted polymers and the number and positions of the attached segments along the chain are unknown[8–10,17,18].

A second method of grafting is termination of a growing chain at a suitable group attached to the surface. This system leads to end-grafted chains with a much better defined structure than the grafted polymers of the former method. The disadvantage of this way of grafting is that the chains grafted at the beginning of the reaction can screen other possible grafting sites. Therefore the graft density (number of chains per unit area) remains relatively low.

Screening of grafting sites can be avoided if polymerization is initiated at the surface, because addition of monomer to the growing chain ends or to a primary radical will be hindered much less by chain molecules already attached to the surface as long as these chains are in good solvent conditions. If initiation is fast compared to propagation, no grafting sites may be screened at all. The way to initiate polymerization at a surface is to immobilize an initiator at the surface. Several workers have used this method in different systems. Dietz *et al.*[11] and Tsubokawa *et al.*[19] used amine groups introduced to the surface of silica and carbon black respectively to initiate the polymerization of *N*-carboxy anhydrides in order to prepare end-grafted polypeptides. Nakatsuka[1], Laible *et al.*[3], Fery *et al.*[4] and Boven *et al.*[12] immobilized an azo-initiator at the surface of silica and glass slides. Large amounts of grafted polymer could be obtained this way. Starting anionic polymerization at a solid surface might combine the advantages of anionic living polymerization as proposed by Szwarc[20,21], and of graft polymerizations starting at the surface. In living anionic polymerization, initiation is fast compared to propagation, and there is no chain transfer or termination. Making block copolymers is relatively easy by adding different monomers one after another. Molecular weights are determined by the monomer/initiator ratio, and the resulting polymer should be monodisperse. Braun *et al.*[13] used a combination of t-butyllithium (BuLi) and tetramethylethylenediamine (TMED) to create initiator sites at the surface of carbon black for the anionic graft polymerization of styrene. Schomaker *et al.*[15] first immobilized a methyl methacrylate (MMA) derivative at the surface of Aerosil A200V. This immobilized monomer was initiated by a Grignard reagent, after which MMA was added.

It is the aim of this work to study the possibility of grafting monodisperse polystyrene and block copolymers of styrene with other monomers onto silica and other Si–OH containing surfaces. The strategy we used was derived from the work of Schomaker *et al.*[15]. After immobilization of a styrene fragment onto the surface, initiation of this fragment was carried out first by a normal anionic initiator, and subsequently new monomer was added. Characterization of the grafted products was done with elemental analysis, Fourier transform infra-red (*FT*i.r.) and ^{1}H nuclear magnetic resonance (n.m.r.)

---

* To whom correspondence should be addressed

0032–3861/92/204394–07

spectroscopies, gel permeation chromatography (g.p.c.) and X-ray photoelectron spectroscopy (X.p.s.)/electron spectroscopy for chemical analysis (e.s.c.a.).

EXPERIMENTAL

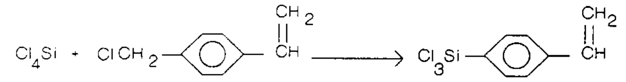
Silica (Aerosil A200V, Degussa; average particle diameter 12 nm, specific surface area 200 $m^2 g^{-1}$) was dried for 2 days at 120°C under vacuum. Glass slides were submerged in chromic acid, rinsed with water (Milli-Q), methanol and ether, and dried at 120°C under vacuum. Silicon wafers, both sides polished, were cleaned in hydrofluoric acid (20%), after which a new silicon oxide layer was allowed to develop: freshly etched silicon exposed to air at room temperature is rapidly covered by a thin oxide layer. The thickness of this layer remains in a convenient range (0.5 to 2.5 nm)[22]. Toluene, tetrahydrofuran (THF) and ether were distilled under nitrogen atmosphere from sodium wire before use. Styrene and 2-vinylpyridine (2VP) were triply distilled under reduced nitrogen pressure from CaH_2 and copper powder, and then degassed before use. MMA was first distilled from CaH_2 and copper powder under reduced nitrogen pressure, and then from trioctylaluminium under reduced nitrogen pressure before use. Isoprene was distilled twice from sodium wire under a nitrogen atmosphere. Chloromethylstyrene (Dow) was distilled under reduced nitrogen pressure. Magnesium was rinsed with dry ether.

Characterization

*FT*i.r. spectra were recorded on a Bruker IFS 88 or a Mattson Galaxy spectrophotometer by the d.r.i.f.t. (diffuse reflectance *FT*i.r.) technique for Aerosil and by simple transmission measurements for silicon wafers. The molar masses of the homopolymers were determined by means of g.p.c. on a Waters ALC/GPC 150C using either THF or chloroform as an eluant and using polystyrene standards in the method of universal calibration. The Mark–Houwink constants used were $K = 1.12 \times 10^{-4}$ dl g^{-1}, $a = 0.73$ for both polystyrene and block copolymers eluting with chloroform, and $K = 1.28 \times 10^{-4}$ dl g^{-1}, $a = 0.70$ for polystyrene and block copolymers with THF as an eluant. The amount of grafted polymer per gram of silica was determined by elemental analysis. Elemental analysis and ^1H n.m.r. spectroscopy were used to determine copolymer composition.

Synthesis of p(m)*-vinylbenzyltrichlorosilane (VBS)*

A Grignard reagent was made from chloromethylstyrene and magnesium in diethyl ether. This reagent was added to an excess of tetrachlorosilane in ether. The reaction mixture was refluxed for an hour and allowed to cool down. Then the magnesium salts were filtered off, and the product, *p*(*m*)-vinylbenzyltrichlorosilane (VBS), was isolated by evaporating the solvent and excess tetrachlorosilane (*Scheme 1*). The crude product was distilled under reduced nitrogen pressure to give a colourless clear fluid. The product was identified with *FT*i.r. and ^1H n.m.r. measurements (*Figure 1*).



Scheme 1 Synthesis of the coupling agent

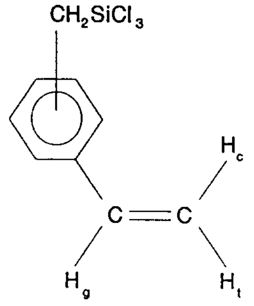
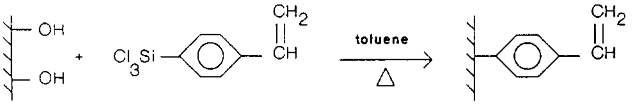
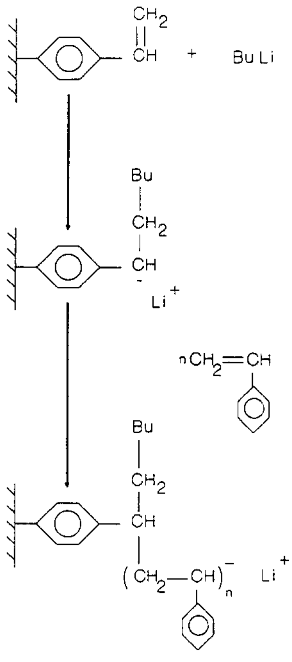


Figure 1 Coupling agent



Scheme 2 Coupling of the coupling agent to glass



Scheme 3 Anionic graft polymerization

Functionalization of silica

VBS was added (1.5 g per 100 ml toluene) to a 5 wt% silica suspension in toluene and the reaction mixture was refluxed for an hour. Then 4 ml of hexamethyldisilazane was added to block the remaining hydroxyl groups at the surface. Refluxing was continued for a further 2 h (*Scheme 2*). The modified silica was washed with toluene (three times), acetone, water and methanol and dried at 100°C under vacuum. The product was characterized by d.r.i.f.t. and elemental analysis.

Graft polymerization

All graft polymerizations onto silica were carried out in toluene under a nitrogen atmosphere at room temperature, except for the polymerizations of the PMMA and P2VP blocks, which were carried out at −80°C. The anionc initiator used was added to the reaction vessel with the silica in toluene (0.5 wt%). The first monomer was added after half an hour to be sure that all immobilized double bonds had been initiated (*Scheme 3*). If block copolymers had to be made, the

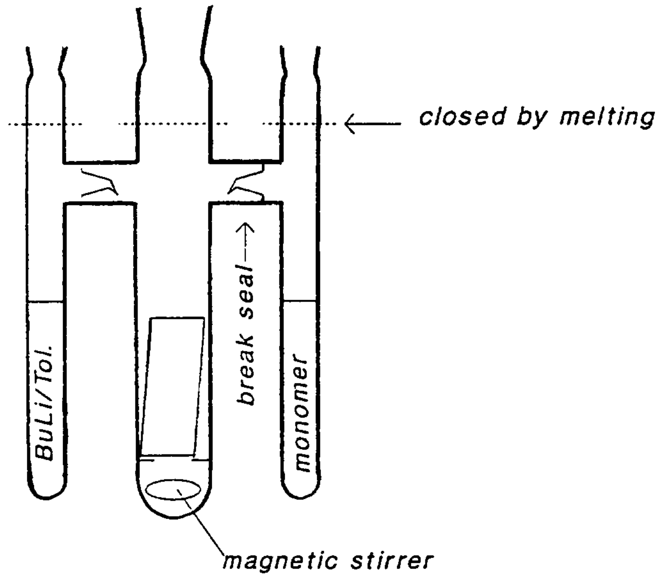


Figure 2 Reaction vessel

second monomer was added after 1 day. The grafted products were washed by extracting several times with chloroform/methanol (4/1 v/v) and centrifuging until no more free homopolymer was found. After the last extraction the product was suspended in chloroform and poured into methanol. The white powder was dried at 70°C under vacuum. Because usually an excess BuLi was used, homopolymer was formed too during the reactions. These polymers were precipitated in methanol and dried at 70°C under vacuum. The graft polymerizations onto glass slides and silicon wafers were performed under a high vacuum (10^{-6} mbar) in a sealed reaction vessel (*Figure 2*). The vessel contained a central reaction chamber in which the glass slide was placed, and four side-arms, closed with break-seals for three monomers and a BuLi solution in toluene. After breaking the seal, the BuLi solution was poured into the central reaction chamber. After an hour the solution was poured back into the side-arm, and the toluene was distilled back into the reaction chamber. Then the arm with the BuLi was melted off. The monomers were added one by one by breaking the seals and distilling the monomers into the reaction chamber. Work-up procedure was like that of silica. The layers formed on the glass slides were too thin to be detected by *FT*i.r. Therefore we used e.s.c.a. to detect the grafted polystyrene.

RESULTS AND DISCUSSION

Synthesis of the coupling agent

The first attempt to immobilize styryl groups onto the surface was done by reacting chloromethylstyrene with a glass surface treated with an amino functional coupling agent. Although a fair amount of styrene could be immobilized this way, subsequent trials to initiate these styryl groups failed, probably because of side-reactions of BuLi with the water-containing surface layer. The reaction of chloromethylstyrene with an amino group at the surface will be difficult to regulate and part of the amino groups will be converted into quarternary ammonium salts. Especially, these ammonium salts will be very difficult to dry. Therefore we prepared a styryl coupling agent without an amino group, and used this in our anionic graft reactions. The method of synthesizing this styryl functional coupling agent was provided by Dr M. Čapka, who made a Grignard reagent out of *p*-bromostyrene and reacted this with tetrachlorosilane using THF as a solvent. However the Grignard reagent of chloromethylstyrene polymerizes quickly in THF but not in ether[23]. Therefore ether was used as a solvent. In order to prepare mainly monofunctional coupling agent, an excess of tetrachlorosilane was used. The reaction product was a yellow oil. After distillation a colourless clear liquid was obtained. The ^{1}H n.m.r. spectrum showed a shift of the methylene group from 4.5 ppm for chloromethylstyrene to 2.8 ppm for the coupling agent. The vinyl double bond stayed intact, as can be concluded in both ^{1}H n.m.r. (6.8 ppm (q) H_g, 5.7 ppm (d) H_c, 5.3 ppm (d) H_t; see *Figure 1*) and *FT*i.r. (1633 cm^{-1}).

Coupling of VBS onto Aerosil

Aerosil could be functionalized with 0.29×10^{-3} mol styryl groups per gram of Aerosil (elemental analysis, titration). Aerosil A200V contains about 10^{-3} mol hydroxyl groups per gram[24]. This means that only 58% of these groups have reacted if we assume that the coupling agent reacts with two surface hydroxyl groups[25]. These results indicate that quite a large amount of hydroxyl groups is still present. Therefore, it is necessary to treat the reaction product with hexamethyldisilazane to block these groups, preventing them from interfering with the anionic polymerization. In the *FT*i.r. (d.r.i.f.t.) spectrum of the coupled product (*Figure 3*) one can see the immobilized double bond (1633 cm^{-1}) and the phenyl groups (1601, 1583 and 1511 cm^{-1}).

Graft polymerizations

Graft polymerizations were carried out in toluene and not in THF because in THF the BuLi initiator was too active: it initiated not only the polymerization, but also reacted with the Si–O–Si bonds, which couple the styryl groups to the silica, and in this solvent we found a loss of coupling agent. This resulted in a lower graft density than usual and traces of Si in the free polymer. In fact

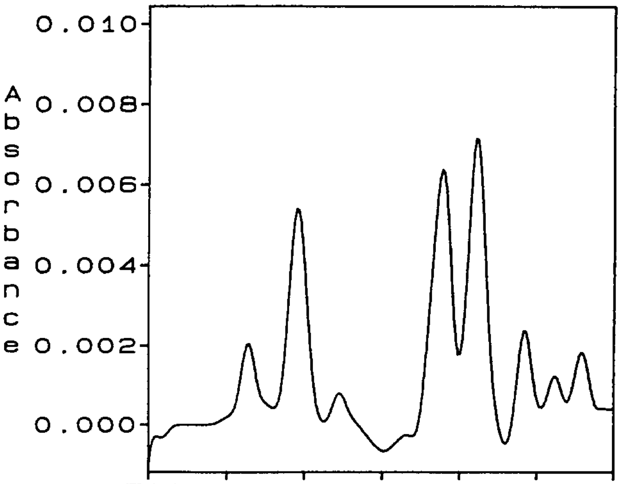


Figure 3 *FT*i.r. (d.r.i.f.t.) of the coupling agent at the glass surface: 1632 cm^{-1}, C=C; 1601 cm^{-1}, phenyl; 1511 cm^{-1}, phenyl; 1493 cm^{-1}, phenyl

this reaction is another way to attach organic groups to the silica surface[18,26]. Using toluene as a solvent, however, has the disadvantage that the BuLi initiator forms aggregates leading to a less reactive initiator, and 'sleeping' polymers during polymerization[27]. Initiation of the double bonds was not instantaneous. In the case of Aerosil A200V this can be seen by a change of colour, and a higher resulting graft density after longer initiation times. Immediately after addition of BuLi the reaction suspension is white, but within a few minutes the colour becomes pale yellow, and then slowly turns into organge/red. After about 15 min initiation time the colour does not change any more, and the graft density at the end of the reaction remains constant. Graft polymerizations onto Aerosil A200V were characterized with elemental analysis and *FT*i.r. (d.r.i.f.t.) measurements (*Figure 4*).

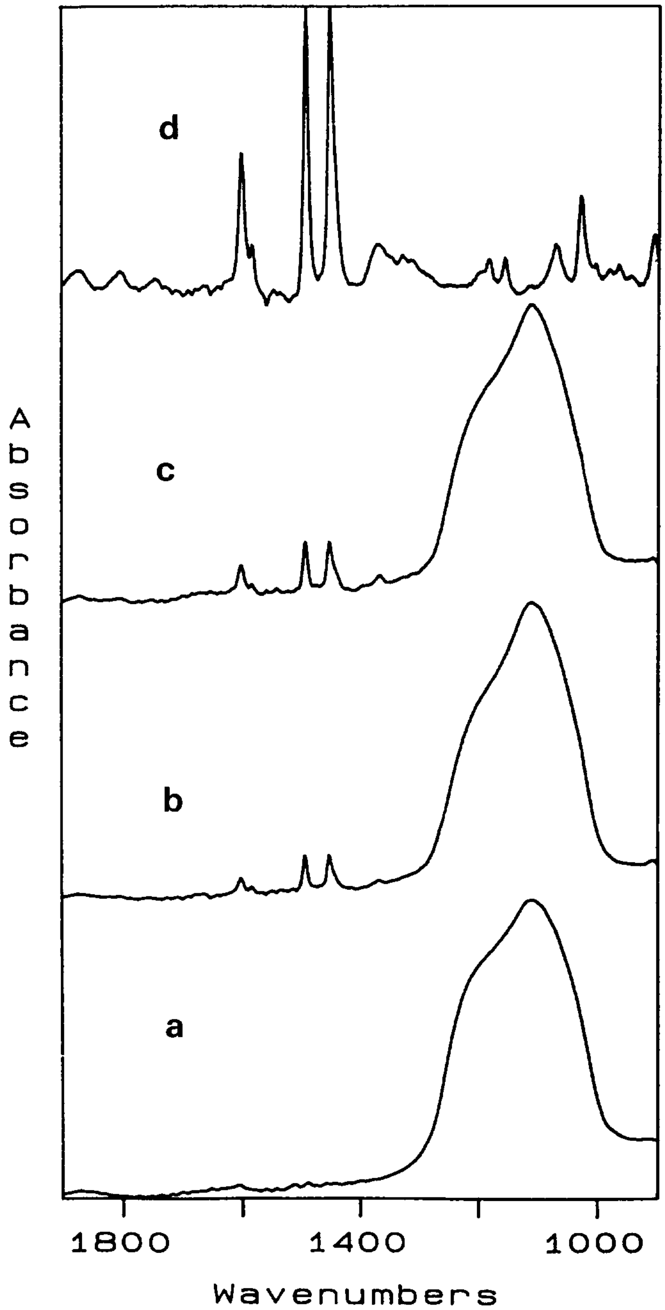


Figure 4 Polystyrene on Aerosil: (a) coupling agent on Aerosil (0.3 mmol g^{-1}); (b) polystyrene on Aerosil (GP-6 0.27 g g^{-1}); (c) polystyrene on Aerosil (GP-17 0.87 g g^{-1}); (d) pure polystyrene

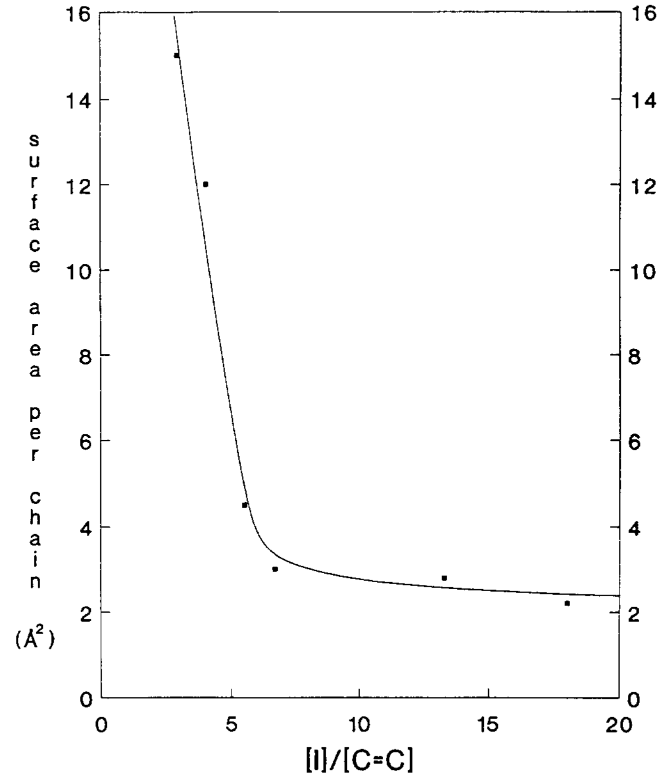


Figure 5 Chain density *versus* excess initiator: [C=C] = number of double bonds at the surface; [I] = number of initiator molecules

In order to be sure that all the polymer as detected by elemental analysis originated from grafted polymers, control experiments have been carried out: physically adsorbed polymer on Aerosil 200V could be washed away completely with chloroform/methanol (4/1 v/v). In the case of flat surfaces the products were finally washed ultrasonically with chloroform. This means that in grafting experiments all the polymer left on the surface after washing must be bound to the surface.

Not all double bonds had been initiated at a BuLi/double bond ratio of 1. This is demonstrated by *Figure 5*, where the surface area per chain is calculated as a function of the initiator/double bond ratio. In fact a maximum chain density is reached at a fivefold excess of BuLi. One possible explanation might be the formation of aggregates of BuLi molecules in non-polar solvents. These aggregates are usually tetramers and hexamers[27], and might also be responsible for the formation of homopolymers during the reaction. Aggregation can be avoided by making the solvent more polar, for instance by adding some THF. However, using a solvent mixture of toluene/THF (9/1 v/v) in our experiments did not improve the results. Increasing the amount of THF also increases the risk of decoupling of the coupling agent, as mentioned before.

The amount of grafted polymer (loading) increases linearly with increasing monomer concentration (*Figure 6*) as was expected for anionic polymerization. The chain density was calculated by dividing the amount of grafted chains, determined by elemental analysis, by the number-average molecular weight of the non-grafted polymer and the surface area, assuming the molecular weights of grafted and non-grafted polymer to be the same. It appeared that the increase in loading was completely due to an increase of the molecular weight

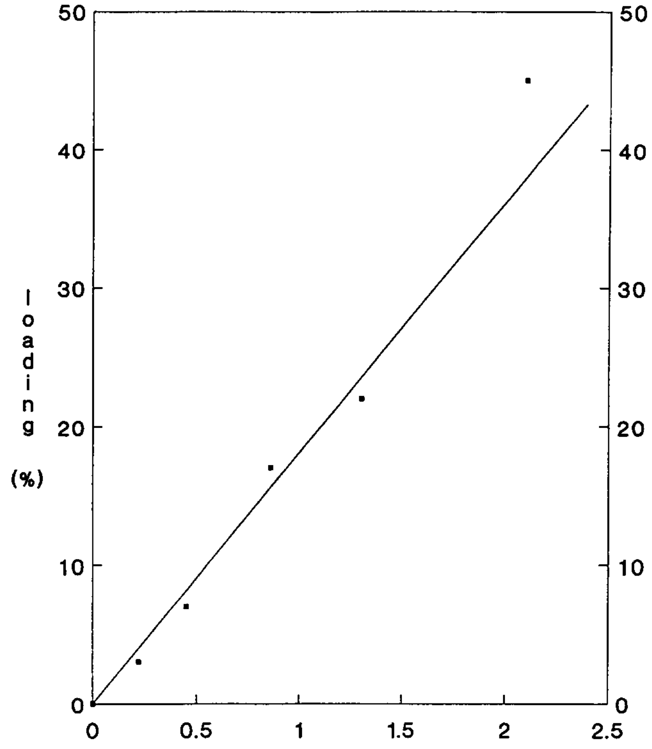


Figure 6 Loading *versus* monomer concentration; [I]/[C=C] = 6

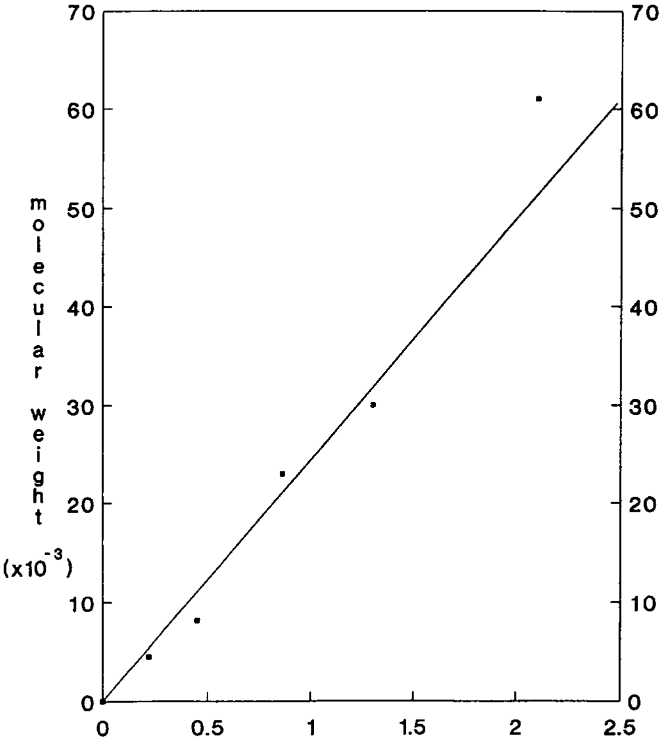


Figure 7 Number-average molecular weight *versus* monomer concentration; [I]/[C=C] = 6

(*Figure 7*) and not to an increase in grafting density. This result is in full accordance with the concept of the living anionic polymerization mechanism. In these reaction products the silica could not be removed by dissolving the Aerosil with hydrofluoric acid (20%) like it can be done with grafted PMMA[12]. Therefore we could not measure the molecular weights of the grafted chains directly. The molecular weights found for the homopolymers were somewhat higher than calculated using the initiator/monomer ratio, and the molecular-weight distributions were somewhat higher than usual for anionic homopolymerization (about 1.3). This is probably caused by free hydroxyl groups, which are still present at the surface, even though a blocking agent has been used, or by impurities (H_2O, CO_2, etc.) adsorbed onto the silica. The latter reason was suggested by Braun *et al.*[13] too, for the broadening of the molecular-weight distributions in the anionic grafting onto carbon black.

Block copolymers have been prepared by adding a second monomer after complete consumption of the first monomer. In this way grafted poly(styrene-*block*-isoprene-*block*-styrene), poly(styrene-*block*-methyl methacrylate) and poly(styrene-*block*-2-vinylpyridine) were prepared. Anionic polymerization of MMA and 2VP had to be carried out at lower temperatures to avoid side-reactions. For 2VP it was also necessary to use diphenylethylene (DFE) as a one-monomer 'block' between polystyrene and poly(2-vinylpyridine). DFE does not itself polymerize, but can initiate 2VP polymerization anionically. ^1H n.m.r. and elemental analysis were used to determine copolymer composition. The formation of the block copolymer can be seen with *FT*i.r. (*Figure 8*). So on Aerosil it was demonstrated that it is possible to use living anionic polymerization to create end-grafted polymers. The next step was to increase the size of the inorganic particles, and eventually try to graft polymers and block copolymers onto large substrates like glass slides and silicon wafers. This increase in size decreases the surface area to be modified, and therefore the total amount of initiated immobilized double bonds is very low in these systems. Consequently, the system was very sensitive to traces of impurities. This meant that very special care had to be taken to exclude all impurities in solvents, monomers and glassware, so we performed the reactions under high vacuum (10^{-6} mbar) in a sealed reaction vessel (*Figure 2*). With glass slides it is

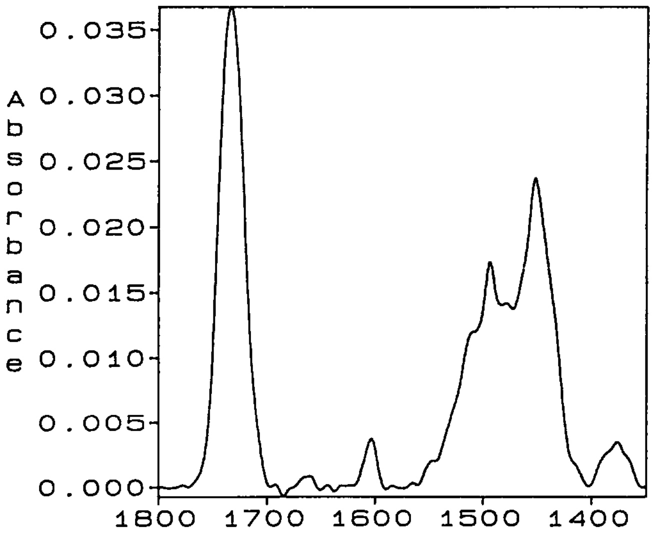


Figure 8 *FT*i.r. (d.r.i.f.t.) spectrum of grafted poly(styrene-*block*-methyl methacrylate); PS:PMMA = 1:1 (elemental analysis); 1733 cm^{-1}, C=O; 1603 cm^{-1}, phenyl; 1493 cm^{-1}, phenyl; 1455 cm^{-1}, $-CH_2-$ (deformation)

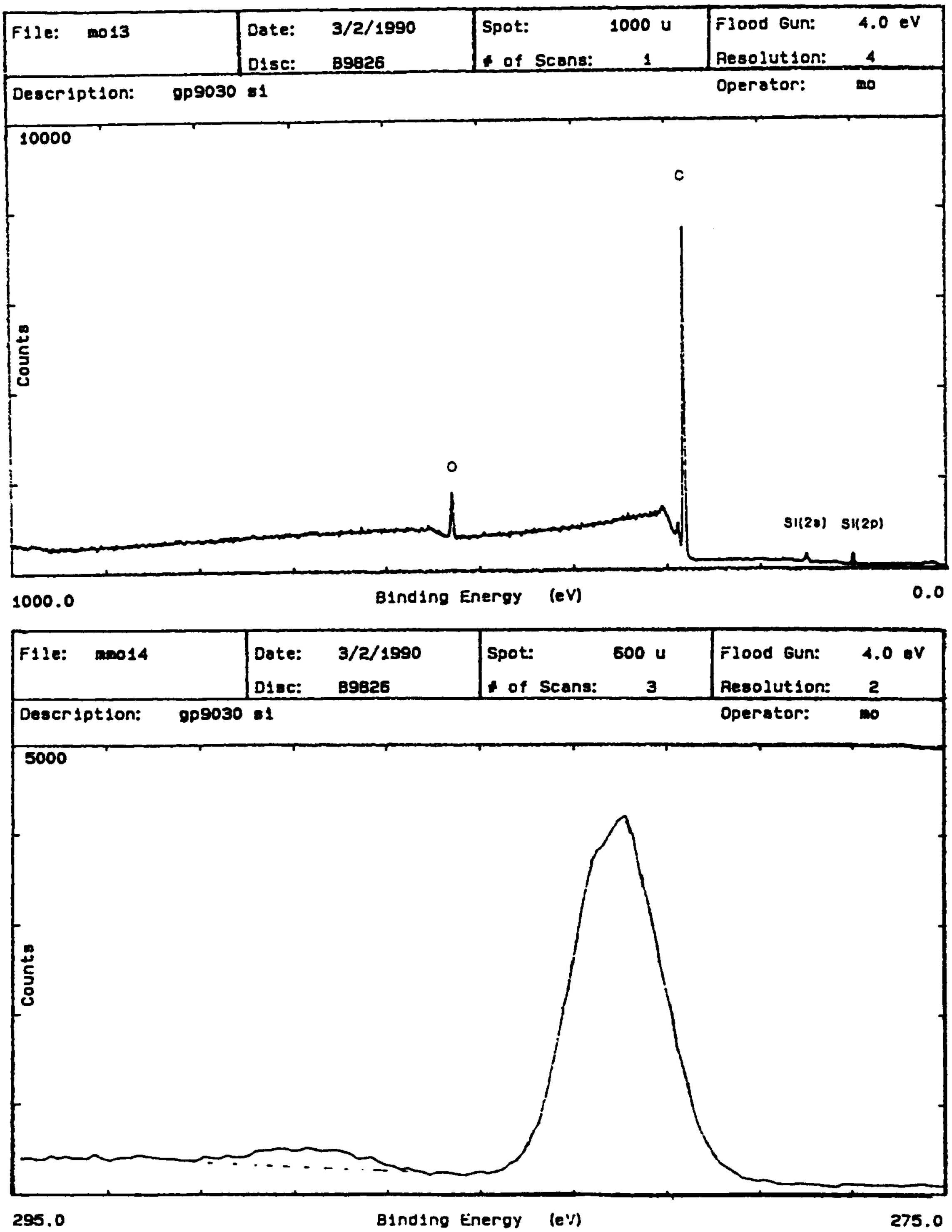


Figure 9 E.s.c.a. spectrum of polystyrene (GP-9030) on a silicon wafer: Si, 100 eV (2p) and 149 eV (2s); C, 284 eV (1s); O, 532 eV (1s); narrow scan, phenyl shake-up

very difficult to detect the grafted layer by *FT*i.r. spectroscopy. Therefore we used e.s.c.a. E.s.c.a. gives information about the top 50–100 Å of a surface. In the e.s.c.a. spectrum (*Figure 9*) the carbon peak (284 eV, 1s) increases and the silicon peaks (100 eV, 2p; 149 eV, 2s) and oxygen peak (532 eV, 1s) decrease as the grafted layer gets thicker. Polystyrene can be identified with e.s.c.a by its shake-up on the high-energy side of the carbon peak, caused by the phenyl π-electrons. The fact that the silicon and oxygen peaks can still be seen means that the polystyrene layer is less than 100 Å thick. Since silicon is transparent to infra-red light, we can confirm the e.s.c.a. measurements by simple transmission *FT*i.r. measurements in the case of grafting onto silicon wafers (*Figure 10*). As mentioned before, special care must be taken to purify all reagents and glassware. Even so, the anionic graft polymerizations onto both silicon wafers and glass slides were less reproducible. Homopolymers were always formed, with molecular weights as predicted, but often very little polymer was left at the surface after washing the reaction product. In e.s.c.a. measurements this could be seen by the silicon and oxygen peaks, which were

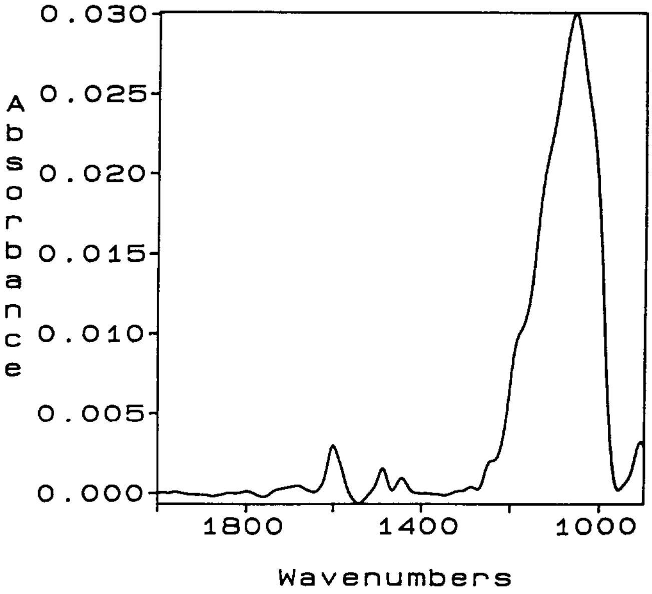


Figure 10 *FT*i.r. (transmission) of polystyrene (GP-9030) on a silicon water; 1601 cm^{-1}, phenyl

nearly as large as in the case of a substrate with just the coupling agent. The results indicate that in principle anionic graft polymerization starting at a flat surface is possible, but it is hard to keep all reaction circumstances under good enough control. Again, surface pollution is probably the main reason for premature termination. Because initiator concentrations and especially the amount of double bonds are so low, even very small traces of impurities have a very big effect on the grafting reactions. Therefore, cleaning of the glass slides and silicon wafers has to be very effective.

CONCLUSIONS

The anionic graft polymerization onto glass was investigated. Double bonds were immobilized at the glass surface, and initiated with an anionic initiator. Adding monomer resulted in end-grafted polymers. Adding two or more monomers one after another resulted in end-grafted block copolymers. The graft polymerizations onto microparticulate silica were reproducible although molecular-weight distributions were a little broader than expected for anionic polymerization. Anionic grafting onto flat surfaces like glass slides or silicon wafers was possible too but less reproducible, even under high-vacuum conditions. Attempts to graft block copolymers onto flat surfaces failed.

ACKNOWLEDGEMENTS

We would like to thank the SON for financial support, without which this work could not have been carried out. We would also like to thank Dr M. Čapka for helpful discussions.

REFERENCES

1 Nakatsuka, T. *J. Appl. Polym. Sci.* 1987, **34**, 2125
2 Hamann, K. and Laible, R. *Fatipec Jahrbuch* 1978, **14**, 17
3 Laible, R. and Hamann, K. *Angew. Makromol. Chem.* 1975, **48**, 97
4 Fery, N., Laible, R. and Hamann, K. *Angew. Makromol. Chem.* 1973, **34**, 81
5 Popov, V. A., Zvereva, Yu. A., Klimov, Ye. S., Palayeva, T. V. and Grishin, A. N. *Vysokomol. Soyed.* (*A*) 1982, **24**, 729 (*Polym. Sci. USSR* 1982, **24**, 808)
6 Popov, V. A., Grishin, A. N., Zvereva, Yu. A., Palayeva, T. V., Fomin, V. A. and Ivanchev, S S. *Vysokomol. Soyed.* (*A*) 1983, **25**, 760 (*Polym. Sci. USSR* 1983, **25**, 883)
7 Eastmond, G. C., Nguyen-Huu, C. and Piret, W. H. *Polymer* 1980, **21**, 598
8 Hashimoto, K., Fusijawa, T., Kobayashi, M. and Yosomiya, R. J. *J. Appl. Polym. Chem.* 1982, **27**, 4529
9 Hashimoto, K., Fusijawa, T., Kobayashi, M. and Yosomiya, R. J. *Macromol. Sci.-Chem.* (*A*) 1982, **18**, 173
10 Trachenko, V. I., Zil'berman, Ye. N., Shatskaya, T. F. and Pomerantseva, E. *Vysokomol. Soyed.* (*A*) 1986, **28**, 580 (*Polym. Sci. USSR* 1986, **28**, 646)
11 Dietz, E., Fery, N. and Hamann, K. *Angew. Makromol. Chem.* 1974, **35**, 115
12 Boven, G., Oosterling, M. L. C. M., Challa, G. and Schouten, A. J. *Polymer* 1990, **31**, 2377
13 Braun, D. and Kamprath, A. *Angew. Makromol. Chem.* 1984, **120**, 1
14 Verlaan, J. P. J., Bootsma, J. P. C. and Challa, G. *J. Mol. Catal.* 1982, **14**, 211
15 Schomaker, E., Zwarteveen, A. J., Challa, G. and Čapka, M. *Polym. Commun.* 1988, **29**, 158
16 Vidal, A. and Donnet, J. B. *Bull. Soc. Chim. Fr.* 1985, **6**, 1088
17 Zaremskii, M. Yu., Stepanyan, A. O., Olenin, A. V., Yarysheva, L. M., Zubov, V P. and Kabanov, V. A. *Vysokomol. Soyed.* (*A*) 1987, **29**, 1242 (*Polym. Sci. USSR* 1987, **29**, 1377)
18 Papirer, E. and Nguyen, V. T. *Angew. Makromol. Chem.* 1973, **28**, 31
19 Tsubokawa, W., Kobayashi, K. and Sone, Y. *Polym. J.* 1987, **19**, 1147
20 Szwarc, M. 'Carbanions, Living Polymers and Electron-Transfer Processes', Interscience, New York, 1968
21 Szwarc, M. *Nature* 1956, **178**, 1168
22 Haller, I. *J. Am. Chem. Soc.* 1978, **100**, 8050
23 Hatada, K., Nakanishi, H., Ute, K. and Kitayama, T. *Polym. J. 1986*, **18**, 581
24 Boehm, H. P. and Schneider, H. Z. *Z. Anorg. Allg. Chem.* 1959, **301**, 326
25 Berendsen, G. E. and de Galan, L. *J. Liquid Chromatogr.* 1978, **1**, 561
26 Papirer, E., Nguyen, T. and Donnet, J. B. *J. Polym. Sci.* 1979, **17**, 1015
27 Brown, J. L. *Pure Appl. Chem.* 1970, **23**, 447