Grafting 1,2-polybutadiene onto porous silica

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1,2-Polybutadiene of moderate molecular weight was grafted onto porous silica by hydrosilylation reaction of a part of its vinyl units, and coupling of the silane with the silanol groups of the silica. Two ways of grafting are discussed: 'grafting from' and 'grafting onto'; the latter gave better results in terms of capacity of residual double bonds grafted onto silica and available for further reactions. However, the capacity was limited to less than 1 meq g^{-1}.

(Keywords: silica; grafting; polybutadiene; hydrosilylation)

INTRODUCTION

1,2-Polybutadiene is a reactive polymer which can be derivatized easily due to the high reactivity of the vinylic double bond of the 1,2 units. It should thus be well suited as a precursor for reagents of catalysts supported on polymers. Many supported catalysts or reagents are prepared from chloromethylated styrene divinylbenzene units which can also be derivatized easily. However, the benzylic moieties of this kind of polymer are sensitive to radical reactions and are a source of chemical instability. Obviously, functional groups attached to a purely aliphatic polymer backbone are expected to be more stable[1]. This statement of radical attack sensitivities is based on the value of transfer constants in radical polymerization.

On the other hand, mineral supports such as silica are widely used in supported catalysis due to their outstanding thermal and mechanical stability, and also to a good control of their morphology (particle size and porous texture). Of course, the use of silica cannot greatly enhance the thermal stability of temperature-sensitive organic moieties grafted onto it. The main drawback of the use of silica as direct support of catalytic moieties is its limited weight or volume capacity. A possible solution to this problem is an increase in the number of active sites when a grafted polymer support is itself supported on silica. The validity of this solution has been demonstrated recently in the grafting of chloromethyl groups onto silica[2].

In this paper, we describe the data obtained in trials to combine these two concepts. Two strategies (*Scheme 1*) have been followed using both trialkoxysilane and hydrosilylation reaction. In the first, a partial hydrosilylation of 1,2-polybutadiene was carried out first and the partly substituted polymer was attached to silica through reaction of the silanol groups of the silica with the alkoxy groups of the silane. In the second strategy the grafting of the silane onto silica was carried out first, and the silane-modified silica was engaged in a hydrosilylation reaction of the polybutadiene. In both cases a limited amount of the double bonds of the polymer is reacted, so that most of these double bonds should remain available for further reactions.

EXPERIMENTAL

Toluene and isopropanol were dried over molecular sieves (3 Å) and tetrahydrofuran (THF) was dried on sodium–benzophenone complex. Silica (Rhône-Poulenc), with diameter 28 nm and surface area 89 $m^2 g^{-1}$, was dried for 4 h at 150°C under vacuum before use; its silanol group content was 5.3 $\mu mol\ m^{-2}$. The hydrosilylation catalyst (Speier) was obtained upon dissolving hydrogen hexachloroplatinate hydrate (Aldrich Gold Label: 99.99%) in isopropanol (0.05 M solution). The silane compounds — triethoxysilane (TES), hexamethyldisilazane (HMDS) and tetramethyldisilazane (TMDS) — are Aldrich products used without further purification. 1,2-Polybutadienes (81% 1,2 units, 19% 1,4 units from ^1H n.m.r.; Polymer Laboratories) with $M_n = 1000$ or 3000 were commercial products also used without further purification.

Polybutadiene hydrosilylations were carried out in toluene with the ratio butadiene unit/silane varying between 10 and 1. The ratio double bond/Pt was about 1000. In a typical experiment, 4.5 g of polybutadiene ($M_n = 1000\ g\ mol^{-1}$; 82 mmol of double bonds) was dissolved in 100 ml of toluene. To this solution was added 2 ml of TES (11 mmol) and about 0.5 ml of the 0.05 M solution of the Speier catalyst. The mixture was stirred at 110°C for 16 h. The modified polymer was then recovered by evaporation of the solvent and the unreacted silane under vacuum. The polymer was analysed by *FT*i.r. (Nicolet 20SX), ^1H and ^{13}C n.m.r. (Bruker 250 MHz) and elementary analyses.

Grafting of silane or hydrosilylated polybutadiene onto silica was also carried out in toluene solution. For example, 1 g of the hydrosilylated polybutadiene and 4 g of pretreated silica were mixed in 50 ml of toluene and the suspension was heated at 110°C for 16 h. The

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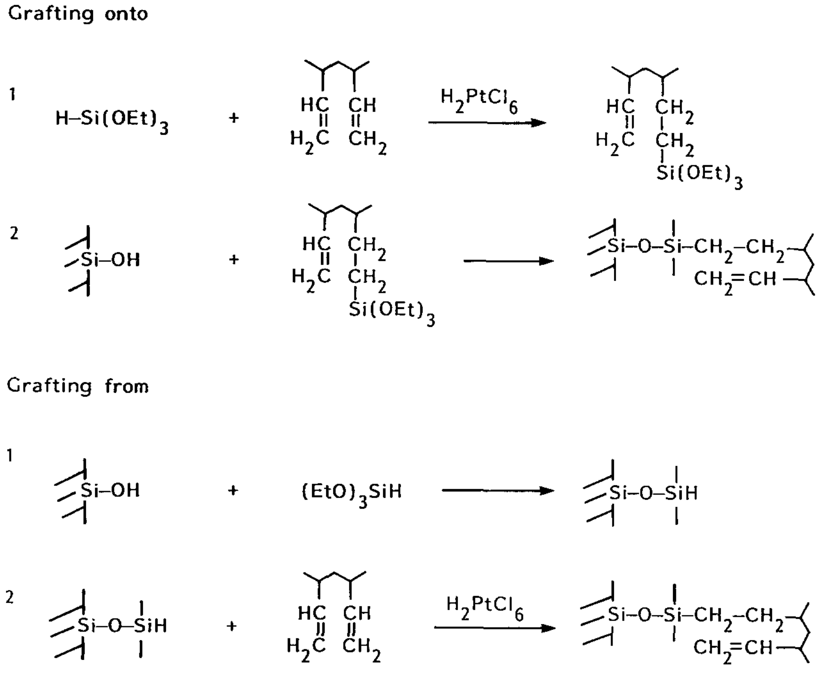

Scheme 1 Strategies for grafting polybutadiene onto silica

suspension was then filtered, and the silica washed with plenty of toluene and dried under vacuum. The modified silica was analysed by elementary analyses and *FT*i.r. (diffuse reflectance).

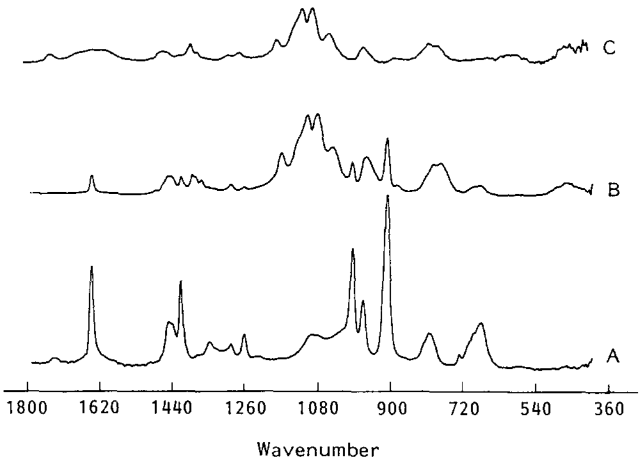

Figure 1 Infrared spectra of polybutadiene before (A) and after hydrosilylation at 19% (B) or 54% (C)

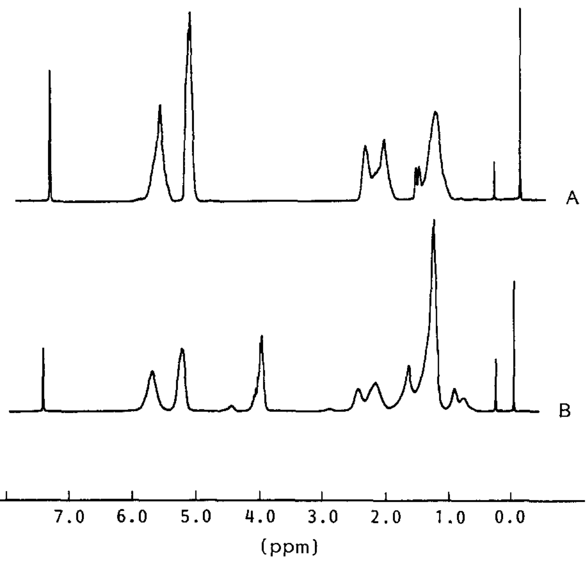

Figure 2 ^{1}H n.m.r. spectra of polybutadiene (A) and 19% hydrosilylated polybutadiene (B)

RESULTS AND DISCUSSION

Hydrosilylation of polybutadiene has been studied in the literature. Using the Speier catalyst, Pinazzi *et al.*[3] showed that the vinyl 1,2 double bonds are much more reactive than the 1,4 configuration; in addition the latter may give some cyclization side reactions. More recently Guo *et al.*[4] used a rhodium–phosphine catalyst highly selective towards the vinyl double bond hydrosilylation. The degree of hydrosilylation can be controlled easily by adjusting the silane/double bond ratio. In our study this ratio was varied from 0.1 to 1.

Figure 1 shows some infrared spectra of the polybutadiene before and after partial hydrosilylation (19 and 54% respectively). The bands corresponding to the vinyl double bond at 1640, 994 and 909 cm^{-1} are strongly reduced. The 967 cm^{-1} bond, corresponding to the 1,4, is broadened but does not disappear. New bands assigned to the ethoxy silane groups are observed at 1043, 1081, 1104 and 1169 cm^{-1}. The latter does not allow observation of the 1170 cm^{-1} band expected for the Si–C bond.

Figure 2 displays the corresponding ^{1}H n.m.r. spectra. Upon partial hydrosilylation, the expected bands do appear at 0.8 ppm (Si–CH_2) and at 3.9 ppm (Si–O–CH_2). The small peak at 0.9 ppm might be attributed to the anti-Markovnikow addition of the Si atom on the vinyl double bond, while another peak appearing at 1.7 ppm might be assigned to some isomerization of the 1,2 double bond, according to Harrod and Chalk[5], or to 1,4 unit cyclization as reported by Pinazzi *et al.*[3].

Figure 3 shows data concerning the hydrosilylation dependence on the ratio silane/double bond. The yield is almost quantitative for low values of this ratio, but decreases for high values, probably due to steric hindrance or to side reaction such as dimerization of the silane. The yield has been estimated from both elementary analyses of Si and ^1H n.m.r. using the peaks at 5.6 and 5 ppm for residual double bonds and the peak at 3.9 ppm for $O-CH_2-$. All the methods agree within experimental error.

The data of the 'grafted onto' materials are reported in *Table 1*. The initial hydrosilylation ratios are obtained from elementary analysis of silicon in the polymer before grafting. Assuming that the hydrosilylation dealt specifically with the 1,2 double bonds, the ratio is higher, because the polybutadiene content of vinyl double bonds was only 81%. The values of carbon content are from experimental analysis. For the capacity, the minimum value assumes that each polymer chain is grafted using only one of its silane groups. It is assumed further that two of the three ethoxy groups have been reacted with the silanol groups of the silica. For the maximum value, one assumes that all the silane groups of the polymer have been grafted by two of their three ethoxy groups. The capacity is concerned with the residual 1,2 double bonds, assuming that all the 1,4 double bonds have remained unreacted. The two values are fairly close and rather small. However, it is interesting to predict the yield of silanol group consumption. In the hypothesis of anchoring the polybutadiene molecule by only one silane group, this yield does vary from about 10 to 17%. In the second hypothesis (all silane reacted), the yield is between 34 and 150%. The actual value is probably in between, with more chance for the highly hydrosilylated molecules to be flat on the surface due to multiple bonds with the silanols.

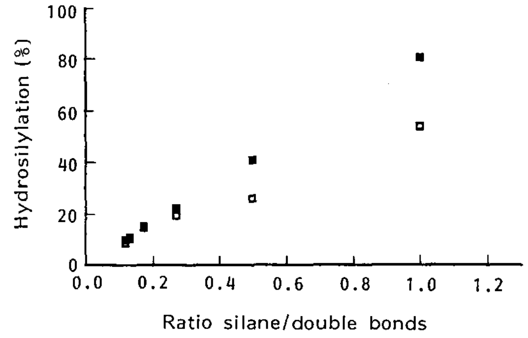

Figure 3 Hydrosilylation yield (□, experimental; ■, theoretical) as a function of the ratio silane/double bonds, assuming for the theoretical values that the reaction is selective to the 1,2-polybutadiene units

Table 1 Capacity of polybutadiene grafted onto silica (meq of residual 1,2 double bond per g)

Initial hydrosilylation ratio		Carbon content (%)	Grafted material capacity (meq g^{-1})	
All double bonds	1,2 double bonds		Maximum	Minimum
10.2	12.6	4.1	0.57	0.54
19	23.5	3.8	0.43	0.38
26	32	3.5	0.33	0.30
54	66	3.9	0.16	0.11

A few experiments have been carried out using the 'grafting from' route of *Scheme 1*. In the first, a small amount of TES was reacted with the silica. The carbon content was then 0.5%. This carbon content reached 1.3% after treatment with HMDS, which means that about 50% of the silanol groups were reacted with HMDS. It may be estimated from this result that around 50% of the silanols have been reacted with TES partly by only one ethoxy group and partly by two. The Si–H bonds can be observed on the infrared spectrum of the modified silica (*Figure 4*). After hydrosilylation in two successive treatments by polybutadiene in the presence of the Speier catalyst, the carbon content increased up to 1.95% which means that only 0.65% of C comes from the polybutadiene, corresponding to 0.11 meq g^{-1} of 1,2 double bond. Slightly better results were obtained using TMDS as silane coupling agents. Then, 87 and 97% of the silanols were reacted to give silane. However, upon reactivity with polybutadiene, the carbon contents increased from 1.1 to 1.5% only. If toluene was replaced by a more polar solvent, THF, the figure was 1.7%, again

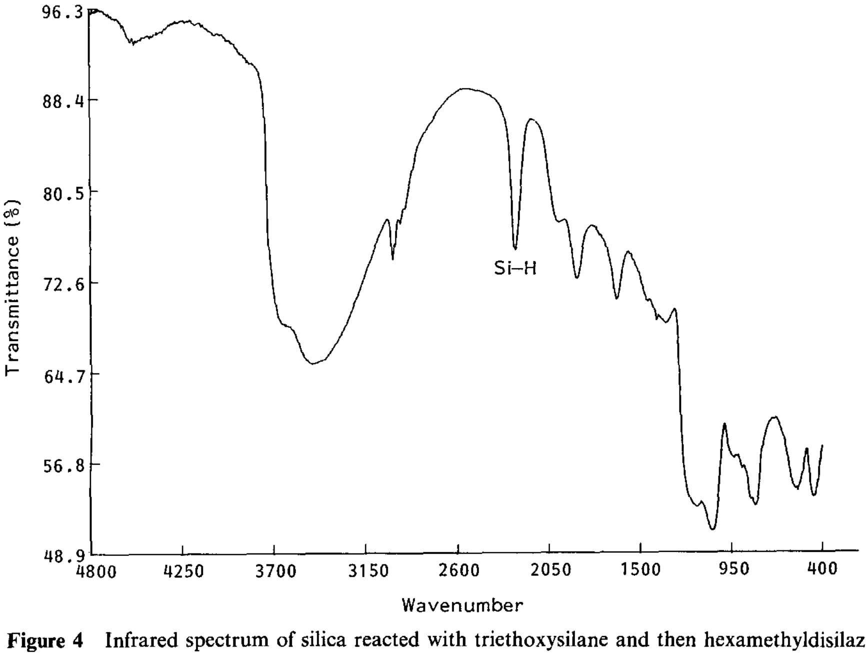

Figure 4 Infrared spectrum of silica reacted with triethoxysilane and then hexamethyldisilazane

corresponding to a capacity of 0.1 meq g^{-1}. However, it was observed that the catalyst remained mostly attached to the silica which contains 1.6 ppm of Pt, which corresponds to half of the Pt engaged. A second treatment was then carried out in the presence of a new charge of catalyst. Some more polybutadiene was hydrosilylated, which accounted for 1.7% of C, i.e. a 1,2 double bond capacity of about 0.3 meq g^{-1}. It must be recalled that this value is a maximum value, neglecting the double bond reacted in the hydrosilylation reaction. Most probably the polybutadiene molecule is reacted by more than one of its double bonds and is anchored flat on the surface. Such flat conformation of the graft may explain the low yield of grafting; another explanation might be the partial inhibition of the catalyst through interaction of the Pt with silica where it remains strongly attached.

CONCLUSION

Anchoring 1,2-polybutadiene on a silica surface through hydrosilylation is a difficult reaction with limited yield. The best method is the 'grafting onto' route using polybutadiene which has been only slightly hydrosilylated by no more than one group per molecule.

REFERENCES

1 Sherrington, D. C. *Pure Appl. Chem.* 1988, **60**, 401
2 Carlier, E., Guyot, A. and Revillon, A. *Reactive Polym.* 1992, **16**, 115
3 Pinazzi, C. P., Soutif, J. C. and Brosse, J. C. *Eur. Polym. J.* 1975, **11**, 523
4 Guo, X., Farwaha, R. and Rempell, G. *Macromolecules* 1990, **23**, 5047
5 Harrod, J. F. and Chalk, A. J. *J. Am. Chem. Soc.* 1962, **86**, 1776