Polymer Bulletin 2, 315-320 (1980)

Polymer Bulletin

Silica-Grafted Polyisobutylene and Butyl Rubber

I. Synthesis and Characterization of Silica-Grafted Polyisobutylene

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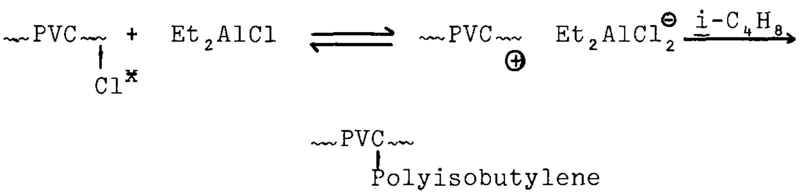
SUMMARY

Silica surfaces have been modified by reaction with $ClSi(CH_3)_2CH_2$-CH_2-$C_6H_4CH_2Cl$ (I) and the solids were used in conjunction with Et_2AlCl to initiate the surface-graft polymerization of isobutylene. Experimental conditions have been defined to obtain respectable grafting rates, grafting ratios and grafting efficiencies.

I - INTRODUCTION

It has been amply demonstrated (KENNEDY 1977) that a large variety of graft copolymers can be efficiently prepared by cationic "grafting from" i.e., by initiating the polymerization of monomers using polymer halides in conjunction with certain Lewis acids (Et_2AlCl, BCl_3). For example, the PVC/Et_2AlCl combination was found to be an excellent initiating system for the polymerization of isobutylene (KENNEDY and DAVIDSON 1977) or styrene (KENNEDY and NAKAO 1977) in solution :



$$\sim\underset{\displaystyle Cl^{*}}{\underset{|}{PVC}}\sim \; + \; Et_2AlCl \rightleftharpoons \sim\underset{\oplus}{PVC}\sim \quad Et_2AlCl_2^{\ominus} \xrightarrow{i\text{-}C_4H_8} \sim\underset{\text{Polyisobutylene}}{\underset{|}{PVC}}\sim$$

where Cl^{*} is an allylic or tertiary chloride present in small quantities in PVC. This grafting principle has recently been shown to be also operative with slurries i.e., solid PVC particles (VIDAL et al. 1977).

This paper concerns the extension of this grafting technique and the use of modified silica surfaces as cationic initiators. It has been demonstrated that suitable chemical modification of silica surfaces yields sites capable of initiating graft polymeriza-

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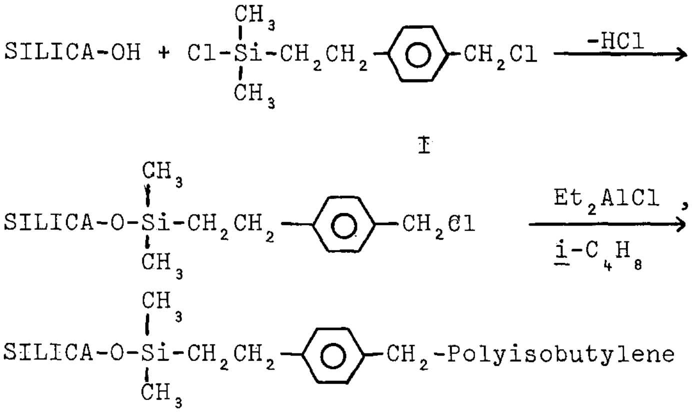
tion of isobutylene. The following equations illustrate the transformations involved :

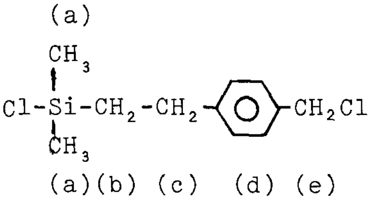


II - EXPERIMENTAL

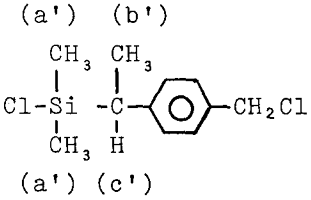
A. Synthesis and Characterization of 2(Chloromethylphenyl)-ethyldimethylchlorosilane (I)

The initiator I was prepared by hydrosilylation of p-chloromethylstyrene (Dow Chemical) with $HSi(CH_3)_2Cl$ (Petrarch System) in presence of chloroplatinic acid in quantitative yield (bp. 202°C/60 mm Hg) (LUKEVICS et al. 1977).

The product was characterized by ^1H NMR (Varian 300 MHz) spectroscopy. In reference to the structures shown, the following resonances have been identified and defined :



(I)



(I')

The multiplet at 7.83 ppm is due to aromatic protons (d) ; the singlet at 4.3 ppm indicates -CH$_2$Cl (e) ; the muliplet (three major resonances) at 2.63 ppm is associated with -CH$_2$- adjacent to the ring (c) ; the multiplet at 1.04 ppm is due to -CH$_2$- adjacent to Si (b) ; the singlet at 0.29 ppm indicates two CH$_3$ - groups on Si (a).

In addition, the three smaller resonances at 0.20, 1.35 and 2.29 ppm, respectively, show CH_3- on Si (a'), CH_3 - (b') and C-H (c') groups in the minor isomer (I') formed by the less favorable hydrosililation route.

According to integration and quantitative analysis, the product is a mixture of 81% I and 19 % I' isomer. It is assumed that due to severe steric inhibition I' is much less reactive than I toward surface silanol groups.

B. Modification of Silica Surfaces by Reaction with I and Characterization

The attaching of I to silica (Lo-Vel HiSil 200, 150 m^2/g ; PPG Industries) was carried out under a stream of pure nitrogen gas as follows : To 70.5 g silica (dried in vacuo at 140°C) rapidly stirred in 1.7 I dry n-heptane in a three-neck flask equipped with high speed stirrer, dropping funnel and reflux condensor were added 3 ml $(CH_3)_3SiCl$ in dry n-heptane followed by 14 ml I. The charge was stirred overnight under gentle reflux. Then 15 ml $(CH_3)_3SiCl$ were added and stirring continued for another 24 hrs. Subsequently n-heptane was removed by distillation and the remaining solid was stored in a vacuum oven until use.

The extent of the reaction between the silane and I was determined by chlorine analysis of the modified silane. The Cl content of the modified product was 0.92_0wt %. which indicates ∿ 1.04 molecule of I per 100 $Å^2$ silica surface.

Further, the modified silica was characterized by IR spectroscopy (Trace A Figure 1). The very weak band at 3750 cm^{-1} is attributed to unreacted -OH groups. The broad band centered at ∿3400 cm^{-1} is due to -OH groups associated by hydrogen bonding. The weak bands at 2950-2960 cm^{-1} are due to CH_3- and $-CH_2$- vibrations indicating attached I on the surface of silica.

C. Grafting Isobutylene From I-Modified Silica Surfaces

A typical experiment was conducted as follows. In a stainless steel enclosure filled with dry nitrogen, a clean test tube was charged with ethyl chloride (24.3 ml), isobutylene (2M) and diethylaluminum chloride (1.73 x 10^{-2} M), and cooled. At the desired temperature (-50°C) the modified silica was rapidly added (0.1000 g, corresponding to 8.6 x 10^{-4} M initiator) to the manually agitated charge. After 30 min. the reaction was quenched by adding 10 ml prechilled methanol and the product was precipitated, filtered and dried under vacuum. The ungrafted PIB was removed by extraction with refluxing n-pentane. The resulting material was characterized by IR analysis and the grafting ratios were determined by gravimetry.

III - RESULTS AND DISCUSSION

It is well known that chlorosilane groups rapidly react with silanol groups on silica surfaces (HAIR and HERTL 1969). Thus it was theorized that cationic grafting could be initiated on silica surfaces by attaching I to the surface of the filler and using these modified silicas II in conjunction with suitable Lewis acids for the polymerization of isobutylene.

Grafting isobutylene from II was carried out as described in the Experimental part. Simultaneously with the grafting reactions, control experiments were run. In these controls, the ingredients were mixed in the same proportion as in the grafting experiment, except that modified silica was omitted. Only when polymer was absent in the control charges were the corresponding grafting experiments accepted and worked up.

Monomer conversion was determined gravimetrically after precipitation of the charge into methanol and drying in vacuo. Subsequently the product was refluxed in *n*-pentane to determine extent of surface grafting. Even prolonged refluxing in *n*-pentane failed to remove all PIB from the silica. The *n*-pentane-insoluble PIB fraction is most likely attached to the surface of silica filler. The amount of *n*-pentane-insoluble PIB was determined gravimetrically and was confirmed by carbon-hydrogen analysis.

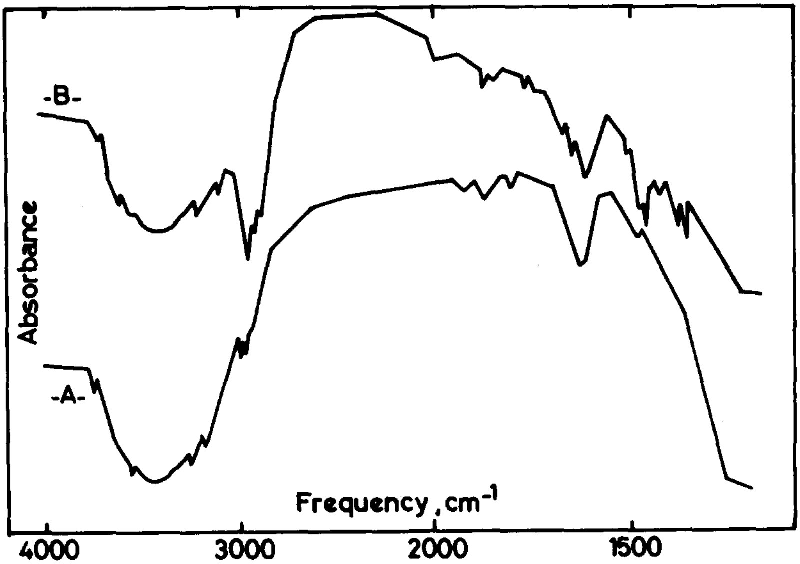


Figure 1 : Infra Red Spectra of Silica Modified with I (trace A) and Silica-g-Polyisobutylene (Trace B)

The silica-g-PIB was characterized by IR spectroscopy. A typical spectrum shown in Trace B of Figure 1 exhibits bands at 1490, 1380 and 1360 cm^{-1} due to CH_3 - and - CH_2 - groups of PIB branches.

Remarkably high grafting rates, grafting ratios and grafting efficiencies have been obtained in experiments using pure C_2H_5Cl solvent, with Al/Cl = 20 at -50° for ∿1/2 hr (cf Table I) highest grafting efficiencies were ∿ 50%.

TABLE I

Grafting Isobutylene from Modified Silica

Et_2AlCl x 10^2M	Al/Cl	T °C	Solvent v/v	t min	conv. %	PIB in Graft%	G.E. %	$\bar{M}_v$ x10^{-3}
2.7	31	-30	50/50	240	0.7	-	-	-
2.7	310	-30	50/50	240	2	-	-	-
2.7	31	-30	0/100	240	4.6	9	6.33	-
13.5	155	-30	0/100	240	15.1	-	-	-
13.5	155	-30	0/100	1440	23.1	8	1	-
1.73	20	-30	0/100	1	2.1	7.8	11.8	-
1.73	20	-30	0/100	3	7	15.4	7.7	-
1.73	20	-30	0/100	105	21	12.7	2	-
1.73	20	-50	0/100	6	2.3	27.3	48.2	-
1.73	20	-50	0/100	30	3.5	38.8	53.9	-
1.73	20	-50	0/100	60	30.8	57	15.5	232
1.73	20	-50	0/100	60	32.7	39.1	6.0	322

|Silica| = 3.33 g/l ; |isobutylene| = 2 M ; Al/Cl = Et_2AlCl/surface Cl due to I ; total volume = 30 ml ; solvent = n-heptane/ethyl chloride. Grafting Efficiency (G.E.) ≡ (g of grafted PIB/g of total IB converted) x 100. $\bar{M}_v$ by viscometry in cyclohexane at 30°C and using KRIGBAUM and FLORY's (1953) equation.

It was of interest to determine whether unreacted surface silanol groups could act as initiation or transfer sites. Thus two experiments were carried out, one in which isobutylene polymerizations were initiated in the homogeneous phase by the t-BuCl/Et_2AlCl initiating system in the absence of virgin silica under conditions used in previous runs, and another in which Et_2AlCl was added to a charge containing untreated silica. Results are shown in Table II.

TABLE II

Polymerizing Isobutylene by t-BuCl/Et_2AlCl in Presence and Absence of Silica

Silica	Silica g/l	t-BuCl x 10^4M	Al/Cl	Conv. %	PIB in graft %	$\bar{M}_v$ x10^{-3}
A300*	3.33	-	-	94.4	2	75
-	-	8.6	20	76.7	-	143

|Et_2AlCl| = 1.73x10^{-2}M; |Isobutylene| = 2M ;Al/Cl = Et_2AlCl/t - BuCl; EtCl; tot.vol. = 3o ml; -5o°C; 6o min

* Fumed silica, Aerosil 300 from Degussa, spec. surface area = 300 m^2/g ; degassed in vacuo at 150° for 48 hrs to remove adsorbed H_2O.

Evidently, untreated silica does not yield graft; the 2 % n-pentane-insoluble PIB may be due to physisorption. Silica may be a chain transfer agent by an undetermined mechanism since the molecular weights obtained in its presence are much lower ($\overline{M}_v$ = 75,000) than those obtained with t-BuCl (140,000) in the absence of silica with I-modified silica (230,000). It is of considerable interest that well dried but untreated silica is an efficient (94.4 %) initiator for isobutylene polymerization in conjunction with Et_2AlCl. This lead is being pursued.

In conclusion it appears that the grafting of cationically responsive monomers from silica surfaces modified by - $Si(CH_3)_2CH_2CH_2C_6H_4CH_2Cl$ is feasible. Topologyeally the silica-g-polyisobutylene obtained by this technique is similar to a "porcupine" comprising solid hydrophylic core attached to flexible hydrophobic branches. This composite should exhibit interesting physical properties whose exploration is in progress.

REFERENCES

1 - HAIR M.L. and HERTL W. : J. Phys. Chem. 73 (7), 2372 (1969)
2 - KENNEDY J.P., Ed. : J. Appl. Polym. Sci., Appl. Polym. Symp. 30 (1977)
3 - KENNEDY J.P. and DAVIDSON D.L. : J. Appl. Polym. Sci., Appl. Polym. Symp. 30, 13 (1977)
4 - KENNEDY J.P. and NAKAO M. : J. Appl. Polym. Sci., Appl. Polym. Symp. 30, 73 (1977)
5 - KRIGBAUM W.R. and FLORY P.J. : J. Am. Chem. Soc. 75, 1775 (1953)
6 - LUKEVICS E., BELYAKOVA Z.V., POMERANTSEVA M.G. and VORONKOV M.G. : J. Organometal. Chem. Library 5, 1 (1977)
7 - VIDAL A., DONNET J.B. and KENNEDY J.P. : J. Polymer Sci., Polymer Letters Ed. 15 (10) 585 (1977)

Received February 12, 1980