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Silica Grafted Polyisobutylene and Butyl Rubber

2. Synthesis and Characterization of Silica Grafted Butyl Rubber

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Summary

Silica surfaces have been modified by reaction with Cl-Si$(CH_3)_2$-CH_2-CH_2-C_6H_4-CH_2Cl and the modified solids were subsequently used in conjunction with Et_2AlCl or $AlMe_3$ coinitiators to initiate the surface graft copolymerization of isobutylene-isoprene mixtures. The experimental conditions have been chosen such that the composition of the rubbery component of the surface-graft be close to that of commercial butyl rubber. The overall composition of silica-grafted butyl rubbers have been characterized.

Introduction

We have shown (VIDAL et al. 1980, VIDAL et al. 1981) that suitably modified silica surfaces in conjunction with certain alkylaluminum compounds are able to initiate the grafting of cationically responsive monomers, e.g., isobutylene and styrene. The modification of silica surfaces was carried out by reacting the surface silanol groups with ClSi-$(CH_3)_2CH_2CH_2$-$C_6H_4CH_2Cl$ 2(chloromethylphenyl)ethyldimethylchlorosilane (I). That benzylic chlorides similar to I are efficient cationic initiators in the presence of certain Lewis acids has been amply demonstrated (KENNEDY, 1975).

With this background information in mind we decided to extend our previous researches, in particular to graft sulfur vulcanizable isobutylene-isoprene (butyl rubber, IIR) branches from various modified silica surfaces. This paper concerns a description of the synthetic procedures together with model experiments and the molecular characterization of these new silica-IIR graft copolymers.

Experimental

A. Materials and General Procedures

The modification of silica surfaces by reaction with I and the characterization of the resulting materials have been described (VIDAL et al. 1980).

The silicas used for modification were fumed silicas (Silica II_A: Lo-Vel HiSil 200, 150 m^2/g PPG Industries and Silica II_B: Aerosil 130, 130 m^2/g Degussa). The absorbed water was removed by degassing the silicas at 150°C. The extent of reactions between silicas and I was determined by

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chlorine analysis of the modified silicas. The Cl content of the modified products indicated, respectively, ∿1.04 and 2.84 molecules of I per 100 Å^2 for silica IIA and IIB.

Solvents and monomers were of highest commercially available purity and were further dried by standard methods. Alkylaluminum compounds (Ethyl Corp.) were purified by vacuum distillation in a nitrogen atmosphere (bp °C/mm Hg: Et_2AlCl 110°/25; $AlMe_3$:80°/160). Prior to distillation, Et_2AlCl was stirred over dried sodium chloride at 80°C for 2 hr to remove possible $EtAlCl_2$ impurity. The distilled Et_2AlCl was stored over NaCl at -30°C.

Syntheses were carried out in a stainless steel dry box under a dry nitrogen atmosphere (VIDAL et al. 1980).

B. Grafting Isobutylene-Isoprene Copolymers from Modified Silica Surfaces

A typical experiment was conducted as follows. A large test tube was charged with 12.15 ml *n*-heptane, 12.15 ml C_2H_5Cl, 5.53 ml (1.95M) isobutylene, 0.17 ml (0.057M) isoprene and Et_2AlCl ($4.32 \cdot 10^{-3}$M), and cooled to -40°C. Subsequently modified silica (0.1000g corresponding to 2.35 x 10^{-3}M initiator) was added rapidly to the manually agitated charge. After 15 min. the reaction was quenched by addition of prechilled methanol. The product was precipitated into methanol, filtered, and dried under vacuum. The ungrafted polymer was removed by extraction with refluxing *n*-pentane. The extracted material was characterized by IR and ^{1}H NMR spectroscopy. Molecular weights of ungrafted polymers were determined by GPC. The GPC instrument was equipped with 4 columns (Chrompack) in series (pore size: 10^2Å, 10^3Å, 10^4Å, 10^5Å). Grafting ratios were obtained by gravimetry and independently by elemental analysis.

Results and Discussion

It has been shown (VIDAL et al. 1981) that cationic grafting can be initiated on silica surfaces by attaching I to the surface of the filler and using these modified silicas in conjunction with suitable Lewis acids for the polymerization of isobutylene. Since polyisobutylene cannot be vulcanized by sulfur, further experiments have been carried out with isobutylene-isoprene mixtures, i.e., with charges known to lead to sulfur vulcanizable butyl rubbers. Silica grafted butyl rubber may be of interest for a variety of applications, i.e., high quality specialty elastomers, and for the study of rubber reinforcement.

To obtain isobutylene-isoprene copolymers whose composition are close to that of commercial butyl rubber, the concentration of isoprene in the charge was 3 volume% in respect to isobutylene. Simultaneously with the grafting reactions, control experiments were also run. In these controls the reactants were mixed in the same manner and proportion as in the grafting experiments except that modified silica was not added. Only when polymer was absent in these controls were the corresponding grafting experiments accepted and worked up.

Conversions were determined gravimetrically after precipitation by methanol, filtration, and drying in vacuum. The silica-grafted butyl rubber was separated from ungrafted rubber by extraction with refluxing n-pentane. The extractions were continued until not even traces of butyl rubber could be detected in the solvent. The extractions were generally complete after 3 days. The quantity of n-pentane-insoluble butyl rubber was determined gravimetrically and confirmed by carbon-hydrogen analysis. The grafted material was characterized by IR spectroscopy. By assuming that the composition and structure of the grafted and ungrafted copolymers are identical, the average molecular weights of the butyl rubber branches were determined by GPC. The amount of incorporated isoprene units and their microstructure were determined by ^{1}H NMR spectroscopy.

Prior to grafting experiments model studies have been carried out to guide our designing of suitable grafting conditions. In these model experiments 1-(chloromethyl)-4 methylbenzene CH_3-C_6H_4-CH_2Cl was used to mimic the cationogenic site on the modified silica. Results of these model experiments are shown in Table I. For comparison purposes a homopolymerization of isobutylene has also been carried out (last line in Table I). Preliminary experiments showed that with Et_2AlCl the most satisfactory controls (i.e., absence of polymer in the absence of I) were obtained with Al/Cl = 10 i.e., when the alkylaluminum to I concentration was 10. With Me_3Al best conditions arose with Al/Cl =20. The molecular weights of IIR's were much lower than with corresponding isobutylene grafts. This finding is in agreement with the observation that the copolymerization of even a few percent of a conjugated diene with isobutylene results in severe molecular weight depression (KENNEDY, 1975).

Led by these model experiments, conditions in terms of solvent composition (polarity), reagent concentrations, temperature, time of reaction have been selected for grafting isobutylene-isoprene copolymers from modified silica surfaces. Representative results are compiled in Table II.

Graft copolymerizations in the presence of modified silica and Et_2AlCl are faster than the corresponding model runs conceivably on account of unreacted surface silanol groups (VIDAL et al. 1980). The extent of reaction can be readily controlled in the case of Me_3Al coinitiator.

Silica II_B modified by relatively high amounts of I is quite reactive and leads to reasonably high grafting efficiencies (G.E.).

After extraction of the ungrafted n-pentane-soluble butyl rubber fraction the grafts were characterized by IR spectroscopy. Thus polyisobutylene (VIDAL et al. 1980) and butyl rubber modified silicas gave essentially identical spectra: The peaks at 2950, 1490, 1380 and 1360cm^{-1} are due to CH_2 and CH_3 groups of IIR.

Table I

Copolymerization of Isobutylene-Isoprene Charges Initiated by 1-(Chloromethyl)-4 methylbenzene/Alkylaluminum Combinations

Coinitiator $\times 10^2$M	Al/Cl	Solvent v/v	t min.	Conversion %	Double bonds mol.%	$\overline{M}_n$ $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
Et_2AlCl; 0.865	10	50/50	5	4.4	-	-	-
Et_2AlCl; 0.865	10	50/50	10	55.5	1.64	24.5	2.4
Et_2AlCl; 1.73	20	25/75	0.25	64.9	-	38.9	2.7
Et_2AlCl; 1.73	20	25/75	0.5	70.8	-	53.3	1.9
$AlMe_3$; 1.73	20	0/100	0.5	5.4	-	18.7	2.5
$AlMe_3$; 1.73	20	0/100	1	4.9	-	25.4	2.1
$AlMe_3$; 1.73	20	0/100	3	8.4	-	27.0	2.3
$AlMe_3$; 1.73	20	25/75	0.5	1	-	-	-
$AlMe_3$; 1.73	20	25/75	2	5.8	-	23.6	2.2
$AlMe_3$; 1.73	20	25/75	5	8.5	-	15.8	2.9
$AlMe_3$; 1.73	20	25/75	11	4.6	1.8	29.7	1.7
$AlMe_3$; 1.73	20	25/75	20	11.9	-	35.7	1.7
$AlMe_3$ a); 1.73	20	0/100	5	19.9	0	40.1	2.0

Total volume: 30 ml; T = -40°C; Solvent = n-heptane/ethyl chloride; $[i\text{-}C_4H_8] = 1.95M$; $[i\text{-}C_5H_8] = 0.057M$; a) $[i\text{-}C_4H_8] = 2M$; $[i\text{-}C_5H_8] = 0$

TABLE II

Grafting Butyl Rubber from Modified Silicas

Initiat.[c)]	Coinitiat. $x10^2M$	Al/Cl	Solv. v/v	t min	Conv. %	IIR in graft %	Branches/100Å $x10^2$	G.E.[d)] %	Double bonds mol.%	$\overline{M}_n$ $x10^{-3}$	$\overline{M}_w/\overline{M}_n$
II_A	Et_2AlCl;0.865	10	25/75[a)]	2	17.1	-	-	-	-	-	-
II_A	Et_2AlCl;0.865	10	50/50[a)]	5	14	34	2.6	11.5	1.8_5	52.4	1.9
II_A	Et_2AlCl;0.432	5	50/50[a)]	30	0.8	-	-	-	-	-	-
II_B	Et_2AlCl;0.432	1.8	50/50[a)]	15	3.2	23	-	30	-	-	-
II_B	Et_2AlCl;0.432	1.8	50/50[b)]	20	0.4	-	-	-	-	-	-
II_A	$AlMe_3$;1.73	20	0/100[a)]	30	1.4	14.2	-	36	-	-	-
II_A	$AlMe_3$;1.73	20	0/100[a)]	60	1.4	19.2	-	50.5	-	-	-
II_A	$AlMe_3$;1.73	20	0/100[a)]	240	3.6	27	4.1	32	1.5_6	26.7	2.5
II_B	$AlMe_3$;1.73	7.4	0/100[a)]	8	4.2[e)]	29	6.8	39.5	2.8	19.7	2.0
II_B	$AlMe_3$;1.73	7.4	0/100[a)]	10	11.6	26	4.4	9.5	1.9	27.2	2.1
II_B	$AlMe_3$;1.73	7.4	0/100[b)]	20	2.3	20	7.2	43	-	12.8	2.1

$[i\text{-}C_4H_8] = 1.95M$; $[i\text{-}C_5H_8] = 0.057M$; Total volume = 30 ml

a) Solvent: n-heptane/ethyl chloride

b) Solvent: n-heptane/methyl chloride

c) Silica = 3.33 g/l; II_A = Lo-Vel HiSil 200; II_B = Aerosil 130

d) G.E. = (g of grafted IIR/g of total IIR formed) x 100

e) Sample whose NMR spectrum is in Figure 1

The number of polymer branches per unit surface area of the silica (grafts/100Å^2) was calculated from the grafting ratios and the number average molecular weight of the ungrafted polymer. It appears that this quantity is dependent on the amount of initiating sites on the surface of the filler and on the molecular weight of the grafts.

The amount of unsaturations in the IIR was determined by ^{1}H NMR spectroscopy and Figure 1 shows a representative spectrum. The measurements were performed with ungrafted polymers. The spectra exhibit two resonances in the double bond region: the signal at 5.1 ppm assigned to the single proton of the unsaturations arising from trans 1-4 enchainments of isoprene units, while the small peak at 4.59 ppm is due to the protons of the vinylidene group corresponding to 3-4 enchainments (CORNO et al., 1980). These spectra provide information as to the microstructure of the butyl rubber. In agreement with Richardson (1954) the isoprene units appear to be ∿92% 1-4 and ∿8% 3-4 enchainments. The total amount of unsaturation in butyl rubber is ∿1.9 mole%.

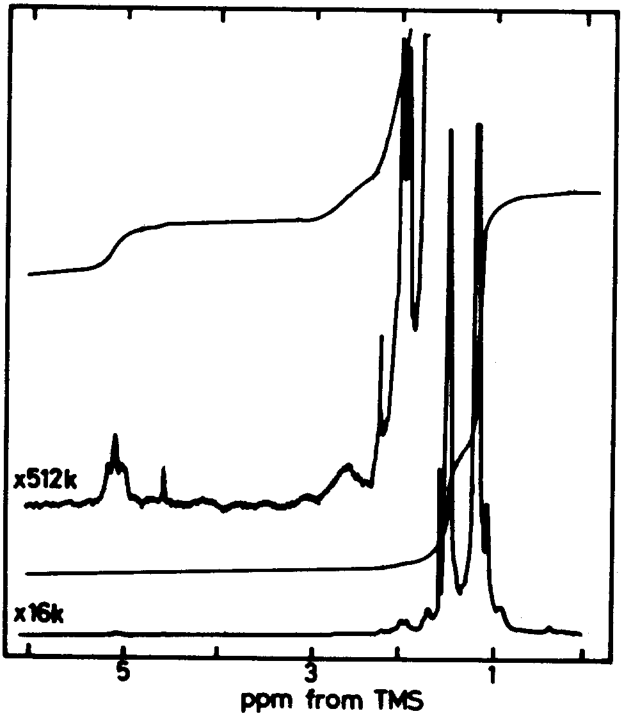

Figure 1: ^{1}H NMR Spectrum of Butyl Rubber (sample (e) in Table II)

Conclusion

Silica surfaces have been modified and used to initiate homopolymerization (isobutylene, styrene) and copolymerization (isobutylene-co-isoprene). Future work will concern an examination of the effect of silica-IIR grafts on the reinforcement of butyl rubber by active fillers.

References

C. CORNO, A. PRONI, A. PRIOLA and S. CESCA: Macromolecules 13(5), 1092 (1980)
J. P. KENNEDY: Cationic Polymerization of Olefins: A Critical Inventory ; Wiley, New York (1975)
W. S. RICHARDSON: J. Polymer Sci. 13, 325 (1954)
A. VIDAL, A. GUYOT and J. P. KENNEDY: Polym. Bull., 2, 315 (1980)
A. VIDAL, A. GUYOT and J. P. KENNEDY: IUPAC Macro 81, Symposium Abstracts, Strasbourg, I, 303 (1981)

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