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Block Copolymers

Syntheses and Characterization of Various Polyisobutylene-Polystyrene Block Copolymers

1. Model Hydrosilylations and Syntheses of Tri- and H-Block Copolymers

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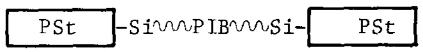
SUMMARY

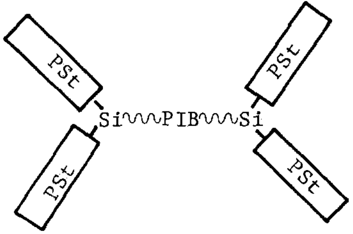
Block copolymers comprising of a central rubbery polyisobutylene PIB segment connected to two or four glassy polystyrene PSt segments (i.e., triblocks or H blocks) have been prepared and characterized. The syntheses were accomplished by coupling living polystyrene anions PSt$^{\ominus}$ to chlorosilane-telechelic PIB's, for example, Cl-Si-PIB-Si-Cl. The latter prepolymers were obtained by hydrosilylating olefin-telechelic PIB's with chlorohydrosilanes. The conditions necessary for the syntheses have been developed with the aid of model kinetic experiments using 2,4,4-trimethyl-1-pentene. The rate of hydrosilylation of this model olefin in the presence of H_2PtCl_6 gave the following reactivity order for the chlorohydrosilanes investigated: $MeSiHCl_2 \gtrsim Me_2SiHCl > HSiCl_3$. Increasing the silane/olefin ratio, temperature, and catalyst concentration enhances the rate of hydrosilylation and conversion. The block copolymers have been characterized by fractional solvent separation followed by RI-UV dual detector GPC, osmometry, and high resolution ^{1}H NMR spectroscopy.

INTRODUCTION

Recent syntheses of a great variety of linear and three-arm telechelic polyisobutylenes have led to many interesting new materials incorporating the rubbery PIB segment, e.g., polyurethanes (1), epoxy resins (2) and iono-networks (3,4). In the course of these investigations we became intrigued by the possibility of synthesizing well defined glassy/rubbery sequential copolymers comprising of a central elastomeric PIB block carrying two, three, four, or six external glassy sequences, for example, with polystyrene PSt as the glassy block:



Triblock Copolymer



Forked (or H) Block Copolymer

We theorized that the synthesis of these and similar structures could be achieved by combining the following three elements:

1. Olefin-telechelic polyisobutylenes (α,ω-diisopropenyl PIB's) of controlled molecular weights and molecular weight distributions carrying exactly two terminal unsaturations (isopropenyl functions) are readily available (5):

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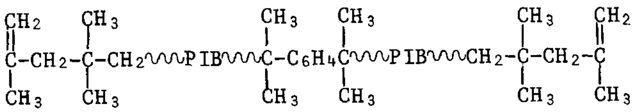
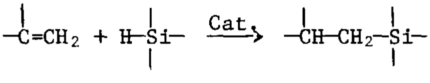


$$\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2\sim PIB\sim\underset{CH_3}{\overset{CH_3}{C}}-C_6H_4\underset{CH_3}{\overset{CH_3}{C}}\sim PIB\sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}$$

C=C-PIB-C=C

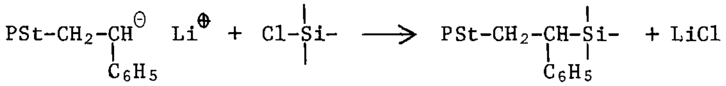
2. Hydrosilylation of olefins by various silanes in the presence of various catalysts may, in certain instances, proceed quantitatively (6):



$$-\overset{|}{C}=CH_2 + H-\overset{|}{\underset{|}{Si}}- \xrightarrow{Cat.} -\overset{|}{C}H-CH_2-\overset{|}{\underset{|}{Si}}-$$

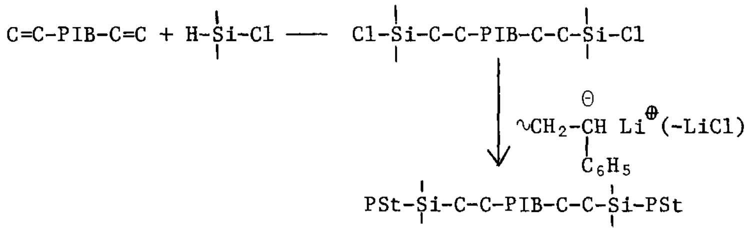
It was of particular significance for our work that hydrosilylation of olefin-telechelic polyisobutylenes by the use of certain chlorohydrosilanes $H-\overset{|}{\underset{|}{Si}}-Cl$ may also proceed quantitatively (see below).

3. Coupling of living polystyrene anions $PSt^{\ominus}$ with the $-\overset{|}{\underset{|}{Si}}-Cl$ function has been demonstrated to proceed quantitatively (7,8):



$$PSt-CH_2-\underset{C_6H_5}{CH^{\ominus}}\ Li^{\oplus} + Cl-\overset{|}{\underset{|}{Si}}- \longrightarrow PSt-CH_2-\underset{C_6H_5}{CH}-\overset{|}{\underset{|}{Si}}- + LiCl$$

Keeping in mind these elements we visualized that various glassy/rubbery block copolymers could be conveniently and cleanly obtained by the following route:



$$C{=}C-PIB-C{=}C + H-\overset{|}{\underset{|}{Si}}-Cl \longrightarrow Cl-\overset{|}{\underset{|}{Si}}-C-C-PIB-C-C-\overset{|}{\underset{|}{Si}}-Cl$$

$$\Big\downarrow \sim CH_2-\underset{C_6H_5}{CH^{\ominus}}\ Li^{\oplus}\ (-LiCl)$$

$$PSt-\overset{|}{\underset{|}{Si}}-C-C-PIB-C-C-\overset{|}{\underset{|}{Si}}-PSt$$

It was further theorized that the number of external PSt sequences could be regulated by the number of chlorines in the chlorohydrosilane, i.e., the use of $H-SiMe_2Cl$, $H-SiMeCl_2$, and $H-SiCl_3$ would result in one, two, or three PSt sequences per end group, respectively.

This paper concerns the synthesis and characterization of PSt-Si-PIB-Si-PSt triblock and $Pst-\underset{PSt}{Si}-PIB-\underset{PSt}{Si}-PSt$ pentablock copolymers by hydrosilylating α,ω-diisopropenyl-PIB with Me_2SiHCl and $MeSiHCl_2$, respectively, and coupling the chlorosilane-telechelic PIB's thus formed with $PSt^{\ominus}$.

EXPERIMENTAL

Materials - Carbon tetrachloride was refluxed with CaH_2 overnight and distilled under nitrogen. The purification of benzene and styrene has been described (9).

Hydrosilanes (Petrarch Systems, Inc.), hexachloroplatinic acid hydrate ($H_2PtCl_6 \cdot 6H_2O$), dimethoxyethans, 2,4,4-trimethyl-1-pentene (TMP), and sec-butyllithium (Aldrich Chemical Company) were used as received. The catalyst solution for hydrosilylation was prepared by dissolving 1 g $H_2PtCl_6 \cdot 6H_2O$ in 9 ml dimethoxyethane and 1 ml absolute ethanol.

The synthesis and purification of α,ω-di(terchloro)polyisobutylene and α,ω-di(isopropenyl)polyisobutylene have been described (5,10).

Model Reaction - In a 100 ml two-neck flask equipped with a thermometer and a condenser (having a nitrogen inlet) were introduced 33.85 ml CCl_4, 0.45 ml benzene (0.0050 mol.), 7.93 ml TMP (0.050 mol.) and 7.77 ml CH_3SiHCl_2 (0.075 mol.). The flask was placed in a thermostated oil bath and when the temperature of the charge reached nearly that of the oil bath, 1 drop ($\sim$0.01 ml) catalyst solution was added to start the reaction.

Hydrosilylation conversion was monitored by ^{1}H-NMR spectroscopy (Varian Associates T-60 NMR Spectrometer) by determining the disappearance of olefin protons with time. Benzene was the internal standard.

Synthesis of Block Copolymers - To 3.5 g olefin-telechelic PIB (PIB-1 $\overline{M}_n$=38,200, $\overline{M}_w/\overline{M}_n$=1.73, or PIB-2 $\overline{M}_n$=3,910, $\overline{M}_w/\overline{M}_n$=2.37, $\overline{F}_n$=1.96), dissolved in 40 ml CCl_4 were added 5.0 ml silane and 5 drops ($\sim$0.05 ml) of catalyst solution. Reactions were carried out under reflux conditions and a blanket of nitrogen. After 24 hours, additional 3.0 ml silane and 5 drops of catalyst solution were added, and the reaction was continued for 24 more hours. For the low molecular weight olefin-telechelic PIB, ^{1}H NMR spectroscopy was used to ascertain that the olefinic double bonds had completely reacted. After removing most of the solvent and unreacted silane by distillation, the residue was dried under vacuum. Then, benzene was distilled into the flask to redissolve the polymer.

The hydrosilylated PIB prepolymers were coupled in benzene solution with a large excess of $PSt^{\ominus}$ (prepared by sec-butyllithium) (9). After destroying unreacted $PSt^{\ominus}$ by the use of degassed methanol, the polymer solution was filtered, the solvent was removed on a Rotovap, and the product was dried under vacuum.

Separation of Homopolystyrene - The crude products of coupling are mixtures of block copolymers and PSt. The separation of PSt was carried out by precipitating benzene solutions using acetone; this procedure was proven to be efficient in previous work (11). Thus, samples were dissolved in 100 ml benzene, and were precipitated by adding 1000 ml acetone. This process was repeated to remove PSt completely.

Block Copolymer Characterization - GPC analyses were performed using a Waters Associates 6000 A high pressure GPC instrument equipped with dual ultraviolet (UV, at 254 nm) and refractive index (RI) detectors. A Varian Associates HR-300 NMR Spectrometer (^{1}H spectroscopy using $HDCl_3$ or/and CCl_4 solvents) was used to determine the PSt content of block copolymers. A HP-503 High Speed Membrane Osmometer was used for $\overline{M}_n$ determination of the high molecular weight block copolymers.

RESULTS AND DISCUSSION

Model Hydrosilylation = Prior to the hydrosilylation of olefin-telechelic polyisobutylenes with different silanes, model experiments have been carried out using TMP, an olefin that exactly mimics the structure of the terminal olefin group in our prepolymers.

Figure 1 shows hydrosilylation rates of TMP with a series of chlorohydrosilanes at 60°C. The concentration of TMP was 1.0 M, the mole ratio of silane/TMP was 1.5, and 0.01 ml catalyst solution/50 ml charge was used. Evidently, the structure of the silanes greatly influences both the rates and conversions. The order of reactivity of these silanes in hydrosilylation is $MeSiHCl_2 \gtrsim Me_2SiHCl > HSiCl_3$. Similar results have also been obtained at 70°C. Hydrosilylation rates observed with Me_2SiHCl and $MeSiHCl_2$ are within what is considered to be experimental variation. The fact that the lowest rate was obtained with $HSiCl_3$ may be due to a combination of inductive and steric effects of the substituents on the silicon. This view is consistent with those expressed by Lukevits and Voronkov (6).

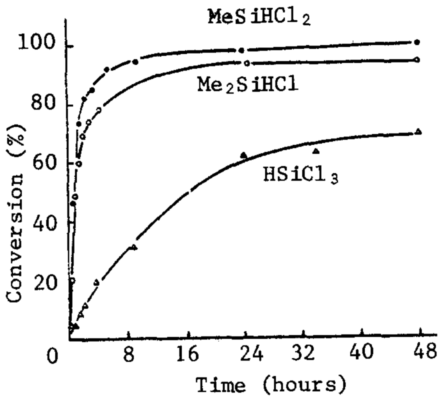


Figure 1: Conversion-time plots for hydrosilylation of TMP at 60°C (Temp. of oil bath)

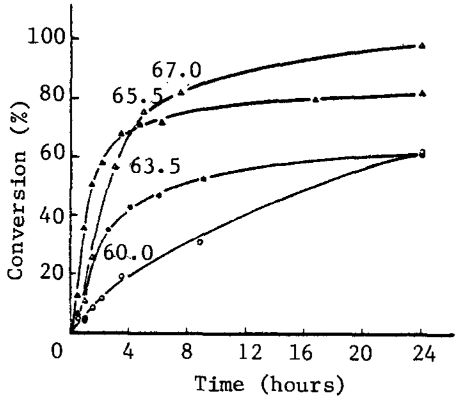


Figure 2: The rate of hydrosilylation with trichlorosilane

o 60°C, silane/TMP 1.5
● 60°C, silane/TMP 3.0
▲ 70°C, silane/TMP 1.5
△ 70°C, silane/TMP 3.0

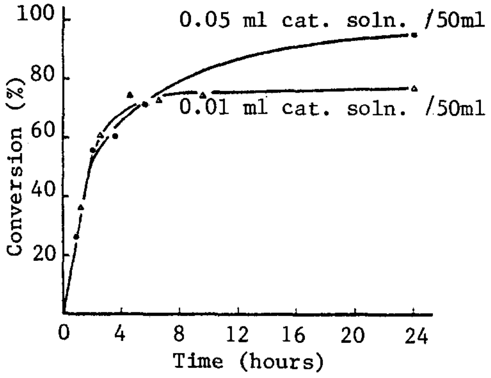


Figure 3: Effect of catalyst concentration on hydrosilylation of TMP with HSiCl$_3$

(60°, [TMP]=0.5 M, silane/TMP=3.0)

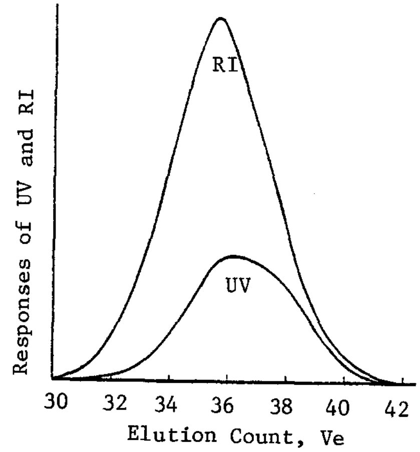


Figure 4: GPC trace of triblock copolymer P-1

Figure 2 shows the effect of $HSiCl_3$/TMP ratio on the rate of hydrosilylation at 60 and 70°C. In the experiment with $HSiCl_3$/TMP=3.0 at 70°C, the reflux temperature of the charge was initially ∿60°C because of the large amount of low boiling $HSiCl_3$ present (b.p. of $HSiCl_3$ is 31-32°C). As hydrosilylation proceeded and $HSiCl_3$ was converted, the temperature gradually increased and after about 14 hours it was ∿70°C (The numbers near the experimental points show the actual temperature of the charge). Evidently, increasing the silane/olefin ratio or the temperature favors hydrosilylation. According to the results shown in Figure 3, increasing the catalyst concentration also increases the conversion of hydrosilylation.

Hydrosilylation of Olefin-Telechelic Polyisobutylene and Coupling with $PSt^{\ominus}$ - Although kinetic experiments with $HSiCl_3$ proved to be quite informative and virtually complete conversion could be obtained even with this silane at relatively high silane/olefin ratio, temperature, and catalyst concentration (see Figures 2 and 3), we preferred to use the more reactive $MeSiHCl_2$ and Me_2SiHCl for polymer hydrosilylation experiments. Guided by the results of model kinetic experiments, reaction conditions were developed for quantitative hydrosilylation of olefin-telechelic polyisobutylenes (see Experimental). The disappearance of olefinic protons in the low molecular weight olefin-telechelic PIB-2 determined by ^1H NMR spectroscopy suggests essentially quantitative hydrosilylation. Moreover, derivatization research (see below), and related work carried out in these laboratories (12) indicate that essentially quantitative hydrosilylation of C=C-PIB-C=C has been achieved. The extent of hydrosilylation could not be determined directly on account of the extreme moisture sensitivity of the terminal Si-Cl group.

Thus, various PIB/PSt block copolymers have been prepared by adding a stoichiometric excess of living polystyryl anions $PSt^{\ominus}$ to chlorosilane-telechelic PIB's obtained via hydrosilylation of C=C-PIB-C=C by Me_2SiHCl and/or $MeSiHCl_2$.

Characterization of Block Copolymers - Information as to the overall composition and structure of our block copolymers has been obtained by a combination of characterization techniques. Figure 4 shows the RI and UV traces (GPC) of a PSt-Si-PIB-Si-PSt triblock copolymer (P-1) prepared by hydrosilylating with Me_2SiHCl a relatively high molecular weight C=C-PIB-C=C (PIB-1), and coupling the product with $PSt^{\ominus}$ ($\overline{M}_n$=800). Homopolystyrene was removed by fractional solvent extraction (see Experimental).

The overall composition of the product can be obtained by the following train of thought. The RI and UV responses obtained by dual-detector GPC may be expressed by the following equations:

$$H_{RI_i} = K_{PSt} \cdot C_{PSt_i} + K_{PIB} \cdot C_{PIB_i} \tag{1}$$

$$H_{UV_i} = k \cdot C_{PSt_i} \tag{2}$$

so that,

$$\left[\frac{H_{RI}}{H_{UV}}\right]_i = \frac{K_{PSt}}{k} + \frac{K_{PIB}}{k} \cdot \frac{M_i - \overline{M}_{PSt} \cdot n}{\overline{M}_{PSt} \cdot n} = \frac{K_{PSt} - K_{PIB}}{k} + \frac{K_{PIB}}{\overline{M}_{PSt}} \cdot \frac{M_i}{k \cdot n} \tag{3}$$

Where H_{RI_i} and H_{UV_i} are the RI and UV responses (heights) at i elution counts of the GPC trace; C_{PIB_i} and C_{PSt_i} are the weight concentrations of PIB and PSt blocks; M_i is the molecular weight at i elution count; $\overline{M}_{PSt}$ is the molecular weight of PSt block; n is the number of PSt block per molecule; K_{PSt}, K_{PIB} and k are constants. According to Eq. 3, a plot of $(H_{RI}/H_{UV})_i$ versus M_i should give a straight line. That this is indeed the case is borne out by the data shown in Figure 5. The molecular weight of P-1 for each elution count was estimated by the use of a GPC calibration curve constructed with PIB standards since the molecular weight of PSt was low and the PSt content in the block copolymer was low. Evidently the number of PSt blocks is the same (i.e., 2) for every copolymer composition along the horizontal axis.

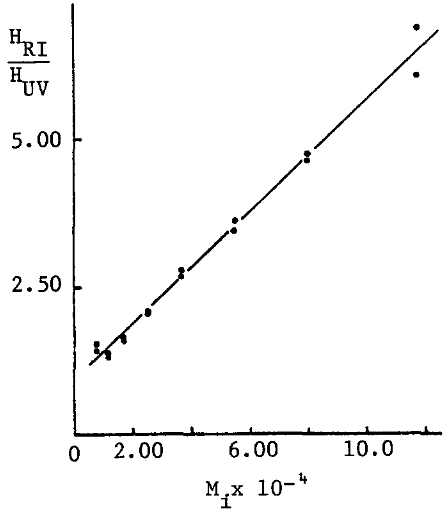


Figure 5: H_{RI}/H_{UV} vs. M_i plot for triblock copolymer P-1

According to high resolution ^{1}H NMR spectroscopy and osmometry, the PSt content and $\overline{M}_n$ of P-1 are 5.3 wt % and 40,500, respectively. These results are well within experimental error with the values expected for a PSt-Si-PIB-Ø-PIB-Si-PSt triblock containing two outer PSt blocks of $\overline{M}_n$=800 and a central PIB segment of $\overline{M}_n$=38,200.

Subsequently, a triblock (P-2) and a pentablock (P-3) copolymer have been prepared by coupling $PSt^{\ominus}$ ($\overline{M}_n$=800) with chlorosilane-telechelic PIB's; the latters were prepared by hydrosilylation of a relatively low molecular weight C=C-PIB-C=C (PIB-2) with Me_2SiHCl and $MeSiHCl_2$, respectively. Figure 6 shows the respective GPC traces, and Figure 7 displays the corresponding $(H_{RI}/H_{UV})_i$ vs. M_i plots. For comparison, the latter figure also contains the line seen in Figure 5 (dotted line). Significantly, the slope of the lines characteristic of the relatively high molecular weight triblock copolymer P-1 and that of the lower molecular weight product P-2 are virtually identical; evidently the overall structures of these materials are virtually the same, i.e., triblocks of n=2. Moreover, the slope of the line characteristic of P-3 is exactly half of those of P-1 and P-2, which indicates that P-3 contains twice as much PSt segments as P-1 or P-2, i.e., n=4.

At a very low molecular weights, i.e., M_i<5000, the data are badly scattered and difficult to analyze. Since sample purification involved acetone precipitation, some PSt rich copolymer may have been lost, leading to erroneous data.

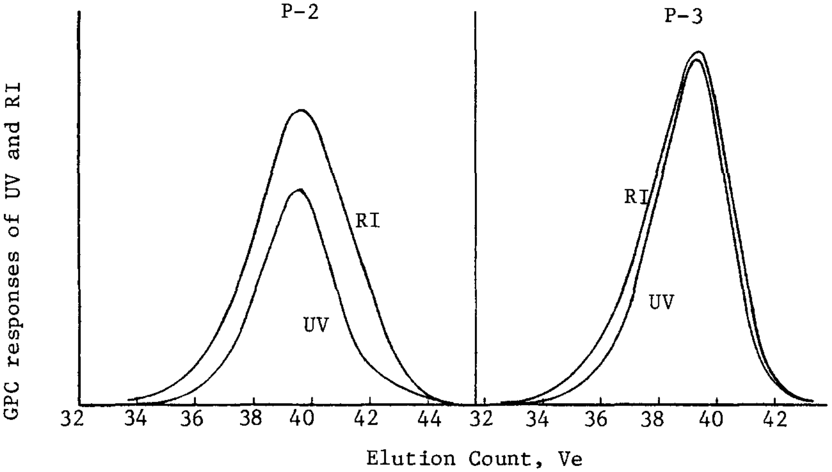


Figure 6: GPC traces of triblock copolymer P-2 and H copolymer P-3

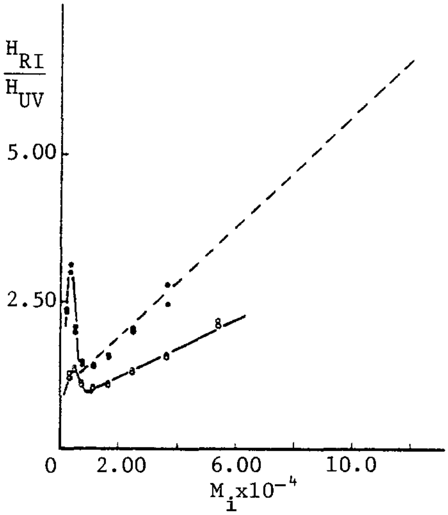


Figure 7: H_{RI}/H_{UV} versus M_i plots of triblock copolymer P-2 and H copolymer P-3

CONCLUSIONS

Model hydrosilylation of TMP using three chlorohydrosilanes in ths presence of $H_2PtCl_6 \cdot 6H_2O$ has been studied by ^{1}H NMR spectroscopy. The order of hydrosilylation activity is $MeSiHCl_2 \geq Me_2SiHCl > HSiCl_3$. Increasing the silane/olefin ratio, temperature, and the amount of catalyst enhances the rate of hydrosilylation and conversion.

Tri- and H block copolymers have been synthesized by hydrosilylation of olefin-telechelic polyisobutylenes with Me_2SiHCl and $MeSiHCl_2$, respectively, followed by coupling with anionic living polystyrene. The resulting copolymers have been characterized by RI-UV dual detector GPC, ^{1}H 300 MHz NMR spectroscopy, and osmometry.

ACKNOWLEDGEMENTS

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