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Side-Loop Polymers Based on the Hydrosilylation of Polybutadiene

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Abstract: Hydrosilylation of hydride-terminated poly(dimethylsiloxane) with polybutadiene in dilute solution yielded polysiloxane side-loops on a hydrocarbon base, a novel polymer architecture. When the ratio of silane to olefin was increased, the inherent viscosity of solutions dropped drastically, and polymer properties changed from tough rubbers to tacky materials. The results are rationalized on the basis of diminishing availability of olefin sites as the reaction proceeds. When one end of a difunctional silane attaches to an olefin site and no other olefin sites are available nearby, molecular motion eventually brings a remote olefin site in the molecule into proximity. Hydrosilylation then results in permanent ring folding. Subsequent hydrosilylations can then result in a dendrimer-like globular molecule. Contact angle measurements of side-loop adducts show temporal stability, indicating that the tendency of poly(dimethylsiloxane) side chains to migrate to or away from the surface, depending on the medium, is circumvented by anchoring both ends.

Introduction

Silicones have become important commercial polymers because of a combination of properties, including high thermal stability,[1] low surface tension,[1,2] low glass transition temperature,[1,2] optical transparency[1−3] and low dielectric constant.[1,2] The materials, however, have relatively poor mechanical strength,[1,4,5] generally requiring high filler loading to obtain acceptable properties. The poor strength is usually attributed to flaws or microcracks that grow readily because of the high mobility of the chains.[5,6]

Recently, silicones have been found to be effective as antifouling marine coatings,[7] providing potential replacements for toxic tin and copper based coatings currently in use. For this application, however, high filler loading is detrimental.

A potential alternative is to attach polysiloxanes as side chains to hydrocarbon polymers. Good fouling release coating properties have been attributed to low surface energy, low glass temperature, and temporal stability in water.[8] When polysiloxane side chains were attached to polymethacrylate backbones, contact angle measurements indicated migration of the side chains to the polymer surface in air, but away from the surface on prolonged immersion in water.[8] The result was unstable surface properties.

The approach taken here was to use a polymer architecture that could inhibit this type of chain migration. It was reasoned that if the polysiloxane chain could be attached to a main-chain polymer at both ends as a *side-loop*, the temporal instability

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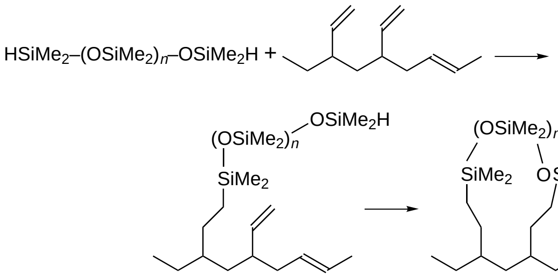
Scheme 1. Side-Loop Formation



would be minimized. Short-chain monofunctional silanes, R_3SiH, have been hydrosilylated onto double bonds of polybutadiene and similar polyolefins.[9−11] Difunctional silanes, such as hydride-terminated poly(dimethylsiloxane) (HPDMS), are available. Intermolecular reactions, however, would result in a highly cross-linked, unmanageable system, but intermolecular reactions should be avoided by high dilution. The formation of side-loops after the initial attachment of HPDMS is depicted in Scheme 1.

Polymer architectures are usually categorized as linear, branched, and cross-linked.[12−14] Recently, the exploration of novel polymer architectures has become one of the most active areas of polymer chemistry, and reviews have appeared covering dendrimers,[15−18] polyrotaxanes,[19] polycatenanes,[19] and cyclic polymers.[20,21] The concept of side-loop polymers has been virtually unexplored. Thus, polymerization of divinyl monomers has yielded polymers with loops consisting of the original spacers between vinyl groups.[22] Also, when cross-linking of polystyrene by alkylation was carried out in dilute solution, only intramolecular cross-linking was obtained.[23]

Experimental Section

Materials. THF and toluene (Aldrich HPLC grade) were used as received. Polybutadiene of M_n 100 000 (93% vinyl olefin) was used as received from Scientific Polymer Products, Inc. Hydride-terminated poly(dimethylsiloxane) (M_n 400) was obtained from Hüls America Inc. Wilkinson's catalyst (tris(triphenylphosphine)rhodium(I) chloride) and chloroplatinic acid were purchased from Aldrich.

Table 1. Hydrosilylation of Polybutadiene[a]

adduct	wt silane	eq silane[b]	wt pbd	eq vinyl[c]	% PDMS	nominal MW[d]
H1V3	8.01	0.0400	6.99	0.1202	53	215,000
H1V2	9.48	0.0474	5.52	0.0949	63	272,000
H1V1	11.62	0.0581	3.38	0.0581	77	444,000
H2V1	13.1	0.0655	1.91	0.0328		

[a] 750 mL of toluene as solvent, 50 mg of Wilkinson's catalyst. [b] Eq wt 200. [c] 93% vinyl content. [d] Based on stoichiometry.

Hydrosilylation of Polybutadiene (General Procedure). Polybutadiene was dissolved in toluene in a 1-L flask equipped with a magnetic stirrer, a reflux condenser, a nitrogen inlet, and a heating mantle. Hydride-terminated poly(dimethylsiloxane) and the catalyst tris(triphenylphosphine)rhodium(I) chloride were added, and the mixture was refluxed under nitrogen until the IR spectra of aliquots indicated the absence of SiH absorption at 2163−2068 cm^{-1} (3−5 days). Details regarding quantities are given in Table 1.

Slide Coatings and Moldings. Portions of the toluene solutions were concentrated with a rotary evaporator to give viscous solutions of 30−45% concentration. These solutions were used immediately, as gelatin resulted on prolonged storage. Microscope slides (1 × 3 in.) were coated with the material by using a spin-coating technique.[24] Silanized slides were taped to the center post of a centrifuge with doubled tape, and the concentrated solution was added dropwise to the center of the spinning slide. The slides were then heated overnight in a 100 °C oven. Moldings were prepared by pouring the concentrated solutions into a Teflon mold and heating at 60−65 °C for several days.

Inherent and Intrinsic Viscosities. Viscometric measurements were performed with a Cannon-Ubbelohde Semi-Micro type viscometer (No.50). The solvent was toluene, and the temperature was maintained at 20 °C with a water bath. The inherent viscosity was measured at 0.5 or 0.1 g/dL, and the elapsed time was recorded with an optical viscosity timer (Model 821, Jupiter Instrument Company, Jupiter, FL). The inherent viscosity of a polymer solution equals the intrinsic viscosity at infinite dilution.[25] For the materials investigated, the difference between the inherent viscosity measured at 0.5 g/dL and the intrinsic viscosity was estimated to be less than 5%.

Gel Permeation Chromatography. The equipment consisted of a Hewlett-Packard Series 1050 pump and two Altex spherogel AE columns (size 103 and 104, respectively) connected in series. The mobile phase was THF or toluene. Polymer contents in the effluent of the columns were detected with a Wyatt/Optilab 903 interferometric refractometer.

Contact Angle. Contact angles were measured with a Cahn Dynamic Contact Angle Analyzer (Model 312). Samples were prepared by dip-coating the material on glass slides (25 × 75 × 1 mm). Water purified with a Barnstead NANOpure water system was used as the probe liquid.

Results and Discussion

Polybutadiene was used as the polyolefin to test the concept of side-loop hydrosilylation. Hydrosilylations have been reported to take place much more rapidly at the vinyl double bonds of polybutadiene than at the internal double bonds.[9] Therefore, polybutadiene with high vinyl content (93%) was used, with 100 000 molecular weight. Commercially available hydride-terminated poly(dimethylsiloxane) of molecular weight 400 was used, and the hydrosilylation was catalyzed with Wilkinson's catalyst (tris(triphenylphosphine)rhodium(I) chloride). The hydrosilylations were carried out in toluene solution and were monitored by the disappearance of SiH absorption in the IR spectrum.

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To avoid intermolecular hydrosilylations, it is desirable to keep the polymer concentration at a level that expanded molecules do not extensively overlap with each other. Correlations between the unperturbed dimension, r0, in cyclohexane and the molecular weight for polybutadienes of different compositions have been reported.[26] According to those correlations, specific volume in cyclohexane at 25 °C for polybutadiene of molecular weight 220 000, containing 25% terminal vinyl groups, is 162 cm^3/g. This number was used to estimate the initial concentrations of the reactants. In actuality the reactions were carried out in toluene, and polybutadiene containing 93% terminal vinyl group was used. Although the effects of solvent are expected to be small, the solubility parameter for cyclohexane, 8.2 (cal/cm^3) = BD, is quite close to the solubility parameter of toluene, 8.9 (cal/cm^3) = BD. For a given molecular weight, the specific volume for polybutadiene increases with an increase in terminal vinyl content.[26] The concentrations used in this study were substantially below the theoretical maximum for total mutual exclusion as derived above.

For ease in comparing the effect of the extent of hydrosilylation of the double bonds of polybutadiene on polymer properties, fixed equivalent ratios of hydride to vinyl double bonds were used. The hydrosilylation reactions are summarized in Table 1; the adducts are designated by the relative equivalents of hydride and vinyl bonds (H1V3 designates a 1:3 ratio). The nominal molecular weights were calculated on the basis of reaction stoichiometry, and are high enough to suggest that good polymer properties could be expected even without cross-linking.

Molded objects were prepared from H1V3, H1V2, and H1V1 by removing solvent under vacuum to give viscous solutions and then drying the solutions in a PTFE mold. The H1V3 samples were tough, strong elastomers, whereas the H1V2 samples were weak and the H1V1 were tacky. The concentrated solutions could not be stored for long periods, and began to gel in several hours. The dried samples did not redissolve completely in toluene. Although IR indicated complete consumption of hydride, it appears that small amounts remained in hindered positions and the accelerated intermolecular reaction on solvent removal resulted in cross-linking. Even extending the hydrosilylation after the normal period with the addition of 3,3-dimethylbutene did not prevent the gelling. Similar results were obtained when the reaction mixture was transferred to an autoclave and treated with ethylene under the same conditions.

The degradation of elastomer properties after sufficient silane is added to consume more than half of the double bonds was unexpected. Depolymerization of the base polymer under the polymerization conditions could be considered. However, Crivello[27] recently showed that, although polybutadiene with 9% vinyl content degrades in the presence of Wilkinson's catalyst in toluene, no such drop in molecular weight is observed with 93% vinyl polybutadiene.

Viscometric Studies. To gain more insight into the reaction, solution viscosities were examined. The results are shown in Table 2. The observed order of the inherent viscosities is opposite the order of the molecular weights expected on the basis of stoichiometry. The most notable viscosity decrease comes after the reaction midpoint (H1V2).

Table 2. Inherent Viscosity of Adducts

adduct	concn (g/dL)	inherent viscosity (dL/g)
H1V3	0.5	0.56
H1V2	0.5	0.32
H1V1	0.5	0.10
H2V1	0.5	0.05

Intrinsic viscosity is related to the molecular weight by the Mark–Houwink equation:

$$\text{intrinsic viscosity} = 3Dk(\mathrm{MW})a \qquad (1)$$

For polybutadiene containing 65% terminal vinyl groups in toluene at 25 °C, the k value is 1.10×10^{-3} dL/g and a is 0.62, the corresponding values for poly(dimethylsiloxane) are 0.22×10^{-3} dL/g and 0.65, respectively.[28] Since for polybutadienes of different vinyl contents, the k value decreases while the a value increases with an increase in terminal vinyl content, the above parameters should apply to the polybutadiene used in these reactions, i.e., 93% 1,2-vinyl, reasonably well. The intrinsic viscosity for the polybutadiene used was 1.23 dL/g, and the inherent viscosity of the hydride-terminated poly(dimethylsiloxane) at 0.1 g/dL was 9.50×10^{-3} dL/g. Both values are in agreement with predictions by the Mark–Houwink equation using parameters cited above. The Mark–Houwink parameters also indicate that toluene is a much better solvent for polybutadiene than poly(dimethylsiloxane). Thus, the reversed inherent viscosity-molecular weight relation observed in the polymers may be due partially to the difference in solubility for polybutadiene and poly(dimethylsiloxane). Polymers prepared with excess hydrides, although of higher molecular weight, are less expansive, as the poly(dimethylsiloxane) contents in these polymers are higher, and poly(dimethylsiloxane) is less soluble in toluene than polybutadiene. Nevertheless, the silane contents of the polymers, as shown in Table 1, are all greater than 53%, and it does not seem likely that this change in solubility properties could result in an order of magnitude reduction in viscosity.

Solubility and refractive index differences between polybutadiene and silicone prevented molecular weight determinations of the adducts by GPC. However, unreacted hydride terminated PDMS (MW 400) could be determined with toluene as the mobile phase. The proportionality obtained from GPC traces for solutions containing the PDMS at known concentration was used to correct the viscosity data. The inherent viscosities for the macromolecular products after the correction were 0.06, 0.11, 0.33, and 0.58 dL/g for runs H2V1, H1V1, H1V2, and H1V3, compared with 0.05, 0.10, 0.32, and 0.56 dL/g before the correction. Thus, the effect of free PDMS on the viscometric measurements was minimal.

Another possible cause of discrepancies in the viscosity data is cross-linking of the adducts on storage before viscosities are measured. This possibility was tested by repeating the hydrosilylation experiments at half the concentration of the previous experiments. The inherent viscosities were 0.28, 0.17, 0.09, and 0.08 dL/g for runs H1V3, H1V2, H1V1, and H2V1, respectively. The values were approximately halved for H1V3 and H1V2, and changes were insignificant for H1V1 and H2V1, which theoretically have no free olefin. Thus, there still is a large unexplained reduction in viscosity as the molecular weight increases as the hydrosilylation proceeds.

A rationalization of the changes in solution viscosity, as well as the characteristics of isolated polymers, is based on the changing availability of vinyl groups as the reaction proceeds. The initial hydrosilylation step is slow because the hydride,

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olefin, and catalyst must unite in dilute solution. After one end of a PDMS molecule is attached, the local concentration of vinyl groups for the remaining end increases enormously, and ring closure takes place rapidly at an adjacent or nearby olefin site. As the reaction proceeds, chain sites with two nearby free vinyl groups ultimately become exhausted, and when a PDMS molecule attaches to an olefin, no additional local sites are available for loop formation. Eventually, motion of the chain brings a distant vinyl group in the polyolefin molecule into proximity for hydrosilylation, and permanent ring folding is the result. Repetitions of the process may "stitch" the molecule into a spherical shape. Thus, as the reaction proceeds, reduced chain entanglement results in lower viscosity in solution, and reduced strength of isolated films.

There is considerable current interest in dendrimers and hyperbranched polymers.[15−18] Hyperbranched polymers are obtained by simple polymerization methods and have some shape similarities with dendrimers. There is little control, however, over uniformity of molecular weight or shape of hyperbranched polymers. Even dendrimers constructed layer by layer have irregularities that become more distorted with each generation. The present method offers an alternative approach to globular macromolecules. The spherical molecule is stitched together from a long polyolefin rather than being built up in layers. Molecular weight uniformity is limited mainly by the uniformity of available polyolefins. Unused olefin sites can potentially be used to introduce other functional groups on the surface. Notably, an extremely simple one-step synthesis method is used, based on commercially available starting materials.

Contact Angle Analysis. Contact angles of water on these materials appear to be independent of the composition. The advancing contact angle of water on the products from run H2V1 was 94° and the receding contact angle was 80°, and the corresponding values were 91 and 79° for run H1V1, 91 and 83° for run H1V2, and 92 and 75° for run H1V3. Interestingly, these properties are temporaily stable. For example, the water contact angles on products from run H1V3 that had been immersed in water continuously for 6 days were 88°, advancing, and 75°, receding. In comparison, water contact angles on freshly prepared polybutadiene film were 108°, advancing, and 86°, receding; the same properties after 8 days' immersion in water were 92 and 20°, respectively. Thus, the tendency of poly(dimethylsiloxane) side chains to migrate into the polymer or to the surface, depending on the medium,[8] is circumvented by anchoring both ends.

Conclusions. As the hydride-to-vinyl ratio is increased in the dilute hydrosilylation of hydride-terminated poly(dimethylsiloxane) with polybutadiene, the inherent viscosity of the solution decreases dramatically, and polymer properties change from tough rubbers to tacky materials. For low hydride-to-vinyl ratio, the results are explained on the basis of the formation of side-loops when attachment takes place between nearby vinyl groups. At higher ratios, hydrosilylation at an isolated olefin site may give a hydride-terminated side chain with no nearby vinyl groups. When molecular motion brings a remote olefin site in the molecule into proximity, hydrosilylation results in permanent ring folding. Subsequent hydrosilylations can then result in a compact, dendrimer-like molecule. Contact angle measurements of side-loop adducts show temporal stability, indicating that the tendency of poly(dimethylsiloxane) side chains to migrate to or away from the surface, depending on the medium, is circumvented by anchoring both ends. The concept of side-loop polymers and the new approach to dendrimers potentially have broader applicability to other systems.

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