least-squares analysis of the ln k versus $1/T$ plots. The slopes, intercepts, and standard deviations from the ln k versus $1/T$ plots are slope = 31.21 ± 0.89 kcal, intercept = 42.0 ± 1.4 ln (s^{-1}) for the M_w 6100 polymer and slope = 31.25 ± 1.38 kcal, intercept = 42.7 ± 2.2 ln (s^{-1}) for the M_w 19 300 polymer.

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Registry No. PMMA, 9011-14-7.

References and Notes

(1) Simha, R.; Wall, L. A.; Blatz, P. J. *J. Polym. Sci.* **1950**, *5*, 615.
(2) Grassie, N.; Melville, H. W. *Proc. R. Soc. London, A* **1949**, *199*, 14.
(3) Cowley, P. R. E. J.; Melville, H. W. *Natl. Bur. Stand. Circ. (U. S.)* **1953**, *No. 525*, 59.
(4) Bywater, S. *J. Phys. Chem.* **1953**, *57*, 879.
(5) Brockhaus, V. A.; Jenckel, E. *Makromol. Chem.* **1956**, *12*, 263.
(6) Boyd, R. H. *Thermal Stability of Polymers*; Conley, R. T., Ed.; Marcel Dekker: New York, 1970; Chapter 3.
(7) Votinov, A.; Kobeko, P.; Marei, F. *J. Phys. Chem. (USSR)* **1942**, *16*, 106.
(8) Madorsky, S. L. *J. Polym. Sci.* **1953**, *11*, 491.
(9) Jellinek, H. H. G.; Luh, M. D. *Makromol. Chem.* **1968**, *115*, 89.
(10) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(11) Sogah, D. Y.; Hertler, W. H.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.

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Regio- and Stereospecific 1,4-Polymerization of 2-(Triethylsilyl)-1,3-butadiene

There is considerable interest in stereoregular polymerization of 1,3-diene monomers. Anionic polymerization of isoprene initiated by alkyllithium reagents in hydrocarbon solvents such as cyclohexane yields polyisoprene of narrow molecular weight distribution whose microstructure has been shown by IR,[1,2] ^1H NMR,[3] and ^{13}C NMR[4] to be predominantly cis-1,4 (~80%). However, appreciable amounts of trans-1,4 (~15%) and 3,4 (~5%) units are also present. Anionic polymerization of isoprene in the presence of donor solvents such as ether and THF leads to a polymer whose microstructure is predominantly 3,4 (~60%).[2,3] Thus the anionic polymerization of isoprene is regio- and stereoselective but *neither* regio- *nor* stereospecific.

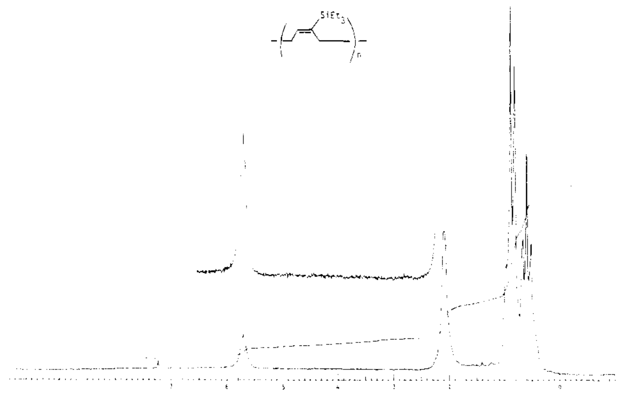
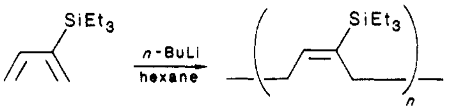


Figure 1. ^1H NMR of 1,4-(E)-poly[2-(triethylsilyl)-1,3-butadiene].

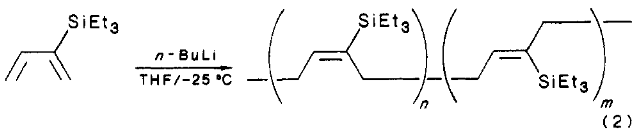
Table I
Anionic Polymerization of I in Hexane at 25 °C

% n-BuLi initiator	time	% yield	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	$\bar{M}_w/\bar{M}_n$
0.5	60 h	62	108.8	67.3	1.61
1.5	30 h	93	18.3	14.0	1.28

Results and Discussion. We should like to report that regio- and stereospecific anionic polymerization of 2-(triethylsilyl)-1,3-butadiene (I) in hexane solvent at room temperature yields (E)-1,4-poly[2-(triethylsilyl)-1,3-butadiene]. Neither (Z)-1,4-poly[2-(triethylsilyl)-1,3-butadiene] nor 1,2 nor 3,4 units are found. The reaction is stereospecific. The results are summarized in Table I. As can be seen, GPC analysis reveals a monomodal molecular weight distribution of low polydispersity ($\bar{M}_w/\bar{M}_n$ = 1.3–1.6). The molecular weight of the polymer depends on the ratio of the monomer to initiator. These results are consistent with relatively rapid initiation and the absence of chain transfer and termination reactions during the course of polymerization of I. The microstructure of this polymer is of considerable interest since physical properties of polydienes depend upon the structure of the repeating units. We have determined the mode of the polymerization (1,4; 1,2; or 3,4) and the geometry of the monomer units by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The ^1H NMR of this polymer can be seen in Figure 1. Note that in the olefinic region only a single peak at 5.70 ppm (1 H) is observed. For comparison the vinyl CH of (E)-3-(trimethylsilyl)-3-octene comes at 5.60 ppm.[6] This strongly suggests that the polymer has an (E)-1,4 microstructure. The stereoregularity of the carbon–carbon double bonds in the polymer chain is supported by the ^{13}C NMR in which only two nonequivalent vinyl carbons as well as two distinct allylic carbons are observed. No peaks which could be assigned to either 1,2 or 3,4 structures were observed in either the ^1H or ^{13}C NMR spectra. Further, only a single silicon resonance is seen in the ^{29}Si NMR spectrum (see Experimental Section for details). Finally, protodesilation of the polymer by treatment with HI in a mixture of water and methylene chloride yields (Z)-1,4-polybutadiene whose structure was determined by infrared spectroscopy.[7] Protodesilation of vinyl silanes has previously been shown to occur stereospecifically with retention of configuration.[8,9] All of these pieces of data are consistent with (E)-1,4-poly[2-(triethylsilyl)-1,3-butadiene]; see eq 1.



(1)



(2)

On the other hand, while anionic polymerization of I in the presence of donor solvents such as THF gave a polymer of 1,4 microstructure, the stereochemistry about the carbon–carbon double bonds was a mixture of E and Z in which the E configuration predominates; see Table II. The ratio of E to Z was determined by integration of the ^1H NMR signals of the vinyl CH protons which are well separated. Thus the Z vinyl CH comes at 5.99 ppm while the E vinyl CH comes at 5.71 ppm. The ^1H NMR of this

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Table II
Anionic Polymerization of I in the Presence of Donor Solvents

% *n*-BuLi initiator	solvent	temp, °C	% yield	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	*E*:*Z*
3	hexane/HMPA 20:1	-25	64	29.0	9.0	2.3
3	THF/HMPA 20:1	-25	44	6.8	4.1	1.25
3	THF	-78	75	18.9	9.17	1.3

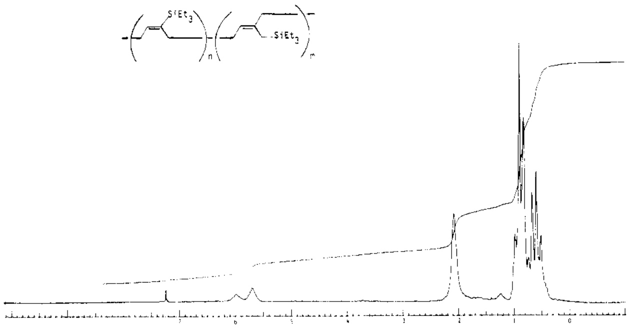

Figure 2. ^{1}H NMR of 1,4-(*E*)- and 1,4-(*Z*)-poly[2-(triethylsilyl)-1,3-butadiene].

polymer can be seen in Figure 2. These assignments are consistent with chemical shifts reported for vinyl CH's of monomeric trimethylsilyl-substituted olefins.[6,10] This latter result is similar to those recently reported for the anionic polymerization of 2-(trimethoxysilyl)-1,3-butadiene in THF which yields 1,4-poly[2-(trimethoxysilyl)-1,3-butadiene] with an *E* to *Z* ratio of 70:30.[11] However, the ^{13}C NMR of 1,4-poly[2-(triethylsilyl)-1,3-butadiene] prepared in THF is more complicated, eight vinyl carbon resonances as well as eight allylic carbon resonances are observed. This is consistent with the ^{13}C NMR previously reported for (*E*)- and (*Z*)-1,4-polyisoprene;[12] see eq 2.

The thermal stability of these polymers has been determined by TGA. 1,4-Poly[2-(triethylsilyl)-1,3-butadiene] is thermally stable to 200 °C. Between 200 and 250 °C about 3% weight loss occurs. Rapid weight loss occurs between 250 and 350 °C. These polymers leave virtually no residue (see Figure 3).

Conclusion. Anionic polymerization of 2-(triethylsilyl)-1,3-butadiene in hydrocarbon media is both regio- and stereospecific. In the presence of donor solvent this polymerization is regiospecific. By comparison, polymerization of isoprene in hydrocarbon is only regio- and stereoselective. The reasons for the greater selectivity in the case of 2-(triethylsilyl)-1,3-butadiene is under active investigation. (*E*)-1,4-Poly[2-(triethylsilyl)-1,3-butadiene] thus joins the small group of stereoregular diene polymers. We are studying various electrophilic substitution reactions on this polymer, since it is well-known that monomeric vinyl silanes undergo regio- and stereospecific substitution reactions by a wide variety of electrophiles.[13]

Experimental Section. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the Fourier Transform mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were obtained on a Brucker WP-270-SY spectrometer operating in the Fourier Transform mode. Ten to fifteen percent solutions in chloroform-d_1 were used to obtain ^{29}Si spectra whereas 5% solutions were used for ^{1}H and ^{13}C spectra. Chloroform was utilized as an internal standard for ^{1}H, ^{13}C, and ^{29}Si NMR spectra. All chemical shifts reported were externally referenced to tetramethylsilane. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have methylene groups bonded to them.[14] IR spectra were recorded on a Perkin-Elmer PE 281 spectrometer. These were taken on chloroform solutions in NaCl cells.

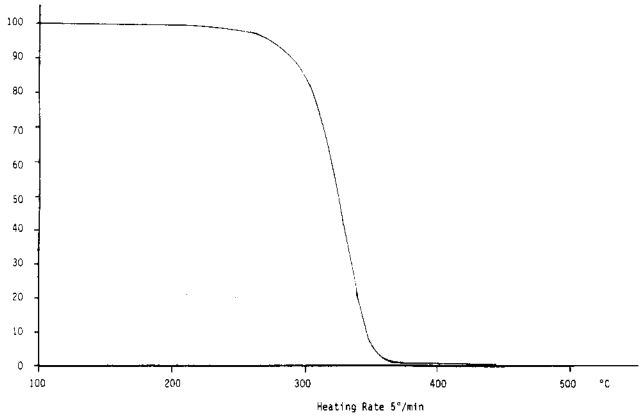

Figure 3. TGA of 1,4-(*E*)- and 1,4-(*Z*)-poly[2-(triethylsilyl)-1,3-butadiene].

GPC analysis of the molecular weight distribution of the polymers was performed on a Perkin-Elmer Series 10 liquid chromatograph equipped with an LC-25 refractive index detector (maintained at 25 °C), a 3600 data station, and a 660 printer. A 32 cm × 77 mm Perkin-Elmer PL 10-μm particle size, mixed pore size, cross-linked polystyrene gel column was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodispersed polystyrene standards: $\bar{M}_p$ 3 600 000, 194 000, 28 000, and 2550 whose $\bar{M}_w/\bar{M}_n$ are less than 1.09.

TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 100 °C for 10 min followed by an increase of 5 °C to 500 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

2-(Triethylsilyl)-1,3-butadiene (I) was prepared in two steps. Chloroplatinic acid catalyzed hydrosilation of 1,4-dichloro-2-butyne with triethylsilane gives (*E*)-1,4-dichloro-2-(triethylsilyl)-2-butene which is dechlorinated by treatment with zinc in ethanol solvent.[15]

Polymerizations were carried out in flame-dried apparatus under an atmosphere of prepurified nitrogen. In a 50-mL round-bottom flask, equipped with a Teflon-covered magnetic stirring bar and a rubber septum, was placed I (6 g, 36 mmol) dissolved in 30 mL of hexane. *n*-Butyllithium (0.1 mL, 1.5 N) was added to this at room temperature. The reaction was stirred for 60 h. Ether was then added, the organic phase washed twice with water, dried over anhydrous magnesium sulfate, and filtered, and the solvent removed by evaporation under reduced pressure. The residue was taken up in THF and the polymer, a viscous oil, was precipitated by addition of methanol. The THF/methanol supernatant was decanted from the polymer. This precipitation procedure was repeated 3 times to obtain analytical samples. The polymer was dried at 57 °C under vacuum overnight. In this way, 3.7 g (62% yield) of polymer was obtained. Removal of the solvents from the supernatant gave 2 g of recovered I.

(*E*)-1,4-Poly[2-(trimethylsilyl)-1,3-butadiene] has the following properties: ^{1}H NMR δ 5.70 (br s, 1 H), 2.10 (br s, 4 H), 0.897 (t, 9 H, J = 6.5 Hz), 0.61 (q, 6 H, J = 6.5 Hz);

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^{13}C NMR δ 141.79, 136.87, 30.14, 29.44, 7.50, 3.22; ^{29}Si NMR δ 1.99; IR ($CHCl_3$) ν 1597, 1450, 1410, 1230, 998 cm^{-1}. Elemental anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 70.87; H, 12.03.

Protodesilation of (*E*)-1,4-Poly[2-(triethylsilyl)-1,3-butadiene]. Five hundred milligrams of polymer was dissolved in 20 mL of methylene chloride in a 50-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar. To this was added 2 mL of a 47% solution of aqueous HI. The mixture was stirred vigorously at room temperature for 4 days. It was then diluted with ether and the organic phase washed with aqueous sodium bicarbonate and water. It was dried over anhydrous magnesium sulfate and filtered and the solvent removed by evaporation under reduced pressure. The (*Z*)-1,4-polybutadiene obtained had the following spectral properties: ^1H NMR δ 5.376 (br s, 2 H), 2.07 (br s, 4 H); ^{13}C NMR δ 129.60, 27.38; IR (film) ν 1650, 1440, 980, 725 cm^{-1}.[7]

Polymerization of I in THF was carried out as above except that the reaction temperature was maintained at −25 °C. The polymer isolated had the following properties: ^1H NMR δ 5.99 (br s, (*Z*)-CH=), 5.71 (br s, (*E*)-CH=), 2.10 (br s, 4 H), 0.89 (t, 9 H, J = 6.5 Hz), 0.60 (q, 6 H, J = 6.5 Hz); ^{13}C NMR δ 144.18, 143.69, 141.90, 141.79, 136.81, 136.64, 135.94, 135.51, 38.48, 33.9, 33.5, 32.63, 30.51, 30.14, 29.43, 28.57, 7.66, 7.50, 4.30, 3.27; ^{29}Si NMR δ 2.06, 1.96, 1.91, 1.89, 0.51, 0.38, 0.30; IR ($CHCl_3$) ν 1600, 1450, 1412, 1233, 997 cm^{-1}. Elemental anal. Calcd: C, 71.34; H, 11.97. Found: C, 70.88; H, 11.87.

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Registry No. I, 112348-69-3; $H_3C(CH_2)_3Li$, 109-72-8.

References and Notes

(1) Tobolsky, A. V.; Rogers, C. E. *J. Polym. Sci.* **1959**, *40*, 73.
(2) Stearns, R. S.; Forman, L. E. *J. Polym. Sci.* **1959**, *41*, 381.
(3) Worsford, D. J.; Bywater, S. *Can. J. Chem.* **1964**, *42*, 2884.
(4) Morèsè-Séguéla, B.; St-Jacques, M.; Renaud, J. B.; Prud'homme, J. *Macromolecules* **1977**, *10*, 431.
(5) Morton, M. *Anionic Polymerization, Principles and Practice*; Academic: New York, 1983.
(6) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623.
(7) Silas, R. S.; Yates, J.; Thorton, V. *Anal. Chem.* **1959**, *31*, 529.
(8) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416.
(9) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825.
(10) Chan, T. H.; Mychajlowskij, W.; Amoroux, R. *Tetrahedron Lett.* **1977**, 1605.
(11) Takenaka, K.; Hirao, A.; Hattori, T.; Nakahama, S. *Macromolecules* **1987**, *20*, 2034.
(12) Tanaka, Y.; Sato, H. *Polymer* **1976**, *17*, 113.
(13) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; pp 79–97.
(14) Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.
(15) Batt, D. G.; Ganem, B. *Tetrahedron Lett.* **1978**, 3323.

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Stoichiometry Effects on Rheology of Model Polyurethanes at the Gel Point

Recent rheological experiments on cross-linking polymers[1–4] lead to a new mechanical definition of the gel point (GP). The network at GP was shown to be characterized by power law stress relaxation and power law dynamic moduli over the entire experimental range. A linear constitutive equation for the stress at GP, the *gel equation*, was formulated[2,4]

$$\tau(t) = S\int_{-\infty}^{t} (t - t')^{-n}\dot{\gamma}(t')\,\mathrm{d}t' \qquad 0 < n < 1 \qquad (1)$$

where τ is the stress tensor, $\dot{\gamma}$ is the rate of deformation tensor, and S and n are two material parameters.

In addition to the newly observed power law behavior, the gel equation also predicts the classical attributes of GP,[5] i.e., infinite steady shear viscosity and zero equilibrium modulus. These commonly used properties are actually poorly suited for determining the gel point since their measurement requires steady-state experiments which cannot be performed near the GP where the relaxation time of the polymer diverges. As a result the GP had to be determined by extrapolation. By contrast, eq 1 predicts a material behavior which can be easily and accurately measured with dynamic mechanical methods. The possible ranges of power law exponent, $0 < n < 1$, and of gel strength, S, allow us to distinguish between different gels.

Surprisingly the stoichiometric ratio, r, of the reactants was found to strongly affect the power law exponent.[4] An exponent value of $n = {}^1/_2$ was measured on a poly(dimethylsiloxane) (PDMS) gel prepared at balanced stoichiometry[1,2] whereas a greater exponent value, $n > {}^1/_2$, was obtained on a PDMS gel with cross-linker deficiency.[4] Three PU gels with *balanced* stoichiometry but with different molecular weight between cross-link points[3] also exhibited the ${}^1/_2$ exponent.

In this study the rheological behavior of PU gels with unbalanced stoichiometry is investigated. The variations of the two material parameters in eq 1, S and n, are followed over the entire range of stoichiometric ratios for which gelation can take place. Our long-term objective is to determine whether eq 1 can be universally used to describe the rheological behavior of cross-linking polymers at the GP. Even though PU and PDMS gels have a different chemistry and a different functionality of the cross-link points, universality principles would require that they respond similarly to variations of the same parameters and especially to variations of the stoichiometry.

Experimental Section. System and Sample Preparation. PU networks were synthesized by end-linking reaction of α,ω-dihydroxypoly(propylene oxide) (PPO) prepolymer with tris(4-isocyanatophenyl) thiophosphate (DRF) cross-linker. Details of the component characterization and of the sample preparation are reported elsewhere.[3,6–8]

In order to avoid the interference of vitrification with gelation and to obtain some reasonably fast reaction rates, PPO1000 was selected as a prepolymer.[3] Its number-average molecular weight and its polydispersity were found to be $M_n = 965$ and $M_w/M_n = 1.007$ as measured by VPO and GPC, respectively. The hydroxyl content was determined by an acetyl chloride titration method. PPO functionality was found to be 1.88. The DRF cross-linker was purified by recrystallization from dry benzene.[8] The isocyanate purity was determined by titration[9] and was found to be 98%.

The stoichiometric ratio, r, of the system is defined here as the initial ratio of isocyanate to hydroxyl groups, [NCO]/[OH]. From Flory's theory of gelation,[5] and assuming an ideal cross-linking process, the PU system is expected to reach gelation for stoichiometric ratios ranging from ${}^1/_2 < r < 2$. The quasi-ideality of this cross-linking reaction at the temperatures of interest (below 90 °C) was verified by showing that the final network with the highest

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