temperature coefficient of $|\eta|$ obtained from eq 2 gives the result

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = (2\alpha_\eta^{\,3}/3)\,\mathrm{d}\ln|\eta|/\mathrm{d}T - {}^2\!/_3(\alpha_\eta^{\,3} - 1)|(2\beta_2 - \beta_1) - ({}^1\!/_2 - \chi_1)^{-1}\,\mathrm{d}\chi_1/\mathrm{d}T| \quad (6)$$

This final equation had the limitation that χ_1 and $\mathrm{d}\chi_1/\mathrm{d}T$ must be known with a reasonably high degree of accuracy. These magnitudes can be obtained from the modified Stockmayer–Fixman equation[15]

$$|\eta|M^{-1/2} = K_\Theta + 0.346\Phi(\bar{v}_2^{\,2}/V_1N_\mathrm{A})(1 - 2\chi_1)\mathrm{M}^{1/2} \quad (7)$$

deduced when eq 3 is used in the original SF work[8] instead of the old equation $\alpha_\eta^{\,3} = 1 + 1.55z$.

For the purpose of evaluating the temperature coefficient of the unperturbed dimension, intrinsic viscosities in cyclohexane at five temperatures were determined for each fraction. The dependence of ln $|\eta|$ on temperature is also shown in Table I.

With the data of intrinsic viscosities and number average molecular weights, eq 7 allows us to obtain χ_1 at different temperatures and consequently $\mathrm{d}\chi_1/\mathrm{d}T$ from the slopes of plots $|\eta|M^{-1/2}$ against $M^{1/2}$. The interaction parameter χ_1 showed a little variation with T and $\mathrm{d}\chi_1/\mathrm{d}T$ was 1.0×10^{-4} K^{-1}.

Finally, α_η is available from eq 3, 4, and 5. We calculated the expansion coefficient at 35 °C as a representative temperature of the considered range. At 35 °C $\chi_1 = 0.222$, $V_1 = 109.9$ cm^3 mol^{-1}, and $\bar{v}_2 = 1.078$ cm^3 g^{-1}. The value of $(\langle r^2\rangle_0/M)^{-3/2} = 1.19 \times 10^{24}$ was taken from the literature.[16]

Substitution of these data in the expression for the temperature coefficient, d ln $\langle r^2\rangle_0/\mathrm{d}T$, gives an average value of $(-1.23 \pm 0.41) \times 10^{-3}$ K^{-1}.

We can compare this result with those obtained by Abe and Flory[3] from a preferred set of configurational energies for PIP chains. The configuration-dependent properties so calculated are largely affected by the location of rotational states such as CH_2–$C(CH_3)$ about the planar trans conformation as a reference. The theoretical value of d ln $\langle r^2\rangle_0/\mathrm{d}T$, calculated for the more realistic location (±70 °C), is between -1.02×10^{-3} and -1.44×10^{-3} for the 100% trans polymer, depending on the configurational energy assumed for the states mentioned above.

As a conclusion, our result is in good agreement with the calculated value, taking into account the composition of our samples. As Flory and Mark[17] pointed out, the viscosity–temperature measurements are reliable methods in obtaining values of the cited coefficient when the solvent–polymer interactions are well considered.

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Star-Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes

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The use of chlorosilanes is well documented[2,3] with regard to the synthesis of star-branched polymers, using anionic polymerization techniques[4-8] and organolithium initiators. The reaction of the silicon–chlorine groups with the carbon–lithium chain end yields a process free from deleterious side reactions. The only potential difficulty encountered is that due to steric hinderance, e.g., it has been reported that poly(styryllithium) will not react completely with silicon tetrachloride[4] or 1,2-bis(dichloromethylsilyl)ethane[6] while poly(isoprenyllithium) fails to react completely with silicon tetrachloride.[9] This latter observation can be rationalized by the fact that the active chain end is known to exist in the 4,1 form in hydrocarbon solvents.[10,11]

Recently, it was reported[12] that 8- and 12-arm polyisoprenes were synthesized using either an octa- or dodecachlorosilane which were synthesized from tetravinylsilane via the hydrosilation reaction involving either methyl dichloro- or trichlorosilane. The Θ temperature behavior, in dioxane, for these materials has been investigated.[13]

We wish to report, in this note, that an extention of the foregoing procedures has led to the synthesis of 18-branch polyisoprene stars, using a specially prepared decaoctachlorosilane.

Experimental Section

The preparation of the linear polyisoprenes was done in cyclohexane, using purified *sec*- or *tert*-butyllithium. The polymerization procedures used are those presented elsewhere. All polymerizations were performed under vacuum conditions.

The decaoctachlorosilane was prepared using the following reactions:

$$Cl_3SiCH_2CH_2SiCl_3 + 6CH_2{=}CHMgBr \rightarrow 6ClMgBr + (CH_2{=}CH)_3SiCH_2CH_2Si(CH{=}CH_2)_3 \quad \mathrm{(I)}$$

$$\mathrm{I} + 6HSiCl_3 \xrightarrow{H_2PlCl_3} (Cl_3SiCH_2CH_2)_3SiCH_2Si(CH_2CH_2SiCl_3)_3 \quad \mathrm{(II)}$$

It should be noted that the hydrosilation reaction generally proceeds in an anti-Markownikoff fashion. Nonetheless, structure II in the above reaction sequence is probably a mixture of isomers due to some addition to the vinyl group in a Markownikoff fashion. This trend was noted for the octa- and dodecachlorosilanes.[12]

The linking reaction was allowed to proceed at ca. 20 °C for approximately 3 weeks. This reaction time was doubtless excessive since it was observed, by gel permeation chromatography, that near complete linking was apparently achieved after 24–40 h, depending on the molecular weight of the arm.[14] Nonetheless, a conservative approach was followed in order to ensure as complete a reaction as possible.

Characterization of the star-shaped polymers and the linear arms was done by a combination of vapor pressure and membrane osmometry as well as light scattering in both dioxane, at $\theta_{A_2} = 0$, and cyclohexane, a good solvent for polyisoprene. The procedures followed have been presented elsewhere.[6-9,12]

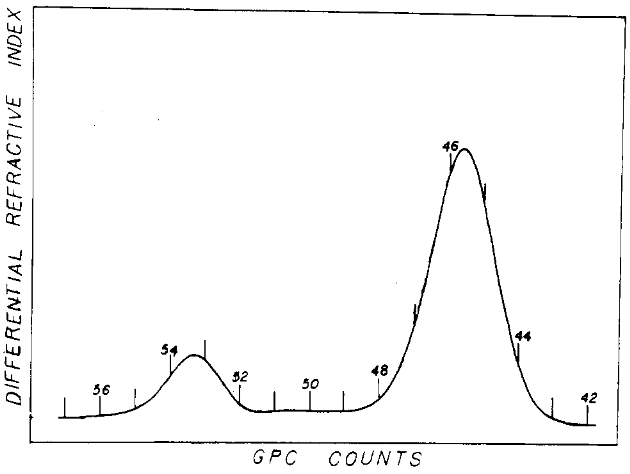

Figure 1. Gel permeation chromatogram of unfractionated star polyisoprene 18-I.

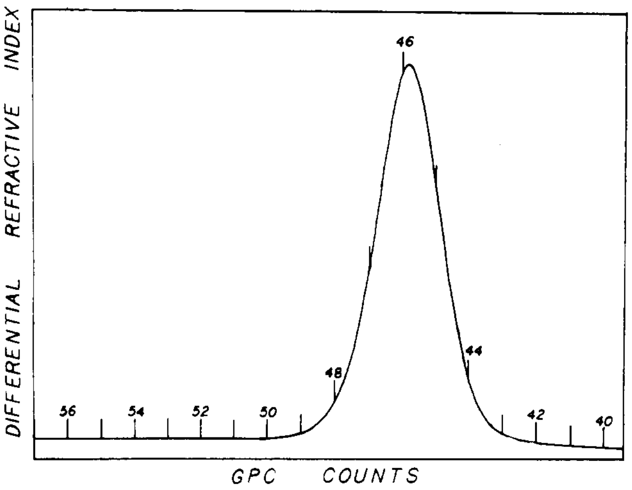

Figure 2. Gel permeation chromatogram of fractionated star polyisoprene 18-IAA.

Supplementary characterization was also done using gel permeation chromatography. A seven-column Styragel set was used with tetrahydrofuran as the carrier solvent at 30 °C.

This column set was calibrated using linear polyisoprene standards synthesized and characterized in our respective laboratories. This calibration was achieved using $^1/_8$ (w/v) solutions. The general characteristics of this seven-column set are available elsewhere.[15,16]

Prior to characterization, the polyisoprenes were fractionated in order to remove linear "parent" material and star-shaped polymer of a low degree of branching. Figure 1 contains gel permeation chromatograms of the unfractionated and the fractionated 18-IAA polyisoprene. There it can be seen that the chlorosilane linking agent contains some lower functional chlorosilane (perhaps the starting material). However, the fractionation process apparently removes virtually all of this lesser branched polyisoprene.

Previously,[12] we advocated the "capping" of poly(isoprenyllithium) chains with several units of butadiene in order to facilitate the reaction with the octa- and dodecachlorosilane compounds. It has been seen on general observation that although the butadienyllithium chain end will react at a faster rate than isoprenyllithium with these chlorosilanes, the *final* degree of branching is the same regardless of the identity of the chain end. Hence, the syntheses of the 18-arm stars were accomplished without the intermediate step of "capping" the isoprenyllithium chains with butadiene.

Results and Discussion

Table I contains the characterization data for the decaocta-star polyisoprenes arms. It can be seen that good agreement was obtained between the osmometric and gel permeation chromatography number-average molecular weights. This agreement was achieved without corrections for column broadening effects. These results are in accord with previous observations[15,16] pertaining to the column arrangement used for this characterization.

Table I
Molecular Weights of Decaocta-Branched Star Polyisoprene Arms

sample	$\overline{M}_n$,[a] 10^{-3} g mol^{-1}	$\overline{M}_n$,[b] 10^{-3} g mol^{-1}	$\overline{M}_w$,[b] 10^{-3} g mol^{-1}	$\overline{M}_z$,[b] 10^{-3} g mol^{-1}
18-I	$18._8$	$18._7$	$19._7$	$20._6$
18-II	$12._0$	$12._4$	$13._1$	$13._8$
18-III	$46._0$	$46._2$	$49._1$	$51._5$
18-VI	$10._7$	$10._7$	$11._2$	$11._6$
18-VII	3.4	3.3	3.6	3.7
18-VIII	5.1	5.2	5.4	5.6

[a] Membrane osmometry; toluene at 37 °C. SαS-08 membranes were used. The molecular weight of 18-VII is from vapor pressure and membrane osmometry. [b] Gel permeation chromatography. Tetrahydrofuran was the solvent at a flow rate of 1 mL min^{-1}. The seven-column set had a porosity range of 2×10^3-5×10^6. The plate count was 1.07×10^3 ppf.

Table II
Molecular Weights of Decaocta-Branched Polyisoprene Stars

sample	$\overline{M}_n$(arm),[a] 10^{-3} g mol^{-1}	$\overline{M}_n$(star),[a] 10^{-5} g mol^{-1}	$\overline{M}_w$(star),[b] 10^{-5} g mol^{-1}	f[c]
18-IAA	$18._8$	3.40	3.44	18.1
18-IIAA	$12._0$	2.16	2.18	18.0
18-IIIAAA	$46._0$		8.00	17.4[d]
18-VIAA	$10._7$	1.93	1.97	18.0
18-VIIA	3.4	0.61_0	0.61_7	17.9
18-VIIIAA	5.1	0.92_0	0.93_0	18.0

[a] Membrane osmometry. [b] Light scattering: average values of measurements done in dioxane (at $\theta_{A_2} = 0$) and cyclohexane (25 °C). The molecular weights obtained from the two solvents differed by no more than 5%. [c] f denotes the degree of branching $\overline{M}_n$(star)/$\overline{M}_n$(arm). [d] $f = \overline{M}_w$(star)/$\overline{M}_n$(arm).

Table II contains the osmometric, where applicable, and the light-scattering molecular weights obtained for these 18-arm polyisoprene stars, along with the degree of branching. It is gratifying to see that this parameter ranges between 17 and 18. Thus, within the limits of experimental error, it has been demonstrated that decaoctapolyisoprene stars can be synthesized having a "near-monodisperse" degree of branching. It should also be noted that the linking reaction will lead to a narrowing of the molecular weight distribution of the polyisoprene stars relative to that observed, via gel permeation chromatography, for the "parent arms". Thus, the combined characterization results indicate that 18-branch polyisoprene stars can be synthesized containing both near-monodisperse degrees of branching and molecular weight distributions. The dilute solution properties of these polymers are being determined.

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A New Estimation of Primary Radical Termination Rate

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In radical polymerization when the initiator concentration is high and/or the monomer concentration is low, a deviation is noticed from the simple expression of the polymerization rate equation

$$R_p = \left(\frac{2fk_d}{\bar{k}_t}\right)^{1/2} k_p[C]^{1/2}[M] \qquad (1)$$

In many papers,[1] such a deviation has been discussed in terms of the concept of primary radical termination. Here, the primary radical termination rate constant is estimated from appropriate approximations of

$$\bar{k}_t[N]^2 = 2fk_d[C]\left\{\frac{(1 - (\bar{k}_{ti}/k_i)([N]/[M]))}{(1 + (\bar{k}_{ti}/k_i)([N]/[M]))}\right\} \qquad (2)$$

Usually, the $\bar{k}_{ti}$ was estimated by application of eq 2 to the kinetic data obtained when [C] was only varied or/and [M] was varied.[1] This means that the $\bar{k}_{ti}$ was calculated as if $\bar{k}_t$ were independent of [C] and [M] although the $\bar{k}_t$ depends on chain length as proposed before,[2] the n being functions of [C] and [M]. In order to treat this dependence, eq 2 was modified by Ito.[3] These modifications show that, if eq 2 was used by assuming that $\bar{k}_t$ was independent of n, the $\bar{k}_{ti}$ should be overestimated. In order to avoid such overestimations, the following two methods were considered. One of them was an estimation of the $\bar{k}_{ti}$ by application of eq 2 to the data obtained by using thiol as a strong transfer agent in order to maintain the condition that n was invariable and therefore that $\bar{k}_t$ was independent of [C] and [M].[4] Recently, this method was doubted on the grounds that the effect of radical transfer to the thiols has not yet been fully understood.[6] The other method was an estimation of $\bar{k}_{ti}$ by using a relationship among [C], [M], R_p, and an average lifetime of radicals, $\bar{k}_t$ being absent from the expression.[5] However, the lifetime was obtained under the condition of nonstationary state, where [N] and $\bar{n}$ were functions of time. Introduction of the lifetime into the stationary state kinetics might yield some error. In the present paper, the $\bar{k}_{ti}$ is estimated by a new relationship among [C], [M], R_p, and $\bar{n}$, where $\bar{k}_t$ is eliminated.

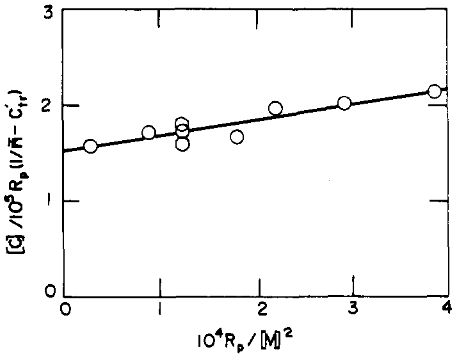

Figure 1. Application of eq 8 to the data[7] in the polymerization of MMA initiated by ABVN at 50 °C in 75% diethyl phthalate.

Theory

The rate equations for the stationary state are:[7]

$$d[R]/dt = 2fk_d[C] - k_i[M][R] - \bar{k}_{ti}[N][R] = 0 \qquad (3)$$

$$d[N]/dt = k_i[M][R] - \bar{k}_{ti}[N][R] - \bar{k}_t[N]^2 = 0 \qquad (4)$$

$$\bar{n} = \frac{k_p[N][M]}{\bar{k}_t[N]^2 + k_{tr}[N][S] + \bar{k}_{ti}[N][R]} \qquad (5)$$

$$R_p = k_p[N][M] \qquad (6)$$

The $\bar{k}_t$ can be eliminated by eq 4 and 5, and we obtain:

$$k_i[M][R] = R_p\left(\frac{1}{\bar{n}} - C_{tr}\frac{[S]}{[M]}\right) \qquad (7)$$

Equations 3, 6, and 7 yield:

$$\frac{[C]}{R_p(1/\bar{n} - C'_{tr})} = \frac{1}{2fk_d}\left(1 + \frac{\bar{k}_{ti}}{k_ik_p}\,\frac{R_p}{[M]^2}\right) \qquad (8)$$

This is independent of any approximation used previously.[1]

Discussion

Equation 8 is applied to the data[7] in the polymerization of methyl methacrylate (MMA) initiated by 2,2′-azobis(2,4-dimethylvaleronitrile) (ABVN) at 50 °C (Figure 1). The values obtained are: $2fk_d = 6.6 \times 10^{-6}$ s^{-1} and $\bar{k}_{ti}/k_ik_p$ = 1090 M s, which is in good agreement with the value of 1420 obtained by using the thiol as a strong transfer agent.[4]

On the application of eq 8 to the data in the polymerization of vinyl acetate (VA) initiated by ABVN[8] at 50 °C (Figure 2), $2fk_d = 7 \times 10^{-6}$ s^{-1} and $\bar{k}_{ti}/k_ik_p$ = 40 000 M s are obtained. The difference between the latter and 68 000 M s obtained[8] by eq 2 is not marked. This means that, as is well known, the VA radicals transfer easily to solvents and therefore this corresponds to the use of a strong transfer agent.[4] Further, the 40 000 is twofold less than 76 000 obtained at very high initiation rates.[9] This is consistent with the hypothesis[3,10] that the $\bar{k}_{ti}$ for reaction between R and small N is larger than that between R and large N, smaller N being formed at a higher initiation rate.

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