dimer species as the chain initiator for **1AS**. It is likely that the solid-state polymerization of all diacetylenes is initiated by a biradical dimer species.

Acknowledgment. The author is grateful to Drs. R. H. Baughman, R. R. Chance, and E. A. Turi for helpful discussions and to Y. P. Khanna for the DSC scans.

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Preparation and Characterization of H-Shaped Polystyrenes[†]

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ABSTRACT: A series of regular H-shaped polystyrenes ranging in molecular weight from 1 × 10^5 to 1.7 × 10^6 has been prepared. Their dilute-solution properties have been determined. They lie between those of regular three- and four-arm star polymers. The unperturbed radius of gyration is smaller by a factor g = 0.70 (g_{th} = 0.712) than that of the linear homologue. For the lower molecular weight H-polystyrenes a small Θ_{A_2} depression is observed. The ratios of the intrinsic viscosities of the H-polystyrenes and the linear polymers, g', are 0.80 and 0.73 in cyclohexane at the Θ temperature and in toluene, respectively. Small but significant deviations from the universal calibration relation log $[\eta]M \propto f(V_e)$ are observed in the exclusion chromatograms of the H-polymers.

Introduction

In order to study the effect of long-chain branching on the properties of polymers well-characterized branched polymers have to be available. For this reason regular star polymers have been prepared and studied.[1,2] Comb polymers consisting of a backbone to which a large number of branches are attached have also been prepared. Although the backbone and the branches are narrow-distribution polymers, the resulting comb polymers are not completely homogeneous in architecture and molecular weight because the placement of the branches along the backbone is by a random process.[3] An attempt has been made to obtain "regular" combs with equidistantly placed branches but the resulting samples were a mixture of comb polymers with an average number of branches.[4] We report now on the synthesis of regular H-shaped polystyrenes with two trifunctional branch points. The five segments that can be distinguished in the H-polymers have approximately equal molecular weights.

Experimental Section

Synthesis. The synthesis of the H-shaped polymers was performed in three steps, using anionic polymerization techniques in evacuated, *n*-BuLi-washed and rinsed vessels. The arms of the H-shaped polymers were prepared in benzene at room temperature, using *sec*-BuLi as the initiator. After the polymerization the living polymer was reacted with CH_3SiCl_3 according to

$$2(\underset{a_1}{\sim\sim\sim StLi}) + CH_3SiCl_3 \rightarrow \underset{a_2}{(\sim\sim\sim St)_2(CH_3)SiCl} + 2LiCl \qquad (1)$$

A small excess of PStLi produced some three-arm star material. The polymer that will constitute the central bridge in (b), H-shaped polymer was prepared separately in a 50/50 mixture of benzene and THF at 0 °C with sodium naphthalenide as the initiator.[5] The molecular weight of this two-ended living polymer, NaSt∼∼∼StNa (b), was matched as closely as possible to that of one arm (a_1).

In the third step the bridge material (polymer b) was slowly added to the arm material (polymer a_2), allowing for complete reaction between successive additions, according to

$$2[\underset{a_2}{(\sim\sim\sim St)_2(CH_3)SiCl}] + NaSt\underset{b}{\sim\sim\sim}StNa \rightarrow (\sim\sim\sim St)_2(CH_3)Si(St\sim\sim\sim St)Si(CH_3)(St\sim\sim\sim)_2 \qquad (2)$$

The second and third steps were executed consecutively and took about 3-4 h.

Presamples were removed from the reactor at various intermediate stages and terminated with $(CH_3)_2CHOH$. This allowed for the independent determination of the molecular weights of the arms (M_a), of the double arm (M_{a_2}), and of the bridge (M_b). It allowed also the monitoring of the course of reactions 1 and 2. The final product was submitted to repeated fractional precipitation. The H-polymer was recovered in the first fraction.

Analysis and Characterization. Polymers and presamples were routinely analyzed by size exclusion chromatography (GPC, Waters 301, equipped with five 4-ft columns of 10^6, 3 × 10^5, 10^5, 10^4, and 10^3 Å). Three-milligram samples were injected in 2 mL of solvent. The flow rate was 1.1 mL/min and the temperature 35 °C. Elution volumes (V_e) were reproducible to within 0.05 count. Either a linear polystyrene standard calibration technique was used to determine the molecular weight and distribution or the GPC was coupled with a low-angle laser light scattering instrument (LALLS, Chromatix KMX-6). THF was the eluting solvent. The dn/dc of polystyrene in THF was found to be 0.190_3 for 633-nm light at 25 °C. The composition of the crude reaction

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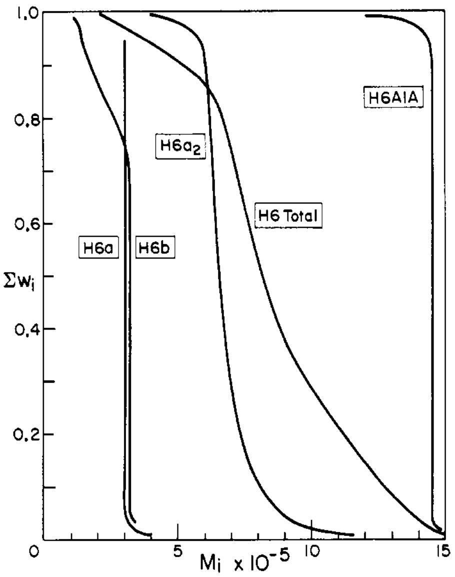

Figure 1. Cumulative molecular weight distribution obtained with the GPC–LALLS instrument during the preparation of an H-shaped polystyrene.

product and of the fractions was analyzed also by sedimentation in a Spinco Model E ultracentrifuge. Cyclohexane at 35 °C was the solvent and the rotor speed was 60 000 rpm. Exact compositions were obtained by extrapolation of the relative areas under the schlieren peaks to zero concentration.

Weight-average molecular weights of the H-polymers were determined by light scattering in cyclohexane and toluene at 35 °C with a Fica 50 instrument using vertically polarized light. The Rayleigh ratio of benzene for the 436-nm wavelength was taken as 50.8×10^{-6} at 35 °C and the dn/dc for the polystyrene is 0.181 mL/g in cyclohexane and 0.114 mL/g in toluene. The radii of gyration were determined as described previously.[6]

Intrinsic viscosities of the samples were measured in semimicro Cannon-Ubbelohde viscometers with solvent flow times larger than 150 s and negligible kinetic energy corrections.

Results

Figure 1 shows typical GPC–LALLS results obtained during the synthesis of an H-shaped polystyrene. Separate GPC injections give the cumulative molecular weight distribution for the arm precursor (a_1) and for its dimeric product (a_2) of reaction 1. The average molecular weight of the latter is 2.28 times that of the arm precursor, indicating the formation of some three-arm star polymer. This is also indicated by the high molecular weight tail in a_2. In Figure 1, the cumulative molecular weight distribution of the bridge material (b) is also shown. This polymer contains about 15% of one-ended material with half the molecular weight. The molecular weight of the two-ended polymer is matched to that of the arm polymer to better than 10%. The numerical data are given in the second and third columns of Table I. The molecular weight distribution of the product of reaction 2 is also shown in Figure 1. A large increase in the high molecular weight tail is evident. It can also be seen that the fractionated H-polymer has a narrow distribution and its molecular weight is approximately equal to $4(M_w)_a + (M_w)_b$.

Table I
Molecular Weight Data for H-Polystyrenes

	precursor[a]		H-polystyrene		
sample	$M_a \times 10^{-5}$	$M_b \times 10^{-5}$	$M_{calcd} \times 10^{-5}$ [b]	$M_{calcd} \times 10^{-5}$ [c]	$M_w \times 10^{-5}$ [d]
H4A1A	0.19_3	0.19	0.96	1.0_4	1.11
H2A1	0.46	0.44	2.3	2.3_5	2.37
H1A1	1.03	1.00	5.1	5.0	4.83
H3A1A	1.32	1.23	6.5	6.6_5	6.7_4
H5A1	2.05	2.04	10.2	10.4	10.4
H6A1A	3.24	3.55	16.5	15.6	16.9

[a] By GPC. [b] $M_{calcd} = 4(M_w)_a + (M_w)_b$. [c] From the stoichiometry of monomer and initiator charged. [d] Light scattering in cyclohexane.

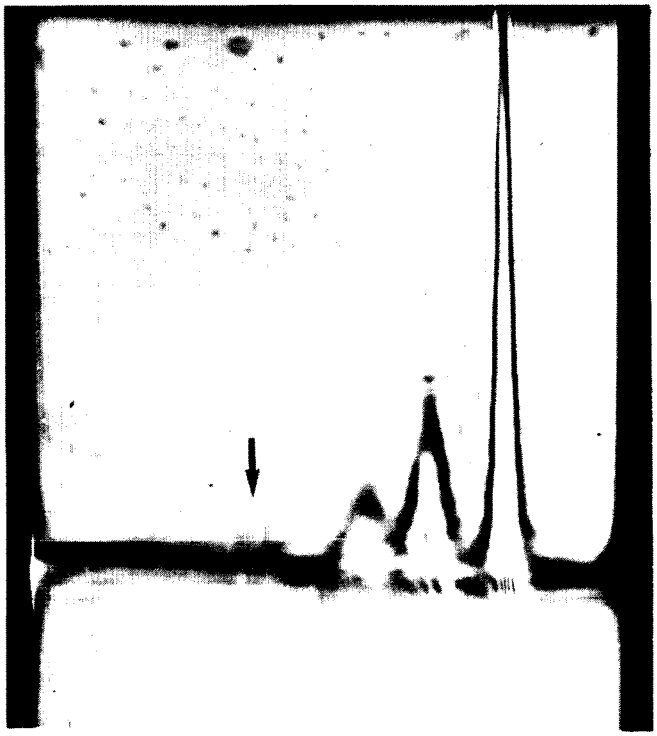

Figure 2. Ultracentrifugation sedimentation of the crude product obtained in the preparation of the H3 polystyrene. From left to right: one-arm precursor (arrow), two-arm precursor, three-arm star, and H-shaped polymer.

Further evidence for the formation of H-shaped polystyrene is obtained from the ultracentrifuge sedimentation pattern of the product of reaction 2 shown in Figure 2. Four sedimenting bands can be distinguished. From left to right one observes a trace of monomeric arm material (indicated by the arrow), the dimeric product of reaction 1, a three-arm star polymer, and the fastest moving H-shaped polymer. The three-arm star polymer may consist of two species: the byproduct of reaction 1 and the product of the reaction of a_2 with one-ended poly(styrylsodium). The latter will have a molecular weight approximately equal to 2.5 times $(M_w)_a$ and is not expected to separate from the other three-arm star. The assignment is corroborated by evaluation of the *apparent* sedimentation coefficients at the beginning of the sedimentation run. The observed ratios of the sedimentation coefficients for the four bands are $1.0{:}1.4_5{:}1.7{:}2.1$ and correspond roughly to $\sqrt{1}{:}\sqrt{2}{:}\sqrt{3}{:}\sqrt{5}$, which are expected in a Θ solvent where $S_0^0 = KM^{1/2}$. A further refinement of the identification cannot be made since the sedimentation coefficients increase slightly with the branch structure[7] but decreases as the polymer is sedimented further in the cell. Also, the different species sediment at different total concentrations and their sedimentation coefficients have different concentration dependencies.

Ultracentrifuge bands of the H-shaped samples shown in Figure 3 indicate that the fractionated polymers have narrow distributions. Ultracentrifugation sedimentation patterns are very convenient for the detection of low molecular weight contaminants due to the Johnston–Ogston effect.[8] The small traces of three-arm star polymer ob-

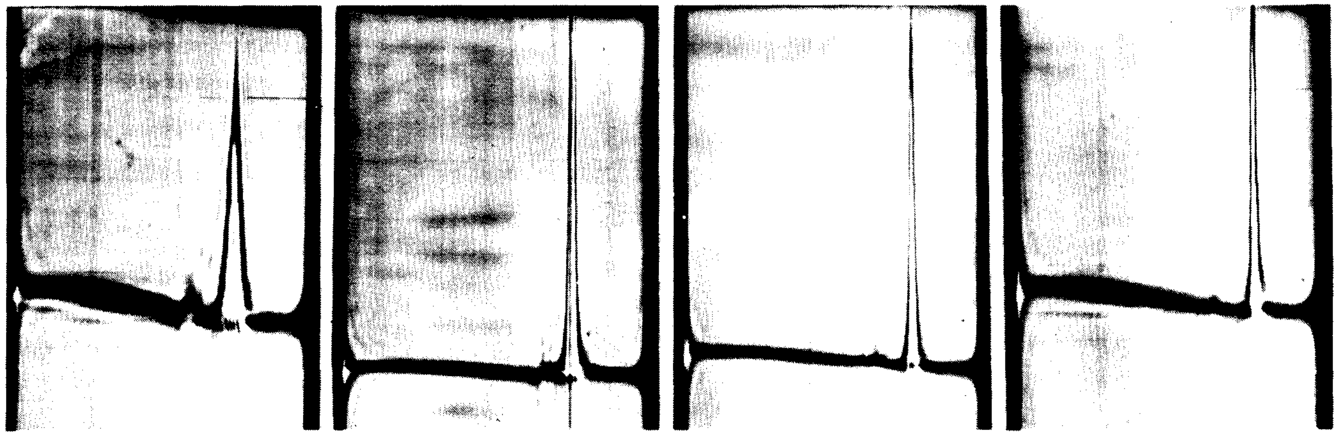

Figure 3. Ultracentrifugation sedimentation of the fractionated H-shaped polystyrenes. From left to right: H1A1, H3A1A, H5A1, and H6A1A.

Table II
Dilute-Solution Properties of H-Polystyrenes

	cyclohexane				toluene			
sample	$M_w \times 10^{-5}$	Θ_{A_2}, °C	$(\Theta_{A_2})_{\text{calcd}}$, °C	$\langle S^2\rangle_{0,z} \times 10^{-4}$, Å^2	$M_w \times 10^{-5}$	A_2, (cm^3 mol)/g^2	$\langle S_2\rangle_{0,z} \times 10^{-4}$, Å^2	Ψ
H4A1A	1.11	31.0	31.7					
H2A1	2.37	32.6	32.6					
H1A1	4.83	(34.0)	33.3	(2.6_5)	4.8_2	2.9_5	0.50	0.46
H3A1A	6.74	*a*		3.6	6.8_2	2.6_4	0.74	0.45
H5A1	10.4	*a*		5.8	10.5	2.4_0	13.0	0.42
H6A1A	16.9	*a*		9.2	17.2	2.1_0	23.7	0.40

[a] $A_2 = 0$ at 34.6 °C.

servable in the sedimentation patterns represent less than 1% of the total polymer. Such small amounts cannot be detected and identified by GPC.

The molecular characteristics of the H-shaped polymers are summarized in Table I. The weight-average molecular weights of the H-shaped polymers agree well with those expected from the method of their synthesis, i.e., $(M_w)_H = 4(M_w)_a + (M_w)_b$. Table II summarizes data on the radii of gyration of the large H-polymers in cyclohexane and toluene. An example of the intramolecular scattering curves from which the radii of gyration are derived is shown in Figure 4. Table II also gives the second virial coefficients measured on dilute solutions of the H-polymers. The low molecular weight H-shaped polymers show positive second virial coefficients (A_2) at the Flory Θ temperature for linear polystyrene in cyclohexane (34.5 °C). As a consequence, the temperature at which A_2 becomes zero, Θ_{A_2}, is lower than for linear polymers. In Table III the measured intrinsic viscosities of the polymers are collected. They can be represented by

$$[\eta] = 6.65 \times 10^{-4} M_w^{0.50}$$

in cyclohexane at 35 °C and

$$[\eta] = 7.47 \times 10^{-4} M_w^{0.73}$$

in toluene at 35 °C. A comparison with the intrinsic viscosities of linear polystyrenes is made in Figure 5.

The delay of the elution from the GPC of the H-shaped polymers relative to linear polystyrenes is shown in Figure 6. This is a consequence of the branched structure of the H-polymers. These data are discussed in terms of the universal calibration hypothesis[9] at the end of the next section.

Discussion

The synthesis of the H-shaped polystyrenes is based on two experimental observations. The first is that the substitution of multifunctional chlorosilanes by living polymer ends occurs in consecutive reactions of which the first two are much faster than subsequent reactions.[10] This makes possible the synthesis of a linear polymer with a central

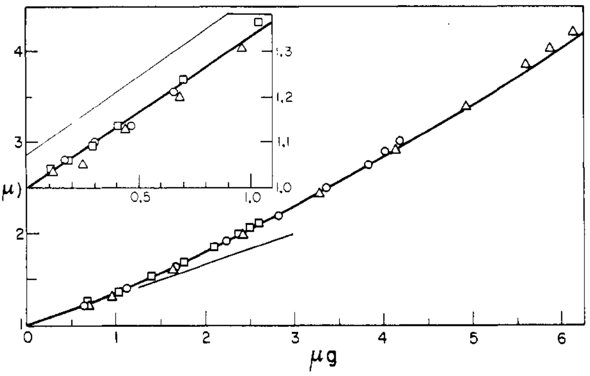

Figure 4. Intramolecular scattering curve obtained for H6A1A in toluene at 35 °C. The insert is an enlargement of the range $0 < \mu g < 1$. (△) 365 nm; (○) 436 nm; (□) 546 nm. The theoretical line is obtained with $\langle S^2\rangle = 2.37 \times 10^5$ Å^2.

Table III
Intrinsic Viscosities of H-Polystyrenes

		[η], dL/g	
sample	$M_w \times 10^{-5}$	cyclohexane 35 °C	toluene 35 °C
H4A1A	1.11	0.21_8[a]	0.35_4
H2A1	2.37	0.31_8[b]	0.62_2
H1A1	4.83	0.45_6	1.04_8
H3A1A	6.74	0.54_5	1.33_5
H5A1	10.4	0.68_7	1.87
H6A1A	16.9	0.88_9	2.67

[a] 0.21_4 at $\Theta_{A_2} = 31.0$ °C. [b] 0.31_3 at 32.6 °C.

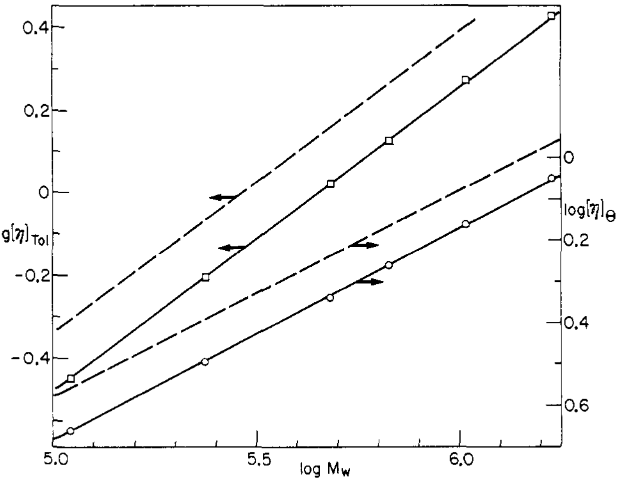

Figure 5. Intrinsic viscosity-weight-average molecular weight relation for the H-shaped polystyrene. The broken lines are for linear polystyrene. Top, toluene at 35 °C; bottom; cyclohexane at 35 °C.

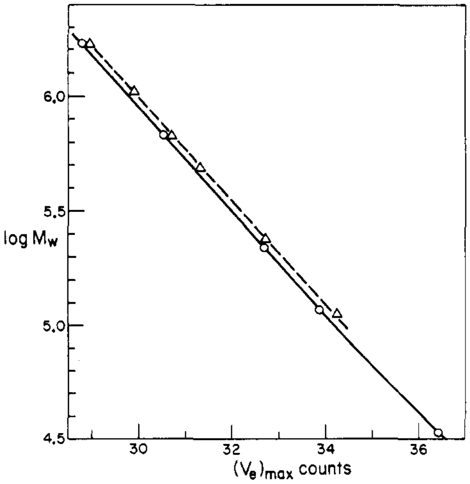

Figure 6. Molecular weight-GPC elution volume relation for linear (○) and H-shaped (△) polystyrenes.

Si-Cl as shown in reaction 1. The second observation is that the rate of substitution of Si–Cl bonds by living ends is much enhanced in the presence of THF.[11] Advantage of this phenomenon is taken in reaction 2. Nevertheless, the preparation of very high molecular weight H-polystyrene occurred only in low yields, indicating that the rate of the final polymer–polymer reaction is dependent on the molecular weight of the polymers.

The yield of the H-polymer cannot be quantitative because a small excess of PStLi has to be used in reaction 1. Failure to do so would lead to the condensation of dichlorosilane containing polymer with bifunctional poly(styrylsodium) during reaction 2 and, as a result, to higher molecular weight polymers of unknown structure.

The molecular weights of the H-polystyrenes compare favorably with the molecular weights expected on the basis of the reactions and attest to the success of the synthesis. In the following discussion the effect on the small differences between $(M_w)_a$ and $(M_w)_b$ on the properties of the H-polystyrenes are considered to be within the experimental uncertainty of the measurements.

The primary property of any branched polymer is its unperturbed radius of gyration, $\langle S^2\rangle_0$. Values of $\langle S^2\rangle_0$ are given in Table II. The ratio, g, of the radius of gyration of a branched polymer to that of the linear polymer of the same molecular weight can be calculated from the architecture of the branched polymer and the assumption of the random walk model for the subchains.[12] For regular comb polymers[13]

$$g_{\mathrm{th}} = \frac{\langle S^2\rangle_{0,\mathrm{br}}}{\langle S^2\rangle_{0,\mathrm{lin}}} =$$

$$\lambda - \frac{1}{p+1}\lambda^2(1-\lambda) + \frac{2\lambda}{p}(1-\lambda)^2 + \frac{3p-2}{p^2}(1-\lambda)^3$$

and in the case of a regular H-shaped polymer with p, the number of branches, equal to 2, and λ, the fraction of the polymer in the backbone, equal to $^3/_5$, $g_{\mathrm{th}} = 0.712$. From the data in Table II it is found that for H-shaped polystyrenes in cyclohexane at the Θ temperature $\langle S^2\rangle_{0,\mathrm{br}}/M = 5.5 \times 10^{-18}$ [(cm^2 mol)/g]. The literature values of $\langle S^2\rangle_{0,\mathrm{lin}}/M$ vary between 7.6×10^{-18} [14] and 8.2×10^{-18}.[15] Using our value of 7.9×10^{-18} for linear polystyrene[16] we find $g = 0.69_6$ for the H-polystyrenes, in fair agreement with the theoretical value. Similar agreement was found for four- and six-arm polymers[10,16] and is typical of lightly branched polymers.

The radii of the H-polystyrenes in toluene are given by $\langle S^2\rangle = 5 \times 10^{-19}M^{1.23}$, compared to $\langle S^2\rangle_{\mathrm{lin}} = 1.66 \times 10^{-18}M^{1.17}$ for linear polystyrene.[3] The high exponent for the H-polystyrenes is almost certainly due to experimental errors. In the range of molecular weights available for $\langle S^2\rangle$ measurements, the average value of g is 0.69 ± 0.02 in toluene, practically unchanged from the value in the Θ solvent. This was also observed for star[10,16] and comb[17] polystyrenes.

The theoretical intramolecular scattering function for regular H-shaped polymers is given by[13]

$$P(\mu) = (2/\mu^2)\{\mu - (1 - e^{-\mu\lambda}) + (1 - e^{-\mu(1-\lambda)/2}) \times [2 - 2(e^{-\mu\lambda/3} + e^{-2\mu\lambda/3})] + (1 - e^{-\mu(1-\lambda)/2})^2 e^{-\mu\lambda/3}\}$$

where $\mu = \langle S^2\rangle[(4\pi/\lambda')\sin(\theta/2)]^2$, with θ the scattering angle and λ' the wavelength of the light in the medium. The experimental scattering functions (e.g., Figure 4) follow the theoretical one well over the range of μ covered by the light scattering measurements, indicating that the branch structure has not caused any major deviations from the random flight statistics for the larger intersegmental distances in the polymer coils.[6]

The Θ_{A_2} temperatures of the H-polystyrenes, which are lower than the Flory Θ temperature of linear polymers, can be rationalized by increased triple-contact interactions in branched polymers.[17] Accordingly, Θ_{A_2} is given by

$$\frac{\Theta}{\Theta_{A_2}} - 1 = \frac{3^{3/2}}{2^4}\,\frac{C'_{\mathrm{M,l}}(^1\!/_3 - \chi_2)}{C_{\mathrm{M,l}}\Psi_1}\,\frac{H(K')}{M^{1/2}\alpha^3 g^{3/2}}$$

where Θ is the Flory Θ temperature (34.5 °C), $C'_{\mathrm{M,l}}$ and $C_{\mathrm{M,l}}$ are molecular constants of the polymer and solvent, Ψ_1 is the entropy parameter, and α is the chain expansion at Θ_{A_2}. In the function $H(K')$ (given in ref 17) K' depends on α and $^1/_3 - \chi_2$. The triple-contact term $^1/_3 - \chi_2 = 0.045$ was obtained previously from the Θ-temperature depressions of four- and six-arm polystyrenes[16] and the α_Θ of comb polystyrenes[3] in cyclohexane. The Θ_{A_2} temperatures for the H-polystyrenes calculated with $^1/_3 - \chi_2 = 0.045$ are given in Table II. The calculated and observed temperatures agree satisfactorily.

The branched nature of a polymer can be well assessed by the value of Ψ

$$\Psi = A_2M^2/4\pi^{3/2}N_A\langle S^2\rangle^{3/2}$$

where N_A is Avogadro's number and Ψ is a measure of noninterpenetration of the polymer coils.[18] For linear polymers in a good solvent $\Psi \approx 0.25$ in the limit of high molecular weight. For star-branched polymers, values of Ψ increase with the number of branches.[2] Also, in combs values of Ψ are substantially higher than for linear polymers.[3] The values of Ψ for the H-polymers are given in Table II. As expected from the branch structure, the average value, 0.43, is somewhat smaller than 0.53 observed in four-arm polystyrenes.[2]

The intrinsic viscosities of the H-polystyrenes are compared with those of linear polystyrenes in Figure 5. The ratio of the intrinsic viscosity of an H-polymer to that of the linear homologue, $g' = [\eta]_{br}/[\eta]_{lin}$, is 0.80 in cyclohexane and 0.73 in toluene, based on $[\eta]_{lin} = 8.3 \times 10^{-4} M_w^{0.5}$ for polystyrene in cyclohexane and $[\eta]_{lin} = 1.02 \times 10^{-4} M_w^{0.73}$ in toluene.[10]

In a relation between g' and g_{th} of the form

$$g' = g_{th}^{m}$$

$m = 0.65$ and 0.92 for the Θ-solvent and toluene data, respectively. These values of m for the H polystyrenes are different from the proposed approximation $m = {}^1/_2$.[19] It was observed that for star polymers in a Θ solvent $m = 0.58$ and this seems also the lower limit for starlike comb polymers with many long branches.[3] The values of m for the H-shaped polymers fall between that of the regular star polymers and that of heterogeneous combs with many branches, for which $m \approx 1$ at $g_{th} = 0.712$.[3] In general, m depends on the structure of the branch polymer as well as on the value of its g_{th}. Notice also that $g'_{Tol} < g'_{\Theta}$ observed for the H-polystyrenes was also found in star polystyrenes.[10,16]

In Figure 6 the molecular weight is plotted logarithmically against the maximum in the elution volume (V_e). Based on the universal calibration concept $([\eta]M_w)_{V_e}$ = constant[9]

$$[(M_w)_{lin}/(M_w)_{br}]_{V_e}{}^{1+a} = g'_{GPC}$$

Since THF is an equally good solvent for polystyrene as toluene, $a = 0.73$ is taken.[20] In the case of the H-polystyrenes $g'_{GPC} = 0.88 \pm 0.02$. This *apparent* ratio of intrinsic viscosities is quite different from that obtained in the good solvent toluene. Similar $g'_{GPC} > g'$ have also been observed for star-branched polymers when toluene was the eluting solvent,[11] and it was found not to be caused by different V_e-concentration dependences for linear and lightly branched polymers. Caution seems therefore required when deducing the polymer branch structure from GPC elution volumes with the aid of the universal calibration principle.

In conclusion, it has been been shown that H-shaped polystyrenes of good quality can be prepared. Their dilute-solution properties resemble those of star-branched polymers. We hope to report on the rheological properties of the H-polystyrenes in another paper.

Acknowledgment. We thank Professor L. J. Fetters for a generous gift of CH_3SiCl_3.

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Salt Linkage Formation of Poly(diallyldimethylammonium chloride) with Acidic Groups in the Polyion Complex between Human Carboxyhemoglobin and Potassium Poly(vinyl alcohol) Sulfate

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ABSTRACT: The salt linkage formation of poly(diallyldimethylammonium chloride) (PDDA) with the acidic groups (carboxyl, mercapto, and phenolic OH groups) in the polyion complex formed stoichiometrically from human carboxyhemoglobin (Hb) and potassium poly(vinyl alcohol) sulfate (KPVS) was investigated by means of colloid titration. The carboxyl group stoichiometrically forms a salt linkage with PDDA ion in the neighborhood of pH 7.7. In the pH range above 12, the PDDA ion binds not only to all of the acidic groups but also to the $^{-}OSO_3$ group which results from the cleavage of the salt linkage between the basic groups and KPVS ions in the KPVS–Hb complex.

Colloid titration is a useful method for obtaining information about the stoichiometry of the salt linkage formation between the ionizable groups in oppositely charged polyelectrolytes.[1,2] Previously we studied the colloid titration of human carboxyhemoglobin (Hb) with potassium poly(vinyl alcohol) sulfate (KPVS) and reported that three kinds of basic groups in Hb, i.e., amino, imidazolyl, and guanidyl groups, stoichiometrically form salt

0024-9297/81/2214-1178$01.25/0