***m*- and *p*-(*N*-Carbazyl)methylstyrenes (6 and 7).** This reaction was carried out by the same procedure as for preparation of **3**[1] using a nominal 60/40 mixture of *m*- and *p*-vinylbenzyl chlorides (**4** and **5**) (Dow experimental monomer XD19152). The reaction mixture was poured into water. Fractional recrystallizations from ethanol led to 29% of the less soluble isomer **6** as fine colorless needles, mp 174.0–174.5 °C. Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.65; H, 6.06; N, 5.08. NMR ($CDCl_3$)δ: 5.05–5.88 (m, 2 H, $=CH_2$), 5.45 (s, 2 H, N—CH_2), 6.4–6.8 (m, 1 H, CH=), 7.0–7.5 (m, 10 H, arom), 8.1–8.2 (m, 2 H, H_4, H_5). IR: 1910 (para-disubstituted benzene[2]), 820 (para-disubstituted benzene[2]), 735 (ortho-disubstituted benzene[2]). UV (CH_3OH): 341 (4.33), 327 (3.69), 317 sh (2.4), 293 (17.9), 287 (12.4), 282 sh (11.1), 258 (32.9), 246 sh (41.2), 236 (53.2).

The more soluble isomer **6** was obtained in 64% yield as nearly colorless stout needles (*n*-hexane), mp 66.5–68.0. Anal. Calcd. for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.11; H, 6.02; N, 4.97. NMR ($CDCl_3$)δ: 4.95–5.65 (m, 2, H, $=CH_2$), 5.18 (s, 2 H, N–CH_2), 6.25–6.8 (m, 1 H, CH=), 6.9–7.5 (m, 10 H, arom), 7.95–8.15 (m, 2 H, H_4, H_5). IR: 1890 (meta-disubstituted benzene[2]), 797, 882 (meta-disubstituted benzene[2]), 735 (ortho-disubstituted benzene[2]). UV (CH_3OH): 341 (4.40), 327 (3.73), 317 sh (2.3), 293 (19.9), 287 sh (11.7), 282 sh (9.83), 258 (2.81), 241 sh (29.2), 236 (41.8).

***p*-(*N*-Phthalimido)methylstyrene (8).** Reaction to 60:40 mixture of **4** and **5** (Dow Chemical Co.) and phthalimide using K_2CO_3/DMF as in the analogous polymer reaction[1] led to a 52% yield of a crude solid. Four recrystallizations from ethanol gave **8** as colorless fluffy crystals, mp 99.0–100.0 °C. Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.52; H, 5.02; N, 5.26. NMR ($CDCl_3$) δ: 4.75 (s, 2 H, NCH_2), 5.03–5.80 (m, 2 H, $=CH_2$), 6.37–6.85 (m, 1 H, CH=), 7.13–7.80 (m, 8 H, arom). IR: 832 (para-disubstituted benzene[2]), 739 (ortho-disubstituted benzene[2]), 1705, 1760 (C=O). The meta isomer present in the product mixture was more soluble and lower melting (~60 °C); it was not isolated in a pure state. IR: 760, 819, 850 (meta-disubstituted benzene[2]), 832 (weaker, para-disubstituted benzene[2]), 739 (ortho-disubstituted benzene[2]), 1710, 1760 (C=O).

Polymerization of Vinyl Monomers. A solution of 3.5 mmol of monomer(s) and 12 ml of dry benzene was purged with dry nitrogen for 20 min. Then 7 mg (0.04 mmol) of AIBN in 2.5 ml of dry benzene was added. The solution was refluxed for 16 h under dry nitrogen and then added dropwise to 200 ml of rapidly stirred methanol. The polymer was isolated by filtration, weighed to give conversion, and purified by three more precipitations from THF into methanol. From the original methanol filtrate unreacted monomer(s) was (were) recovered.

Poly[*m*-(*N*-carbazyl)methylstyrene] (9). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05. Found: C, 88.23; H, 5.82. IR: 885 (meta-disubstituted benzene[2]), 1625 (weak, C=C). UV (THF): 344 (4.61), 330 (4.16), 318 sh (2.76), 295 (16.5), 290 sh (11.3), 284 (9.71), 262 (19.6), 246 sh (26.9), 237 (40.8), 230 (39.2). GPC: $\overline{M}_n = 11.0 \times 10^3$, $\overline{M}_w = 19.4 \times 10^3$, MWD = 1.75.

Poly[*p*-(*N*-carbazyl)methylstyrene] (10). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05. Found: C, 89.01; H, 6.01. IR: 800, 990, 1010 (para-disubstituted benzene[2]), 1415 (?), 1618 (weak, C=C). UV (THF): 344 (4.53), 330 (4.02), 318 sh (2.76), 275 (16.0), 290 sh (11.1), 284 sh (9.24), 262 (19.7), 246 sh (27.4), 237 (41.2), 230 (44.4). GPC: $\overline{M}_n = 9.69 \times 10^3$, $\overline{M}_w = 24.4 \times 10^3$, MWD = 2.51.

Poly[*p*-(*N*-phthalimido)methylstyrene] (11). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98. Found: C, 77.28; H, 4.93. IR: 1710, 1770 (C=O). UV (THF): 300 sh (1.82), 293 (2.03), 253 sh (1.66), 240 sh (11.1). GPC: $\overline{M}_n = 8.63 \times 10^3$, $\overline{M}_w = 14.4 \times 10^3$, MWD = 1.70.

Poly[*p*-(*N*-carbazyl)methylstyrene-*co*-*p*-(*N*-phthalimido)methylstyrene] (12). Anal. Calcd for $C_{21}H_{17}N \cdot C_{17}H_{13}NO_2$: C, 83.49; H, 5.53; N, 5.12. Found: C, 82.97; H, 5.24; N, 5.05. IR: 1710, 1770 (C=O). UV (THF, ϵ based on carbazole): 344 (4.93), 330 (4.70), 318 sh (3.79). GPC: $\overline{M}_n = 7.28 \times 10^3$, $\overline{M}_w = 15.1 \times 10^3$, MWD = 2.03.

References and Notes

(1) H. W. Gibson and F. C. Bailey, *Macromolecules*, **9**, 688 (1976).
(2) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962, pp 24–27.
(3) W. W. Limburg and D. A. Seanor, U.S. Patent 3 877 936, assigned to Xerox Corp.

Synthesis and Characterization of Poly(styrene-*g*-isoprene) Copolymers

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ABSTRACT: Poly(styrene-*g*-isoprene) copolymers have been prepared by a modification of the standard chloromethylation process. The active CH_2Cl sites on the backbone were converted to $CH_2OSi(CH_3)_2Cl$ groups before coupling with polyisoprenyllithium. More quantitative coupling is obtained in this way. The graft copolymers produced were studied in solution in several solvents by light scattering and intrinsic viscosity techniques. It was found that such graft copolymers have a much less segregated structure in solution than do the corresponding two-block copolymers. The changes in intrinsic viscosity produced by adding side chains of increasing length can be roughly predicted in terms of a compositional and a branching effect.

Despite the many efforts that have been put into the preparation of well-characterized, homogeneous, narrow molecular weight distribution comb polymers, a completely satisfactory method has not yet been developed. A detailed study of the effect of branching on physical properties requires, if possible, a quantitative coupling reaction. In this way, a series of polymers of varying branch length with a constant number of branches on a given backbone can be prepared. The series can be completed if necessary by repetitions using different backbones. Most workers have recognized that the direct coupling of polystyrylpotassium with chloromethylated polystyrene gives the best results. However, the substitution reaction is accompanied by backbone–backbone coupling as a result of metal–halogen exchange, leading to comb polymers of higher than the theoretical molecular weight. At the same time, incomplete substitution produces less than the theoretical number of branches in these combs.[2–4] In order to attain the objectives outlined above and to increase the probability of obtaining more homogeneous products, both difficulties have to be overcome. The reaction of low molecular weight chlorosilane compounds with polystyryllithium and polyisoprenyllithium is known to produce regular star-branched polymers without complicating side reactions.[5–7] The same reaction has been applied to the preparation of comb polystyrenes[8] with less success. No satisfactory explanation could be given for the fact that only about 70–80% of the theoretical number of branches was found in the comb polymers. In addition, the molecular weight distributions of the graft copolymers were wider than is desirable. This was only partly caused by starting from backbone poly-

Table I
Characteristics of Backbone Polystyrenes

Sample	10^{-6} M_w[a]	wt % chlorine[b]	wt % benzyl acetate[c]	p(Cl)	p(acetyl)
P3	0.41_8	0.20	0.86_2	23	24.1
P4	0.81_7	0.14	0.65_5	32	35.7

[a] Before modification. [b] After chloromethylation. [c] After acetylation.

Table II
Refractive Index Increments for Polystyrene and Polyisoprene at 35° and 4358 Å

Solvent	Polystyrene	Polyisoprene
Chlorobenzene	+0.084	−0.004
Bromoform[a]	+0.010	−0.082
Tetrahydrofuran	+0.208	+0.148
Cyclohexane	+0.181	+0.117

[a] At 5460 Å.

mers which were fractions of a styrene–vinyl acetate copolymer produced by free-radical polymerization and hence slightly polydisperse. The same basic method has now been substantially improved for the synthesis of poly(styrene-*g*-isoprene) copolymers.[9] The backbone material is an anionically prepared narrow molecular weight distribution polystyrene which is modified to contain a known number of chlorosilane groups. Analysis of the weight fraction of polystyrene in the graft copolymers allows an independent evaluation of the branching efficiency not available in ordinary comb polymers.

Experimental Section

(a) Preparation and Modification of the Backbone Polystyrene. Narrow molecular weight distribution polystyrenes were prepared under vacuum in benzene using *sec*-butyllithium as the initiator.[10] Gel permeation chromatography (GPC) of the polymers indicates $M_w/M_n < 1.05$. Their molecular weights are given in Table I.

Chloromethylation. Following the work of Pepper[11] and Candau,[12] typically 10 g of polystyrene was dissolved in 250 mL of CCl_4. To the solution 20 mL of chloromethyl methyl ether and 0.75 mL of $SnCl_4$ was added and the mixture was stirred at room temperature. The degree of chloromethylation is determined by the reaction time. The chlorine content in the polymers was determined by x-ray fluorescence (Table I).

Acetylation. The classical method for acetylating chloromethylated polystyrene[13] was replaced by a modification of the work of Liotta.[14] Chloromethylated polystyrene (10 g) was dissolved in 200 mL of benzene–acetonitrile (50/50 v/v) and 5 g of vacuum dried (110 °C) CH_3COOK and 800 mg of dicyclohexyl-18-crown-6 (Aldrich) were added. The reaction is complete after stirring for 24 h at 70–75 °C. The acetate content (Table I) of the polymers was determined from the C=O IR absorption band at 1730 cm^{-1}. Benzyl acetate was used for calibration.

Hydrolysis. To 10 g of acetylated polystyrene in 200 mL of dioxane, water was added to just keep the polymer in solution. NaOH (8 g) was then added and the mixture was stirred for 3 days at 40 °C.[15] The polymer was precipitated in water, acidified, redissolved in benzene, precipitated in methanol, and thoroughly dried under high vacuum. The absence of acetate groups was checked by means of IR.

Chlorosilylation. The subsequent chlorosilylation was performed under high vacuum as described.[8] The hydroxymethylated polystyrene was dissolved to form a 2–3% solution in benzene. Degassed dichlorodimethylsilane (Eastman) in 100-fold excess over hydroxyl groups was added, and after mixing an equivalent amount of CaH_2 dried and degassed pyridine was immediately added. The reaction mixture was left for 3 h and the polymer was freeze dried. The freeze drying was repeated once with fresh benzene. The filtration previously performed[8] was deleted as it was found that pyridinium chloride sublimes easily during freeze drying. The dry polymer was stored at −20 °C until required.

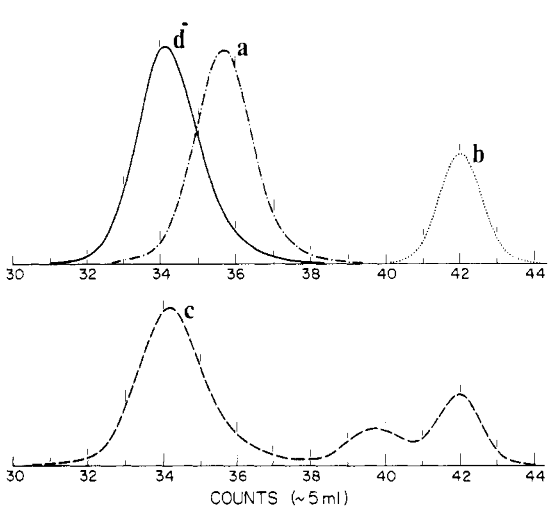

Figure 1. GPC diagrams of (a) polystyrene backbone, (b) polyisoprene side chain, (c) product of the grafting reaction, (d) fractionated product of the grafting reaction.

(b) Preparation of Poly(styrene-*g*-isoprene) Copolymers. Polyisoprenyllithium was prepared in benzene with s-BuLi.[10] A sample was removed for the molecular weight characterization of the individual branch. A fraction of the benzene was distilled from the polyisoprenyllithium on to the chlorosilylated polystyrene. After the latter had dissolved, the solution was added dropwise to the polyisoprenyllithium solution under vigorous stirring. Initially the concentration of polyisoprenyllithium (UV absorption at 290 nm) decreased rapidly, but a further slow decrease was observed for about 5 days. Excess polyisoprenyllithium was then terminated with methanol.

The polymer was immediately subjected to fractionation in the presence of 0.02% (w/v) 2,6-di-*tert*-butyl-4-methylphenol. First, methanol was added to the dilute benzene solution until a faint cloudiness developed at 35 °C. The temperature was then gradually lowered until the supernatant contained branch polyisoprene only. The total supernatant was then removed and the precipitated graft copolymer was redissolved in benzene and fractionally precipitated.

(c) Measurements of Physical Properties. The various stages of the poly(styrene-*g*-isoprene) copolymer preparation were monitored by GPC. A waters 301 instrument equipped with eight 3-ft columns of 3×10^6, 5×10^5, 6.5×10^4, 2.5×10^4, 8.5×10^3, 2.5×10^3, 500, and 60 Å was used. Toluene at 35 °C was the eluent. Osmotic molecular weights were determined on a Mechrolab 503 osmometer in toluene at 35 °C. Light scattering measurements were made with a Fica 50 photogoniometer at 436 nm. Vertically polarized light was used; the Rayleigh ratio of benzene at 35 °C was taken as $R_{90} = 50.79 \times 10^{-6}$ at 436 nm. Refractive indices were calculated from the styrene analysis and the values for the pure polymers (Table II).[16] The polystyrene content of the polymers was measured spectrophotometrically at 269 and 262 nm according to the method of Meehan.[17]

The purification of solvents for solution property measurements has been adequately described in previous publications from this laboratory[16] except for bromoform. This was washed with water, dried over K_2CO_3, and fractionally distilled at 10 mm of pressure taking a middle cut. Diphenylamine (0.01%) was added as stabilizer. It was found essential to protect the solutions from normal laboratory illumination at all times. As little as 10 min exposure would cause a yellow-brown coloration. The light scattering measurements in bromoform alone were made at a wavelength of 546 nm (R_{90}(benzene) = 17.9×10^{-6}).

Results

Figure 1 shows the GPC pattern of a typical product together with those of the original backbone and branch polymers. A peak at $V_e = 40$ corresponds to twice the molecular weight of the branches and is probably caused by coupling of polyisoprenyllithium with residual $(CH_3)_2SiCl_2$ in the backbone polymer. Fractionation of the crude material gives a first

Table III
Characteristics of Poly(styrene-*g*-isoprene) Copolymers

Sample	x^a	p_{uv}	$10^{-4}M_n$ branch	CH $10^{-6}M_w$	CH 10^{-4} $\langle S^2\rangle_{app}$, Å^2
P3	1.00			0.43	3.26
P3C4	0.47_2	24.5	1.91	0.93	7.9
P3C2	0.29_2	26.9	3.77	1.54	12.6
P3C1	0.21_4	22.7	6.77	1.97	15.6
P4	1.00			0.82_4	6.75
P4C3	0.75_0	31.7	0.85	1.05	10.1
P4C2	0.49_7	38.0	2.16	1.70	15.7
P4C1	0.26_4	36.0	6.32	3.10	27.3

[a] Weight fraction polystyrene from UV analysis. CH = cyclohexane.

cut (~10%) in which a small amount of copolymer of double the expected molecular weight is found. This can be traced to some dimerization during the chlorosilylation process, since GPC analysis of the chlorosilylated backbone shows its presence. To ensure the absence of side products, only the middle fractions were retained for study. These (comprising 50% of the product) are free of measurable quantities of impurities (Figure 1). Their characterization is given in Table III.

The degree of branching achieved (p) can best be determined from the weight fraction of polystyrene in the polymer (x) and the molecular weights of the backbone and branch.

$$p = \frac{M_{bb}}{M_{br}}\frac{(1-x)}{x}$$

The alternative method which involves measurements of M_{bb}, M_{br}, and M_{comb} is less accurate for polymers with small weight fractions of branches. It also suffers from the disadvantage that unless the polymers are homogeneous their molecular weights determined by light scattering are not real and vary with the refractive index of the solvent.[18] Our measurements on the graft copolymers, however, suggest (Tables III and IV) that the products are homogeneous in molecular weight and composition, for the measured molecular weights are nearly independent of solvent. These lead to values of p in acceptable agreement with those obtained from the above equation. In all solvents the measured radii of gyration of copolymers composed of two components A and B are apparent ones[19] because of the different refractive index increments of the two homopolymers.

$$\langle S^2\rangle_{app} = y\langle S^2\rangle_A + (1-y)\langle S^2\rangle_B + y(1-y)l^2 \quad (1a)$$

whereas

$$\langle S^2\rangle_{true} = x\langle S^2\rangle_A + (1-x)\langle S^2\rangle_B + x(1-x)l^2 \quad (1b)$$

For graft copolymers we may write $\langle S^2\rangle_A \equiv \langle S^2\rangle_{bb}$, $\langle S^2\rangle_B \equiv \langle S^2\rangle_{br,t}$, and $\langle S^2\rangle_{true} \equiv \langle S^2\rangle_{comb}$, where $\langle S^2\rangle_{bb}$ is the mean square radius of gyration of the backbone and $\langle S^2\rangle_{br,t}$ that of the total branch material. l^2 is the mean square distance between the two centers of gravity. $y = x\nu_A/(x\nu_A + (1-x)\nu_B)$, ν being the appropriate refractive index increment. In tetrahydrofuran and cyclohexane, y is a positive fraction somewhat higher than x.

The light scattering measurements in chlorobenzene and bromoform are of particular interest. In these two solvents with polyisoprene and polystyrene respectively, the major contribution to scattering is made by the other part of the molecule. In terms of eq 1 for chlorobenzene y is slightly greater than unity but in bromoform $(1-y)$ is slightly greater than unity. In both cases the other two terms are small and negative, e.g., when x is 0.5, y is 0.609 in cyclohexane, 0.584 in tetrahydrofuran, 1.051 in chlorobenzene, and −0.139 in bromoform. Hence $\langle S^2\rangle_{app}$(chlorobenzene) $\approx \langle S^2\rangle_{bb}$ and $\langle S^2\rangle_{app}$(bromoform) $\approx \langle S^2\rangle_{br,t}$.

The Zimm plot for polymer P3C4 in chlorobenzene is given in Figure 2. It should be compared with the one shown in Figure 2 of ref 16 for a two-block styrene–isoprene copolymer of nearly the same composition and molecular weight. The extreme distortion shown by the latter polymer is absent in the present case. A reversal of slope of the angular dependence does however occur at the highest concentration which would not occur with a homopolystyrene in this solvent. Nevertheless, the results indicate a much smaller difference between total molecular volume and scattering volume than in two-block copolymers. Only with polymer P4C1 (Figure 3) where only 26% of the molecule is scattering light does the situation approach that observed in ref 16. In bromoform the Zimm plots of graft copolymers of 50/50 composition are close to those expected from a homopolymer in a good solvent (Figure 4).

A comparison of the radii of gyration of the backbone and of the derived graft copolymers in chlorobenzene indicates some expansion of the backbone is caused by the polyisoprene branches. Although the measured values of the graft copolymers are not exactly those of the polystyrene component, an examination of eq 1 shows that they are minimum estimates of $\langle S^2\rangle_{bb}$ since $\langle S^2\rangle_{br,t} \geqslant \langle S^2\rangle_{bb}$ and $l^2 \geqslant 0$ and both $(1-y)$ and $y(1-y)$ are negative in this solvent. The equality signs are valid for Gaussian statistics if the number of branches is large and they are relatively short (see below). Otherwise the inequality signs apply, an effect which will be reinforced if incompatibility of the two components causes intra-molecular phase separation. The bromoform results indicate that $\langle S^2\rangle_{br,t}$ is indeed larger than $\langle S^2\rangle_{bb}$.

Figure 5 shows intrinsic viscosity results in dioxane, cyclohexane, and toluene. With increased branch length, the intrinsic viscosities in cyclohexane and toluene approach each other. In the limit of extremely long branch length, the polymers approximate to a 24–27 branch star polyisoprene in a

Table IV
Light Scattering Measurements on Poly(styrene-*g*-isoprene) Copolymers in Three Good Solvents ($\langle S^2\rangle$ Units (Å)^2)

Sample	THF $10^{-6}M_w$	THF $10^{-4}\langle S^2\rangle_{app}$	PhCl $10^{-6}M_w$	PhCl $10^{-4}\langle S^2\rangle_{app}$	CHBr$_3$ $10^{-6}M_w$	CHBr$_3$ $10^{-4}\langle S^2\rangle_{app}$
P3	0.42	6.2	0.43	6.4		
P3C4	0.90	11.3	0.95	7.3	0.94_5	11.0
P3C2			1.86	9.2_4		
P3C1	1.98	23.5			1.90	24.0
P4	0.76	14.0	0.83_6	14.3		
P4C3			1.06_5	12.9		
P4C2	1.68	26.2	1.71	16.2	1.80	23.7
P4C1			3.13	17.2		

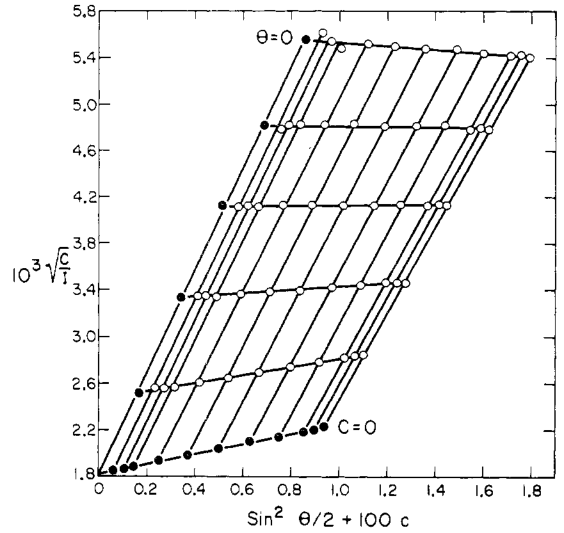

Figure 2. Zimm plot of polymer P3C4 in chlorobenzene.

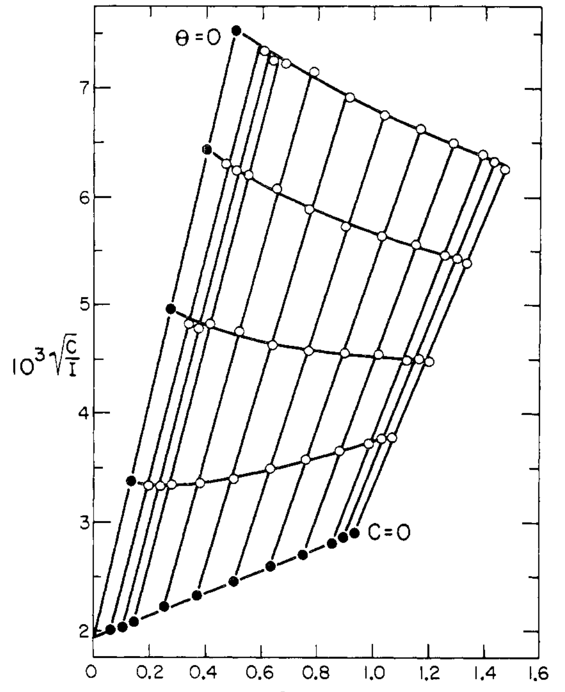

Figure 3. Zimm plot of polymer P4C1 in chlorobenzene.

good solvent. In dioxane there is little change in intrinsic viscosity with increasing branch length and polyisoprene content, the solvent power being much weaker for polyisoprene.

Discussion

The improvements made in the synthesis of graft copolymers compared to the earlier process[8] are clearly shown by the good agreement between the expected number of branches (Table I) and the number actually found (Table III). The deficiencies in that process[8] can now be more easily understood. The 18 h allowed for the coupling reaction is insufficient. The unexpectedly wide molecular weight distributions found in the final product were at least partly caused by the presence of some high molecular weight material produced by a small amount of backbone coupling.

It is at least qualitatively clear from the present Figure 2 and that of ref 16 that the configurations in solution of graft and two-block polymers are different. The question arises for all nonrandom copolymers as to the extent of segregation of the two components. In the Gaussian chain approximation for two-block copolymers l^2 is rather large and equal to $2(\langle S^2\rangle_A + \langle S^2\rangle_B)$.[19] Repulsive interaction between the two components will force an even greater separation of the centers of gravity. In contrast, taking the simplest model for the graft copolymer, that of a regular comb[20] (branches equidistant along the backbone) again in the Gaussian-chain approximation, it can be simply shown that;

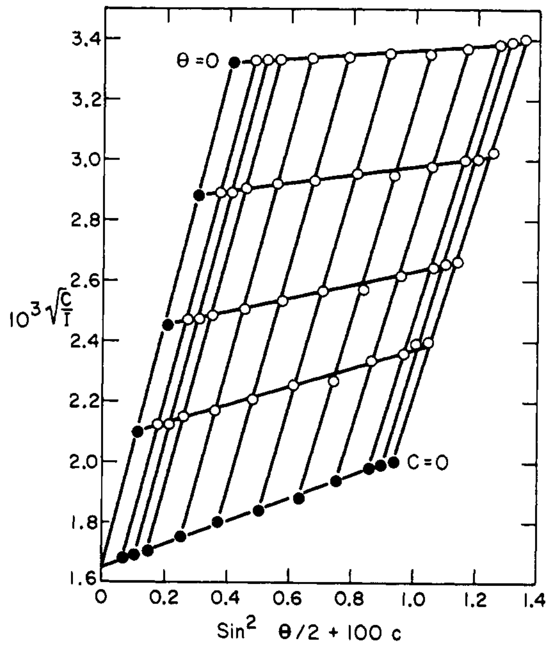

Figure 4. Zimm plot of polymer P3C4 in bromoform.

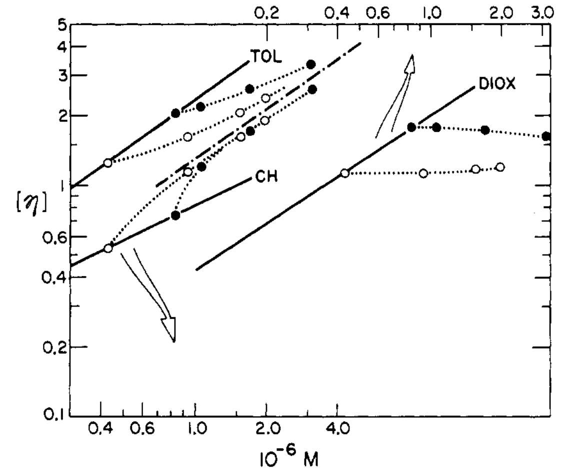

Figure 5. Change in intrinsic viscosity of polystyrene by the addition of polyisoprene branches. (—) [η] of linear polystyrene in toluene (TOL), cyclohexane (CH), and dioxane (DIOX). (○) graft copolymers of the P3 series and (●) of the P4 series. (- · -) estimate of [η] of a star branched polyisoprene containing 27 branches (see text).

$$l^2 = \langle S^2\rangle_{bb}(2/p^2) + \langle S^2\rangle_{br}(2/p) \tag{2}$$

where $\langle S^2\rangle_{br}$ is the mean square radius of gyration of a *single* branch. For p values near 30 it is clear that l^2 will be very small compared with $\langle S^2\rangle_{bb}$ or $\langle S^2\rangle_{br,t}$. In addition the mean square radius of gyration of the total branch material will be

$$\langle S^2\rangle_{br,t} = \langle S^2\rangle_{bb}(1 - 1/p^2) + \langle S^2\rangle_{br}(3 - 2/p) \tag{3}$$

i.e., very little above that of the backbone for $p \sim 30$ and for

$\langle S^2\rangle_{\mathrm{br}} \ll \langle S^2\rangle_{\mathrm{bb}}$. The overall radius of gyration is given by,

$$\langle S^2\rangle_{\mathrm{comb}} = \langle S^2\rangle_{\mathrm{bb}}\left(1+\frac{N_y}{p^2}-\frac{2N_y^2}{p^2}\right) + \langle S^2\rangle_{\mathrm{br}}N_y\left(3-\frac{2N_y}{p}\right) \quad (4)$$

which transforms to the equation given by Orofino[20] if backbone and branch units are identical. Also, $N_y = (1 - x)$. Equation 4 predicts little change in $\langle S^2\rangle$ for $p \sim 30$ until the branch length becomes very long. The formula for randomly branched molecules[21] predicts results which would be experimentally indistinguishable from eq 4.

Obviously the present results were not obtained under theta conditions for both types of segment as would be required for the proper use of eq 2 and 3. In addition repulsion between unlike units may also cause deviations from Gaussian statistics. Some expansion of the backbone seems to have been caused by the presence of foreign side chains and there also appears to be a significant difference between $\langle S^2\rangle_{\mathrm{br,t}}$ and $\langle S^2\rangle_{\mathrm{bb}}$ which is not predicted by the above equations if we assume that the results in bromoform and chlorobenzene give close to the real values of the two radii of gyration. This argument implicitly assumes that chlorobenzene and bromoform are equally good solvents for both polystyrene and polyisoprene. In order to check on this assumption, four polystyrenes and two polyisoprenes were examined in chlorobenzene, bromoform, toluene and tetrahydrofuran, either by light scattering techniques or by intrinsic viscosity measurements. The latter technique only is available for the polymer–solvent pairs polyisoprene/chlorobenzene and polystyrene/bromoform. The radius of gyration of polystyrene was found to be identical within experimental error in toluene, chlorobenzene, and tetrahydrofuran. Bromoform was found to be a slightly better solvent for polystyrene with intrinsic viscosities on the average 6% higher than in toluene. For polyisoprenes, the intrinsic viscosities in toluene and chlorobenzene were virtually identical, but in bromoform they were about 7% lower and in tetrahydrofuran 5% higher. Correspondingly $\langle S^2\rangle$ was about 8% higher in THF than in bromoform. In summary all are very good solvents for both homopolymers but bromoform is a slightly better solvent for polystyrene and slightly worse for polyisoprene.

If we assume that the small differences for bromoform are not likely to produce serious error, eq 1 can be solved for the three unknowns using data obtained in tetrahydrofuran, chlorobenzene, and bromoform. This procedure leads to the following results

P3C4: $\langle S^2\rangle_{\mathrm{bb}} = 7.9 \times 10^4$ Å^2; $\langle S^2\rangle_{\mathrm{br,t}} = 11.6 \times 10^4$ Å^2; and $l^2 = 7.1 \times 10^4$ Å^2

P4C2: $\langle S^2\rangle_{\mathrm{bb}} = 17.8 \times 10^4$ Å^2; $\langle S^2\rangle_{\mathrm{br,t}} = 25.8 \times 10^4$ Å^2; and $l^2 = 20.8 \times 10^4$ Å^2

The values of $\langle S^2\rangle_{\mathrm{bb}}$ and $\langle S^2\rangle_{\mathrm{br,t}}$ evaluated are slightly higher than the apparent values obtained in chlorobenzene and bromoform, respectively. This seems reasonable considering that the two correction terms in eq 1 should be small and negative. Only the value obtained for l^2 seems to be larger than expected although of course much lower than would be predicted for a two-block copolymer. Even though the results indicate a tendency of the polyisoprene segments to be concentrated closer to the perimeter of the molecule, a symmetrical structure would be expected to maintain a very small value of l^2. The magnitude of the error introduced by the combination of data from three solvents of not exactly the same solvent power is unknown. The estimate of l^2 is very dependent on the data obtained in tetrahydrofuran, the only case where it has an appreciable contribution to the apparent mean square radius of gyration. Qualitatively at least $\langle S^2\rangle_{\mathrm{app}}$ in tetrahydrofuran would have to be between the values obtained in chlorobenzene and bromoform if l^2 is really zero. This seems not to be the case. It seems probable that although the value of l^2 obtained may be inaccurate the true value is probably nonzero.

The measurements of mean square radius of gyration in cyclohexane cannot be compared in the same manner because of the wide difference in solvent power for the two components. Measurements in this solvent (and in tetrahydrofuran) are of most value in establishment of an accurate value of the molecular weight since the refractive index increment is high. The y values in cyclohexane and tetrahydrofuran are not widely different being about 4% higher in the former solvent. In both cases the apparent values approximate the true radii of gyration although they are somewhat biassed toward contributions from polystyrene segments. The smaller values in cyclohexane compared to those in THF reflect the contraction of the backbone in a theta solvent. In THF, the apparent radii of gyration fall below those of linear polystyrenes of the same molecular weight as is normal for a branched polymer but in cyclohexane the values are slightly higher than is found for such polystyrenes. The latter effect must be caused by the polyisoprene side chains which are in a very favorable environment in cyclohexane.

The intrinsic viscosities in cyclohexane and toluene show trends which conform to those observed for $\langle S^2\rangle_{\mathrm{app}}$. In toluene, a good solvent for both types of segment, viscosities drop below those of linear polystyrenes of the same molecular weight but in cyclohexane the trend is reversed (Figure 5). Nevertheless, even in toluene the intrinsic viscosities are higher than would be the case for equivalently branched homopolystyrenes as can be seen by a comparison of the present data with that reported in ref 8. In both cyclohexane and toluene the fact that polyisoprenes have higher intrinsic viscosities than polystyrenes is of importance. In fact the trends in intrinsic viscosity on branching can be predicted qualitatively in terms of a compositional plus a branching factor. The former can be calculated from data on linear polystyrenes and polyisoprenes[22] as was done for block copolymers and the latter from data on branched polystyrenes.[8] The actual values of $[\eta]$ calculated are of course in error because of the oversimplified model used.

In the limit of infinite side chain length, the intrinsic viscosities in toluene and cyclohexane must become equal to the values expected for a 25–30 branch star polyisoprene. From the results of Noda[23] and Roovers[8] this is about 30% of the intrinsic viscosity of a linear polyisoprene of the same molecular weight. By accident toluene and cyclohexane are almost equally good solvents for polyisoprene so the intrinsic viscosities are nearly identical. In the limit of long side branches, therefore, the intrinsic viscosities of the graft copolymers must become equal in the two solvents.

In dioxane, close to theta conditions for polyisoprene, adding polyisoprene branches produces very small changes in intrinsic viscosity over that of the polystyrene backbone. The situation is similar to that observed previously[8] with branched polystyrenes under theta conditions. In the latter case this is caused by $\langle S^2\rangle_0^{3/2}/M$ and Φ remaining fairly constant at least until the branch length becomes very large. With poly(styrene-*g*-isoprene) copolymers both compositional and branching effects mentioned previously will have the effect of reducing the intrinsic viscosity below that of a linear polystyrene of the same molecular weight. The simple additive scheme described above predicts that the intrinsic viscosity will be nearly independent of branch length in the region studied but lower than that of the backbone. At longer branch lengths an upward trend with increasing M must, however, finally take over as the molecule begins to approximate the configuration of a multibranch star polymer. Such behavior is not observed in the range studied; presumably the approach is much slower when the side chains are in an unfavorable environment and the backbone expanded than when the reverse occurs as in cyclohexane.

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Effect of Diffusional Resistance upon Gas Chromatography in Capillary Columns

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ABSTRACT: A theoretical investigation indicates the effect stationary-phase mass-transfer resistance has on thermodynamic properties as obtained from chromatographic measurements utilizing open-tubular columns. The model applies to a wide range of experimental conditions. Parameters for the system are: carrier-gas flow rate, column length, solute diffusivity, absorbent layer thickness, ratio of tube radius to absorbing layer thickness, and the true Henry's constant. A plot has been developed which allows simple determination of the true Henry's constant from the experimentally observed Henry's constant. The analysis predicts lower true Henry's constants than those predicted by previously presented reduction methods. As a result, Flory's χ parameters determined by packed and by capillary columns for the benzene- and cyclohexane–polyisobutylene systems are brought into better mutual agreement. The analysis indicates that both the diffusivity and the true Henry's constant for a given solute–solvent system may be determined from a single set of chromatographic experiments.

Gas–liquid chromatography (GLC) has long been recognized as a useful tool for the separation and identification of the components constituting a chemical sample. In recent years, however, GLC has also gained acceptance as a technique for the accurate determination of the solubility of vapors in a liquid phase.[1,2] This method is especially well-suited to polymeric solvents, where the time for a single measurement by conventional bulk-equilibration methods may be several days, in contrast to only minutes by chromatography. In addition, GLC offers the advantage of allowing solubility measurements at much lower concentrations than can be achieved in the static method. As a result, measurements reflect the properties of a system more closely resembling the conventional thermodynamic standard state, infinite dilution.

The solubility (or Henry's constant) of the solute is determined by measuring the net retention time for a solute "probe" passing through a column which contains the stationary liquid (or polymeric) phase. Experimentally determined solubilities have, however, been found to be dependent on the carrier-gas flow rate,[3,4] film thickness,[5] and the temperature of the system relative to the glass-transition temperature of the polymer.[6,7] This implies that a kinetic or transport effect exists in such measurements. The chromatographic measurements must be extrapolated to the value where the flow-rate effect no longer exists in order to determine purely thermodynamic properties.

It has been recognized from the earliest theories of chromatography that one of the causes of departure from the ideal of instantaneous equilibrium of gas and stationary phases is the diffusional resistance of the solute through the stationary phase. This effect is usually relatively minor in the case of a liquid absorption layer. However, in the case of a polymeric absorption phase, this phenomenon is magnified as a result of the greatly reduced solute diffusion in the solvent.

Effect of Equilibrium. The fundamental principle of gas chromatography is that solutes are selectively absorbed by the liquid or, as in this work, the polymer phase:

$$u_{\mathrm{sp}} = uf + u_{\mathrm{p}}(1 - f) \qquad (1)$$

where u is the linear velocity of the carrier gas (cm/s), f is the fractional time that the solute spends in the gas phase, subscript sp signifies *solute peak,* and subscript p signifies *polymer phase.* From ensemble theory, for a large number of molecules, f also represents the fraction of solute molecules in the gas phase at any given time.

In gas–liquid chromatography, the linear velocity of the polymer phase is zero, and eq 1 may be simplified to

$$u_{\mathrm{sp}} = uf \qquad (2)$$

Due to the difference in these two velocities, u and u_{sp}, a sample of solute will elute from the column at a longer time, t_{R}, than the retention time of the pure carrier gas, t_{G}.

A solute probe, passing through a column under the conditions of instantaneous equilibration, is represented in Figure 1. The carrier gas and solvent probe proceeded down the column with velocities of u and u_{sp}, respectively. The solute in