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Brill transition appears to be characterized by two energy states and to occur in a space corresponding to about 25 chemical repeat units.

The Size of the Crystals in Nylon 66

Having shown that the elemental unit involved in the Brill transition contains about 25 chemical repeat units or 50 amide groups, it is of interest to compare this quantity with the size of the crystals.

The long period determined by small-angle X-ray diffraction on three samples crystallized from solution in methanol varied from 61 to 69 Å, corresponding to 5.0 ± 0.3 repeat units along the chain.[2] These results are consistent with those of Hinrichsen[9] who studied the dependence of the long period on the temperature of crystallization from solution. He reported 53–54 Å for crystallization temperatures of 60–130 °C, 55.5 Å for 140 °C, and 60 Å for 147 °C.

Estimates of the lateral dimensions can be calculated from the breath of the (100) and (010) peaks in the wide-angle diffraction pattern obtained for an earlier study using the Sherrer equation. This method gives minimum values because there may be other causes of broadening. The underlying amorphous diffraction is a complicating factor. The estimated sizes at room temperature are about 130 Å in the hydrogen bond direction and 85–125 Å normal to the hydrogen-bonded sheets, corresponding to widths of 29 and 23–34 chains, respectively. Above the Brill transition, there is a single, relatively sharp peak in this region which becomes more narrow as the temperature is increased. The apparent crystal size increases from 170 Å or 40 chain widths at 202 °C to 290 Å or 68 chain widths at 240 °C. Thus, it can be estimated that the number of repeat units in a crystal is of the order of 4000 at room temperature and much more at higher temperatures. The important point is that it is much larger than the active quantity of 25 repeat units deduced by deconvoluting the excess heat capacity for the Brill transition. This means that the transition does not involve a cooperative motion of an entire crystal but only a quantity equivalent to about five stem segments traversing the relatively thin nylon crystals. We conclude that the Brill transition occurs point by point involving small groups of adjacent stems.

Acknowledgment. Small- and wide-angle X-ray diffraction data were received from F. C. Wilson and G. A. Jones, respectively.

Registry No. Nylon 66, 32131-17-2.

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Synthesis and Characterization of Poly(methylphenylphosphazene)-*graft*-polystyrene Copolymers[1]

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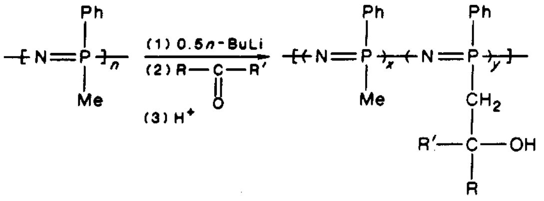
ABSTRACT: The polymeric anion formed by the deprotonation of poly(methylphenylphosphazene) was used to initiate the anionic polymerization of styrene to form new polyphosphazene-*graft*-polystyrene copolymers with compositions ranging from 65 to 90% polystyrene. These new materials were characterized by elemental analyses, ^{1}H and ^{31}P NMR spectroscopy, dilute solution techniques (size exclusion chromatography, membrane osmometry, and viscosity), and thermal analysis (differential scanning calorimetry and thermal gravimetric analysis).

Introduction

While the preparation of block and graft copolymers comprised of very different polymers has been widely used in organic polymer chemistry to develop new materials with optimum properties, relatively few copolymers have been reported that contain the class of inorganic polymers known as polyphosphazenes, $[R_2P{=}N]_n$. Polyphosphazenes have a number of useful properties, such as flame retardancy and unusual thermal and radiation stability, that could substantially enhance more commonly used organic materials and are, therefore, useful candidates for block or graft formation. Some work has been directed toward the preparation of polyphosphazene/polysiloxane graft and block copolymers,[2] and a recent paper[3] reports the preparation of polystyrene/polyphosphazene grafted systems using a radical initiation process. These reports have made use of ring opening reactions of $[Cl_2P{=}N]_3$ or poly(aryloxyphosphazene) products of the ring opening/substitution method.

Recent work in our laboratory[4] has demonstrated that the deprotonation of a polyphosphazene prepared by a condensation polymerization, $[Ph(Me)P{=}N]_n$,[5] is easily accomplished by treatment with BuLi. Subsequent quenching of the resulting anion sites along the polymer backbone with various electrophiles (e.g., eq 1) has produced several new derivatized polyphosphazenes in which



$$-[N{=}P(Ph)(Me)]_n- \xrightarrow[(2)\ R-C(=O)-R' \quad (3)\ H^+]{(1)\ 0.5n\text{-BuLi}} -[(N{=}P(Ph)(Me))_x-(N{=}P(Ph)(CH_2C(OH)RR'))_y]- \quad (1)$$

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Table I
Analytical Data

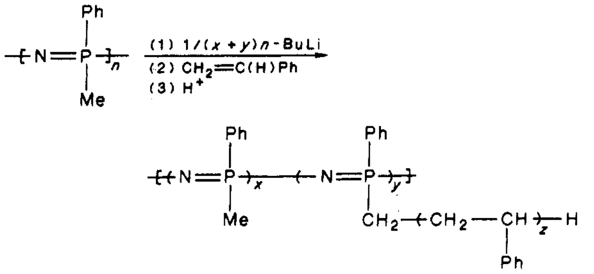
copolymer	% styrene[b]	% yield	analyses[a]		
			C	H	N
3	66	98	79.21 (81.58)	7.16 (7.10)	3.36 (3.52)
4	66	80	79.90 (81.58)	7.19 (7.10)	3.59 (3.52)
5	66	87	78.35 (81.58)	7.22 (7.10)	3.48 (3.52)
6	66	87	78.93 (81.77)	7.24 (7.11)	3.52 (3.46)
7	75	95	82.88 (84.54)	7.33 (7.28)	2.69 (2.55)
8	68	98	80.91 (82.33)	7.18 (7.14)	3.31 (3.28)
9	92	88	89.43 (89.77)	7.83 (7.59)	0.85 (0.82)
10	88	92	89.03 (89.79)	7.67 (7.59)	1.18 (0.81)

[a] Calculated values in parentheses. [b] Based on weights of styrene and polyphosphazene used in the reaction.

all the substituents along the P–N backbone are attached by direct P–C linkages. The ease and control of degree of deprotonation suggested that these anion sites would be suitable for the initiation of anionic polymerization of selected monomers. Because the anionic polymerization of styrene occurs at conditions that are compatible with deprotonation of the polyphosphazene, this study focused on the grafting of this well-known, versatile organic polymer segment to the inorganic polymer backbone. Our goals were (1) to study the feasibility of using anionic grafting reactions to further expand the technological applications of polyphosphazenes, (2) to prepare a series of polyphosphazene-*graft*-polystyrene copolymers in which the ratios of the two components were varied by controlling the number and the length of the polystyrene grafts, and (3) to characterize and compare the properties of these copolymers.

Results and Discussion

A series of polyphosphazene-*graft*-polystyrene copolymers **3–10** were prepared via an anionic grafting process that involved the following three-step reaction sequence (eq 2). First, partial deprotonation of the methyl substituents in the parent polymer $[Ph(Me)PN]_n$ (**1**) was carried out in THF by the addition of 0.1–0.2 equiv of BuLi at −78 °C. Second, the resulting polymeric anion **2** was treated with varying amounts of styrene (ca. 1–15 equivs). The final step was the quenching of the living styrene anions on the grafted chains with ethanol. These copolymers **3–10** may be grouped into two sets: (a) those with ca. 20% ($x = 4$ and $y = 1$) of the P=N backbone units having grafted chains consisting of 13–20 (z) styrene monomer units (**3–7**) and (b) those with ca. 10–14% ($x = 6.3$–9 and $y = 1$) of the PN units having grafted chains of 20, 100, or 150 monomer units (**8–10**). The composition of the graft copolymers ranged from 65 to 92% styrene by weight.



(2)

3-10

3: $x = 4.0$; $y = 1$; $z = 13$
4: $x = 4.0$; $y = 1$; $z = 13$
5: $x = 4.0$; $y = 1$; $z = 13$
6: $x = 4.3$; $y = 1$; $z = 14$
7: $x = 4.0$; $y = 1$; $z = 20$
8: $x = 6.3$; $y = 1$; $z = 20$
9: $x = 6.3$; $y = 1$; $z = 110$
10: $x = 9.0$; $y = 1$; $z = 153$

A number of control reactions using BuLi to polymerize styrene and several trial grafting experiments were conducted to determine procedures that optimized the grafting process. These efforts indicated that, in addition to the usual care in purity and dryness of reagents that is necessary for anionic polymerization of styrene, the best and most consistent results were obtained when (1) the polyphosphazene anion was prepared by using dilute BuLi (ca. 0.5 M) for accuracy in measurements, by using polymer solutions of concentrations of ca. 1 M in THF, and with stirring for at least 1.5 h at −78 °C to ensure complete anion formation; (2) the mixture was stirred for at least 6 h to allow for sufficient mixing of the growing graft and the styrene monomer; and (3) precipitation of the graft copolymer within 3–5 h after quenching. A polystyrene control reaction was also carried out simultaneously with each grafting reaction using identical conditions and quantities of BuLi, THF, and styrene to verify the purity of the reagents and solvent and to provide an estimate of the chain length of the grafted side chains.

Typically, when the polystyrene control reactions worked well (i.e., gave polystyrene with narrow molecular weight distributions and M_n no higher than twice the theoretical values), the graft copolymer reactions also worked well giving 80–98% yields after at least one reprecipitation from THF in hexane. The graft copolymers were off-white materials that were soluble in THF, toluene, benzene, and CH_2Cl_2. Unlike polystyrene, the graft copolymers did not readily precipitate when concentrated acetic acid added to THF solutions. Slow evaporation of solvent from THF or CH_2Cl_2 solutions gave flexible, transparent films.

The NMR spectroscopic data for the graft copolymers provided little information about the new copolymers. The ^{31}P NMR spectra were very similar to that of the parent polymer with signals at ca. δ 1 and the ^1H NMR spectra contained the overlapping signals of phenyl and aliphatic C–H protons found in both components of the grafts. On the other hand, the elemental analyses of the grafts (Table I) indicated that significant amounts of styrene had been incorporated into the copolymers since the carbon analyses were much higher (ca. 78–89%) than in the parent (ca. 61%) and the nitrogen analyses (1–4%) were considerably lower than in the parent (10%).

Stronger support for successful grafting of polystyrene onto the polyphosphazene comes from three molecular weight studies that involved dilute solution techniques. In all cases the data (Table II) show quite sizable increases in the molecular weights of the grafts relative to the parent homopolymer. First, the intrinsic viscosities of the copolymers (116–313 mL/g) were determined in toluene at 30 °C and were markedly higher than that of the parent polymer (ca. 41 mL/g). Furthermore, when the viscosity of a graft was compared to the value obtained for a blend with a similar polystyrene:polyphosphazene composition, it was evident that the graft copolymer was a higher molecular weight material. In some cases the viscosities were also determined in THF, another good solvent for both components of the polymer, and the values were within

Table II
Viscosity, Membrane Osmometry, and Size-Exclusion Chromatography Data

			SEC analyses[c]		
copolymer	$[\eta]^a$	$M_n{}^b$	M_n	M_w	M_w/M_n
3[d]	130	3.3×10^5	3.8×10^5 (2.5×10^5)	5.0×10^5 (3.3×10^5)	1.3
4[d]	137	3.1×10^5	3.8×10^5 (2.5×10^5)	4.7×10^5 (5.0×10^5)	1.2
5[e]	116	3.4×10^5	1.8×10^5 (2.7×10^5)	3.3×10^5 (4.0×10^5)	1.8
6[f]	197	3.5×10^5	1.6×10^5 (2.8×10^5)	3.4×10^5 (5.2×10^5)	2.1
7[g]	190	3.8×10^5	1.4×10^5 (2.4×10^5)	3.0×10^5 (5.4×10^5)	2.0
8[f]	150 (140)	4.3×10^5	2.3×10^5 (3.8×10^5)	4.5×10^5 (6.8×10^5)	2.0
9[g]	292 (308)	1.8×10^6	4.2×10^5 (1.0×10^6)	1.5×10^6[h] (1.7×10^6)	3.6
10[f]	313 (295)	8.0×10^5	5.6×10^5 (1.2×10^5)	1.7×10^6[h] (1.5×10^6)	3.1

[a] Intrinsic viscosities in mL/g in toluene. Values in parentheses were obtained in THF. [b] Determined by membrane osmometry. [c] Theoretical values are in parentheses. [d] Parent polymer: M_n, 8.5×10^4; M_w, 1.7×10^5; M_w/M_n, 2.0. [e] Parent polymer: M_n, 9.4×10^4; M_w, 1.4×10^5; M_w/M_n, 1.5. [f] Parent polymer: M_n, 9.5×10^4; M_w, 1.7×10^5; M_w/M_n, 1.8. [g] Parent polymer: M_n, 8.1×10^4; M_w, 1.4×10^5; M_w/M_n, 1.7. [h] A 10^6-Å μ Styragel column was added to the system.

10% of those obtained in toluene. In all cases, the plots of η_{sp}/c versus c (c is concentration) were linear with Huggins constants in the range of 0.39–0.74.

A second indication of successful grafting was molecular weight information obtained by size exclusion chromatography (gel permeation chromatography) (Table II). When compared to the parent polymers (Figure 1), the SEC traces of the graft copolymers showed shifts toward significantly higher molecular weights, broadened distributions of molecular weights, as is typical for branched polymer systems,[6] and increased amounts of tailing, especially for the larger copolymers. The weight-averaged molecular weights (M_w) obtained from the SEC traces were measured relative to narrow molecular weight polystyrene standards and were only slightly lower than the theoretical M_w values (determined by adding the M_w of the parent polymer to the additional weight of the grafted polystyrene chains, assuming complete incorporation of styrene). Because extensive branching affects the coiling ability of the polymers and thus decreases the molecular size, the SEC molecular weights are expected to be somewhat lower than the actual molecular weights of the copolymers.

Hence, the absolute number-averaged molecular weights (M_n) provide a more accurate measure of the molecular weights of these grafts. The M_n values, determined by membrane osmometry in toluene at 35 °C, were typically slightly higher than the SEC values and were within the range of the calculated values for the grafts. Furthermore, no significant diffusion through the membranes was observed. This is indicative of the absence of low molecular weight materials that might have been present due to some homopolymerization of styrene.

The presence of homopolymers must always be considered in grafting processes, but in this case the possibility of homopolymerization is minimized by two factors. First, previous work with the polyphosphazene anion shows that anion formation is relatively complete at the reaction conditions used in these experiments because quenching of the polymeric anion consistently produces polymers with the proper degree of substitution.[4,7] Indeed, this is the case for 10, 20 and even 50% deprotonated poly(methylphenylphosphazene). It is, therefore, highly unlikely that unreacted BuLi remained to initiate the polymerization of the styrene in these grafting reactions. Secondly, the formation of homopolystyrene through chain transfer is also unlikely since these reactions involved anionic polymerization.[8]

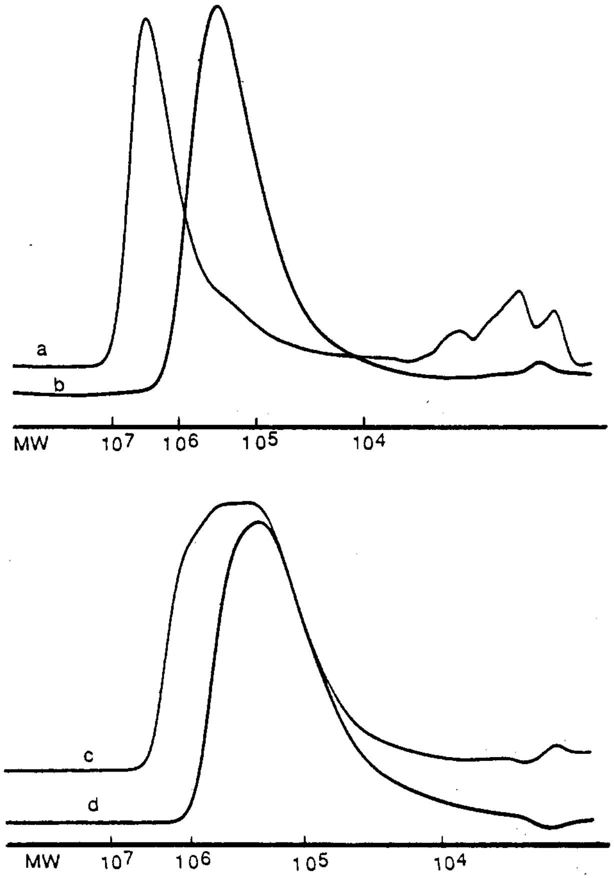


Figure 1. Molecular weight distributions (determined by SEC): (a) of graft copolymer **10**; (b) of parent $[Ph(Me)P{=}N]_n$ for **10**; (c) of graft copolymer **6**; (d) of parent $[Ph(Me)P{=}N]_n$ for **6**.

Despite the fact that homopolymerization was unlikely and the molecular weight data discussed above indicate that grafting was successful, a series of simple precipitation studies were done to attempt to separate any homopolymers from the grafts. This was somewhat complicated by the nearly identical solubilities of the polyphosphazene and polystyrene in common solvents. However, the coordination ability of the backbone nitrogen in the polyphosphazene offers a striking difference between the homopolymers and renders the phosphazene to be quite soluble in acetic acid. In fact, dissolution of the polyphosphazene in CH_3COOH produced the protonated polymer which was readily identified by the downfield shift (ca. δ 8) in its ^{31}P NMR spectrum.[9] The corresponding insolubility of polystyrene in acetic acid thus facilitates the separation of the homopolymers. The addition of acetic acid to a THF solution of pure polystyrene or a blend of polystyrene and $[Ph(Me)P{=}N]_n$ readily caused precipitation of the polystyrene. However, addition of up to five times as much acetic acid to a solution of a graft of similar composition and concentration as the blend produced an iridescent solution with a bluish tint from

Table III
Thermal Analysis Data

copolymer	DSC T_g[a]		TGA[b] onset	TGA[b] 50% weight loss
control		93	387	413
$[Ph(Me)P{=}N]_n$	37		394	433
blend	34	93	391	416
3	43	105	397	425
4	37	96		
5	38	96	402	422
6	43	108		
7	37	100		
8	43	105		
9	38	105	393	419
10	39	100	389	413

[a] Glass transition temperatures (T_g) in degrees Celsius (inflection point). [b] Onset of decomposition and 50% weight loss temperatures in degrees Celsius.

which only a small quantity of precipitate could be isolated. This material displayed a strong signal at δ 8.8 in the ^{31}P NMR spectrum indicative of the presence of the graft copolymer with a protonated backbone. While it is reasonable to first assume that any homopolystyrene would readily precipitate without the addition of such large quantities of acetic acid, this was not substantiated by a similar precipitation experiment with a blend of the graft and homopolystyrene. Unlike the blend of the homopolymers where precipitation of polystyrene occurred readily, it was necessary to add an even larger quantity of acetic acid than was used for the pure graft to obtain sufficient precipitate for ^{31}P NMR spectroscopic analysis. Since this material contained no phosphorus, it is evident that the graft copolymer, which contains a large number of long polystyrene chains, served to solubilize the pure homopolystyrene. Hence, it cannot unequivocally be concluded that the grafted materials did not contain small, undetectable quantities of homopolystyrene.

The data obtained from thermal analyses (DSC and TGA) of the graft copolymers are summarized in Table III. Thermogravimetric analyses (TGA) conducted in argon consistently indicated onsets of decomposition of ca. 390 °C with 50% weight loss values of ca. 410–425 °C. Comparable values were obtained for the homopolymers and for a blend. Hence, these grafting reactions offer negligible enhancement of thermal stability over that of the individual homopolymer components.

Only two transitions were observed in the DSC scans, with these corresponding closely to the glass transition temperatures (T_g) of the polystyrene and polyphosphazene components. Slight variations in the T_g's occurred (i.e., 36–43 °C and 96–108 °C), but no discernible trends could be ascertained.[10] Nonetheless, the observation of two distinct transitions suggests that two well-separated phases exist in these graft copolymers. The DSC scan of a blend of the homopolymers was somewhat different with both of the transitions being several degrees lower than in the grafts. Similar observations were reported for a blend of poly[bis(4-isopropylphenoxy)phosphazene] and polystyrene.[4]

In summary, the successful grafting of polystyrene to the polyphosphazene backbone via anionic polymerization reactions can be carried out with some degree of control of the length and number of grafted chains. Moreover, unlike the related grafts obtained from radical polymerization,[4] this approach leads to soluble, uncrosslinked materials. More importantly, the anionic grafting reactions on the polyphosphazene backbone could be extended to a variety of monomer systems, thereby providing access to a variety of new inorganic–organic and inorganic–inorganic polymeric materials. Further studies of the synthesis of such materials are in progress.

Experimental Section

Poly(methylphenylphosphazene) was prepared as described elsewhere[5,11] and purified by reprecipitation from THF into hexane. Styrene was purchased commercially and was stored over and distilled from CaH_2 at 80 °C/40 mmHg (N_2 atmosphere) immediately before use. The BuLi was also purchased commerically (2.5 M in hexane) and was diluted with hexane (distilled from CaH_2 under N_2) to ca. 0.5 M. The exact concentration was established by titration using a published procedure.[12] Tetrahydrofuran was distilled from Na/benzophenone under nitrogen just prior to use. All glassware used for solvents and for the reactions was flamed dried under vacuum, and all manipulations were carried out under an atmosphere of nitrogen, until the reactions were quenched.

The ^1H and ^{31}P NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$. Elemental analyses (Table I) were performed on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106 or by Galbraith Laboratories, Knoxville, TN. Size exclusion chromatography measurements (Table II) were made on a Waters Associates GPC II instrument equipped with UV and refractive index detectors and with a Nelson Analytical data handling system using 500, 10^4, and 10^5 Å μStyragel columns. Where noted a fourth column (10^6 Å μStyragel) was added to the system. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% $Bu_4N^+Br^-$, a flow rate of 1.5 mL/min, a temperature of 30 °C, and a sample size of 0.05 mL of 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the range of ca. 10^3–10^6. Membrane osmometry data (M_n in Table II) was obtained at 35 °C in toluene by using a Wescan Model 230 recording membrane osmometer equipped with regenerated cellulose membranes (Type RC-52). Intrinsic viscosities (Table II) were determined in toluene or THF at 30 °C using a Cannon-Ubbelohde dilution viscometer immersed in a thermoregulated water bath.

Glass transition temperatures (Table III) were determined by differential scanning calorimetry using a Du Pont Model 910 instrument equipped with a Du Pont 1090 thermal analyzer data station. Measurements were made under nitrogen against an aluminum reference from −40 °C or −120 °C to 130 °C by using a sample of ca. 10 mg and a heating rate of 10 °C/min. Each experiment was repeated at least once on the same sample. Thermal gravimetric analysis (Table III) were performed on a Du Pont TGA Model 951 instrument equipped with a Du Pont 1090 thermal analyzer data station. The polymer samples (ca. 50 mg) were heated at a rate of 10 °C/min under argon from ambient temperature to 900 °C.

Synthesis of Poly(methylphenylphosphazene)-*graft*-polystyrene. In a typical procedure, a three-neck 250-mL round-bottom flask equipped with a stopcock gas-inlet adapter, stopper, rubber septum, and a magnetic stir bar was flame-dried under vacuum, cooled, purged with nitrogen, and charged with 10.9 mmol (1.5 g) of $[Ph(Me)P{=}N]_n$. After the polymer sample was dried in a vacuum oven at 120 °C for ca. 18 h, THF (10 mL) was added to the flask. Upon complete dissolution (ca. 4 h) of the parent polymer, the solution was cooled to −78 °C and BuLi (2.1 mmol, 0.48 M) was added via syringe. The mixture was allowed to stir for a minimum of 1.5 h at this temperature, and then styrene (27.9 mmol, 3.2 mL) was added to the −78 °C polymer anion solution. This mixture was allowed to warm slowly and was stirred overnight at room temperature. The reaction was then quenched by addition of ethanol (2.1 mmol, 0.2 mL). This mixture was stirred for ca. 1 h, and the graft copolymer was precipitated by slow addition of the THF mixture to hexane (ca. 600 mL). Subsequent reprecipitations from THF into hexane, decantation of the solvents, and drying in a vacuum oven for 2 days at 150 °C, afforded off-white materials that readily formed flexible films by slow evaporation of the solvents from THF or CH_2Cl_2 solutions.

Polystyrene Control Reactions. For each grafting reaction, a simultaneous preparation of polystyrene was performed as a control. The THF (10 mL) was transferred by syringe into glassware equipped as described above and was cooled to −78 °C. Then BuLi (2.1 mmol, 0.48 M) was added, the solution was stirred for 1.5 h at −78 °C, and styrene (27.9 mmol, 3.2 mL) was added via syringe. The reaction mixture was stirred overnight at room temperature and quenched and purified as described above.

Fractional Precipitation. The graft copolymer (1.0 g) was dissolved in ca. 30 mL of THF. Concentrated acetic acid was added dropwise (ca. 20 mL) until a bluish white iridescent solution persisted. Several aliquots were centrifuged, and the combined precipitates were analyzed by ^{31}P NMR spectroscopy (δ 7.9). A blend [10% poly(methylphenylphosphazene) and 90% polystyrene by weight] was treated in the same manner. Polystyrene was completely precipitated after addition of ca. 4 mL of acetic acid (no ^{31}P signal). A second blend [50% poly(methylphenylphosphazene)-*graft*-polystyrene and 50% polystyrene] was also treated in the same manner. In this case, the addition of ca. 10 mL of acetic acid gave a cloudy solution, but it was necessary to add ca. 40 mL of acetic acid to acquire sufficient precipitate for ^{31}P NMR spectroscopic analysis (no signal).

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Registry No. BuLi, 109-72-8; $(\mathrm{Me_3SiN{=}P(Ph)(Me)OCH_2CF_3})(\mathrm{PhCH{=}CH_2})$ (graft copolymer), 118336-37-1.

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Notes

Effect of Cross-Links on the Swelling Equation of State: Polyacrylamide Hydrogels

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Introduction

In the literature there exists a body of rather precise experimental observations of vapor pressure differences between swollen polymer networks and the equivalent polymer solutions.[1-3] The clearly distinguished deviations in thermodynamic activity between these two states are attributed to an anomalous elastic contribution to the total free energy of swollen gels, the mixing contributions being assumed to be the same for the two states. This anomaly has been taken as qualitative evidence in favor of the junction fluctuation model of networks,[3] but quantitative agreement with this or any other single model remains elusive,[4] and the additivity of elastic and free energy terms has been called into question.

The conclusions drawn from the investigations of ref 1–3 are founded on the Flory–Rehner theory of polymer network swelling, the only allowed adjustable parameters of which are the second-order interaction parameter χ and the volume elastic modulus G_v. In this theory, interactions of an order higher than 2 follow a fixed protocol defined by the series expansion of a mixing term $\log(1-\varphi)$, where φ is the polymer volume fraction. Difficulties arise when the additional restrictive assumption is adopted that χ is the same in the un-cross-linked solution as in the cross-linked gel.

The purpose of this note is to show that network cross-linking can severely perturb the potentials between polymer segments, not only in the second order but also in higher order interactions. Consequently, for the purpose of deducing the elastic contribution to the chemical potential of the network, the use of the un-cross-linked solution as a reference state is not necessarily valid and could be misleading.

One can write for the osmotic pressure Π_u of a neutral un-cross-linked polymer solution (indicated by the subscript u)

$$\Pi_u = RT\rho\varphi/M + A_{2u}\varphi^{9/4} + A_{3u}\varphi^3 + \sum_{n>3} A_{nu}\varphi^n \qquad (1)$$

in which R is the gas constant, T the absolute temperature, ρ the density of the pure polymer, and M the mass of the polymer chains. The 9/4 power in the second-order term is the consequence of polymer–polymer correlations in the semidilute excluded volume condition (i.e., large M, $\varphi \ll 1$, $A_{2u} \gg A_{3u}\varphi^{3/4}$) for which simple scaling theory applies.[5] This nonintegral power loses its theoretical justification close to and below the Θ temperature ($A_{2u} < 0$), since the simple scaling used to derive it does not hold in this region, but this consideration is not important for the purposes of this note. The terms in eq 1 with $n > 3$, neglected in simple scaling, must be included to describe the higher order interactions at concentrations above the semidilute range.

In the cross-linked network (designated by the subscript c), the thermodynamic activity is defined by the swelling pressure, ϖ

$$\varpi = \Pi_c - G_v = A_{2c}\varphi^{9/4} + A_{3c}\varphi^3 + \sum_{n>3} A_{nc}\varphi^n - G_{vo}\varphi^{1/3} \qquad (2)$$

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