# Arborescent Polystyrene-*graft*-poly(2-vinylpyridine) Copolymers: Synthesis and Enhanced Polyelectrolyte Effect in Solution

**R. Andrew Kee and Mario Gauthier***

*Institute for Polymer Research, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

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ABSTRACT: A technique is described for the preparation of arborescent copolymers containing poly(2-vinylpyridine) (P2VP) segments. 2-Vinylpyridine is first polymerized with 1,1-diphenyl-2-methylpentyllithium in tetrahydrofuran in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). The graft copolymers are obtained by titration of the P2VP anions with a solution of a chloromethylated polystyrene substrate. Copolymers incorporating either short ($M_w \approx 5000$) or long ($M_w \approx 30\,000$) P2VP side chains were prepared by grafting onto linear, comb-branched (G0), G1, and G2 chloromethylated arborescent polystyrenes. Branching functionalities ranging from 14 to 3880 and molecular weights ranging from $8.2 \times 10^4$ to $6.7 \times 10^7$ were obtained for the copolymers, while maintaining a low apparent polydispersity ($M_w/M_n \approx 1.06-1.15$) after grafting. Characterization data for these materials from size exclusion chromatography and light scattering indicate that they have a highly compact structure. Dynamic light scattering results show that the arborescent poly(2-vinylpyridine) copolymers expand much more in solution than the linear homologous polymers when protonated with HCl. This is attributed to the higher charge density attained in the branched copolymers.

## Introduction

Dendritic polymers are an interesting class of macromolecules with a cascade-branched structure including dendrimers, hyperbranched, and arborescent polymers.[1] Arborescent polymers are prepared from successive grafting reactions incorporating well-defined polymeric building blocks. This “graft-on-graft” approach makes it possible to obtain macromolecules with a high branching functionality and molecular weight in a few reaction steps, while maintaining a narrow molecular weight distribution ($M_w/M_n \approx 1.1$).

The first step in the synthesis of arborescent polymers is the random introduction of reactive grafting sites along a linear substrate. Living polymer chains are then coupled with the linear substrate to generate a comb-branched (generation 0 or G0) polymer. The functionalization and coupling reaction cycles are repeated to obtain the higher generation (G1, G2, etc.) arborescent polymers. This grafting strategy has been applied to the synthesis of arborescent polystyrenes,[2] using cycles of chloromethylation and coupling with polystyryl anions. Similar methods have also been developed to prepare “comb-burst” polyethylenimines[3] and arborescent polybutadienes.[4] In all cases, the syntheses relied on living polymerization techniques providing precise control over the molecular weight and polydispersity of the grafted polymer segments. The number of reactive functional groups can also be predetermined, allowing control over the branching density for each generation.

Other anionically polymerizable monomers have been incorporated into arborescent copolymers. A grafting-from approach has been described for the preparation of arborescent polystyrene-*graft*-poly(ethylene oxide).[5] More recently, a grafting-onto approach was used to prepare arborescent polystyrene-*graft*-polyisoprene copolymers.[6] An important feature of arborescent copolymers is that the number and size of the grafted side chains can be varied independently. This translates into extensive control over the morphology and the physical properties of the copolymers. The incorporation of monomers such as 2-vinylpyridine in the synthesis of arborescent copolymers is of considerable interest, because the pyridine moieties can undergo protonation to yield a polyelectrolyte.

The preparation of graft polymers containing P2VP segments has so far been limited to comb-branched structures. Copolymers consisting of a polystyrene backbone and poly(2-vinylpyridine) side chains have been prepared using both grafting-from[7] and grafting-onto[7,8] schemes. The grafting-from strategy, based on the metalation of poly(*p*-bromostyrene) with lithium naphthalenide to serve as a polyfunctional initiator, suffers from the formation of a significant amount of nongrafted poly(2-vinylpyridine). Greater control over the structure of the copolymers is attained when a grafting-onto strategy is employed. The reaction of poly(2-vinylpyridinyl)lithium with partially chloromethylated polystyrene yielded copolymers with a poly(2-vinylpyridine) content ranging from 30 to 72% w/w.[7] However, a significant portion (16−29% w/w) of the poly(2-vinylpyridine) side chains was prematurely terminated by residual impurities or through side reactions.

The synthesis of two series of arborescent copolymers consisting of poly(2-vinylpyridine) segments of different molecular weights grafted onto linear, comb-branched (G0), G1, and G2 randomly chloromethylated arborescent polystyrenes is now reported. Interesting physical properties related to their highly branched structure are observed for these copolymers. For example, their very compact size leads to enhanced molecular expansion upon ionization of the P2VP side chains in solution. This phenomenon was investigated using dynamic light scattering measurements.

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* To whom correspondence should be addressed. E-mail: gauthier@uwaterloo.ca.

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## Experimental Section

**Reagents.** Styrene (Aldrich, 99%), 1,1-diphenylethylene (DPE; Aldrich, 97%), tetrahydrofuran (THF; Caledon, ACS Reagent), and $CCl_4$ (Caledon, ACS Reagent) were purified as previously described.[5] *N*,*N*,*N′*,*N′*-Tetramethylethylenediamine (TMEDA; Aldrich, 99%) and 2-vinylpyridine (2VP; Aldrich, 97%) were first purified by stirring with $CaH_2$ and distillation under reduced pressure. An additional purification step for both reagents, completed immediately before use, is described subsequently. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) and *tert*-butyllithium (Aldrich, 1.7 M in pentane) were used as received. The exact concentration of the *sec*-butyllithium solution was determined using the procedure of Lipton et al.[9] Purified chloromethyl methyl ether (CMME) was prepared as described earlier.[5] The procedures using CMME should be carried out with due caution in a well-ventilated fume hood, since it is a known carcinogen.[10] All other reagents were used as received.

**Partially Chloromethylated Polystyrene Substrates.** Linear, comb-branched (G0), G1, and G2 partially chloromethylated polystyrene samples were synthesized as previously described.[6]

**Arborescent Copolymers.** 2-Vinylpyridine was further purified, prior to polymerization, on a vacuum line using three freezing−evacuation−thawing cycles with $CaH_2$, followed by slow distillation to a glass ampule with a poly(tetrafluoroethylene) (PTFE) stopcock. The ampule was then filled with purified nitrogen and stored at −5 °C until needed. TMEDA was purified on a high-vacuum line using three successive freezing−evacuation−thawing cycles, titration with *tert*-butyllithium until a persistent yellow end point was observed, and slow distillation to a glass ampule with a PTFE stopcock.

The first step in the synthesis of a graft copolymer is the polymerization of 2-vinylpyridine in a stirred glass reactor. After evacuation, flaming, and filling of the reactor with nitrogen, purified THF and the TMEDA solution were added, followed by the DPE solution in THF. The initiator 1,1-diphenyl-2-methylpentyllithium was generated in situ from *sec*-butyllithium and DPE. 2-Vinylpyridine in THF was added dropwise to the solution, resulting in a rapid color change from bright to dark red. After 30 min, a sample of the side chains was removed from the reactor and terminated with degassed methanol. The polymer solution was then warmed to −30 °C and titrated with a solution of chloromethylated polystyrene in THF until a pale orange color was observed. The polymer solution was warmed to room temperature, leading to further fading of the color over 30 min. Residual anions were terminated with degassed methanol. Nongrafted P2VP side chains were removed from the crude grafting product by precipitation fractionation using THF/methanol (4/1 v/v) as a solvent and *n*-hexane as a nonsolvent.

**Characterization.** Size exclusion chromatography (SEC) served to characterize the polystyrene substrates and poly(2-vinylpyridine) side chains, the raw grafting products, and the fractionated graft copolymers. The instrument used consists of a Waters 510 HPLC pump, a Jordi 500 mm DVB linear mixed bed column, and a Waters 410 differential refractometer detector. Tetrahydrofuran containing TMEDA (5% v/v, to prevent the adsorption of P2VP on the column)[11] served as eluent at a flow rate of 1 mL/min. A linear polystyrene standards calibration curve was used to provide apparent (polystyrene-equivalent) molecular weights and molecular weight distributions for the grafting substrates, the graft copolymers, and the poly(2-vinylpyridine) side chains.

The composition of the arborescent copolymers was determined by $^1H$ NMR spectroscopy on a Bruker AM-250 spectrometer after dissolution in $CDCl_3$ at a concentration of 5% w/v.

The absolute weight-average molecular weight ($M_w$) of the polystyrene grafting substrates and of the arborescent graft copolymers was determined from static light scattering measurements. Refractive index increments (d*n*/d*c*) for the graft copolymers were measured in methanol at 25.0 ± 0.1 °C using a Brice-Phoenix differential refractometer with a 510 nm bandpass interference filter. A Brookhaven BI-200 SM light scattering goniometer equipped with a Lexel 2 W argon ion laser operating at 514.5 nm was used for the static light scattering measurements.[5] The absolute $M_w$ was determined by Zimm extrapolation to zero angle and concentration for a series of measurements for 6−8 samples at angles ranging from 30° to 150°.

**Table 1. Characteristics of the Polystyrene Grafting Substrates**

| polymer | $M_w^{br}$ (SEC)[a] | $M_w/M_n^{br}$ (SEC)[a] | $M_w$ (LS)[b] | $f_w$ | $CH_2Cl$[c]/ mol % | grafting sites |
|---|---|---|---|---|---|---|
| PS (linear) | 5420 | 1.09 | n/a | 1 | 26 | 14 |
| G0PS | 5220 | 1.07 | 66 700 | 12 | 22 | 140 |
| G1PS | 6160 | 1.06 | 727 000 | 108 | 20 | 1390 |
| G2PS | 5210 | 1.07 | 5 030 000 | 826 | 16 | 7730 |

[a] Values from SEC analysis using linear PS standards calibration. [b] Absolute $M_w$ of the graft polymers from laser light scattering. [c] Chloromethylation level from $^1H$ NMR spectroscopy.

The hydrodynamic radius of the graft copolymers was determined from dynamic light scattering measurements, for comparison to values obtained for linear poly(2-vinylpyridine) samples (Polymer Source, Inc.). A Brookhaven BI-2030AT 201-channel correlator was used for the measurements. The hydrodynamic radius was determined from the *z*-average diffusion coefficient obtained from cumulant analysis. The results from the first- and second-order cumulant analyses were always compared, to ensure that aggregation of the macromolecules did not occur. Solutions of the copolymers and linear P2VP samples were prepared in methanol and in methanol containing 0.1 N HCl. Both solutions contained 1% v/v water. The concentration of the solutions was adjusted to <0.4% (w/v) to provide a reasonable photon counting rate (≈$10^5$ counts/s). Prior to analysis, each polymer sample was filtered three times through a 0.5 μm PTFE membrane filter into a scintillation vial.

## Results and Discussion

The characteristics of the linear and branched polystyrene substrates used in the preparation of the graft copolymers are summarized in Table 1. The branching functionality of the polymers, defined as the number of chains added in the last grafting reaction, is calculated from the equation

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \qquad (1)$$

where $M_w(G)$, $M_w(G-1)$, and $M_w^{br}$ are the absolute weight-average molecular weight of graft polymers of generation G, of the preceding generation and of the side chains, respectively. All grafting substrates were synthesized using $M_w^{br} \approx 5000$ side chains. The number of potential grafting sites introduced on the substrates is calculated from their molecular weight ($M_w(G)$) and chloromethylation level. In keeping with previous nomenclature,[6] sample identification for the grafting substrates and the graft copolymers specifies their composition and structure. For example, G1PS-P2VP30 refers to a graft copolymer with $M_w^{br} \approx 30\,000$ poly(2-vinylpyridine) (P2VP) side chains grafted onto a G1 (twice-grafted) arborescent polystyrene substrate.

The coupling reaction used in the preparation of the copolymers is provided in Scheme 1. It involves simple nucleophilic displacement of chloride anions by the living macroanions under conditions selected to minimize side reactions. Copolymers with different structures can be synthesized, depending on the generation (linear or G0−G2) of the partially chloromethylated

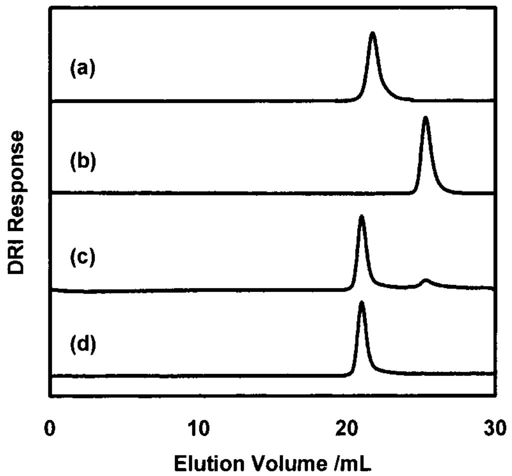
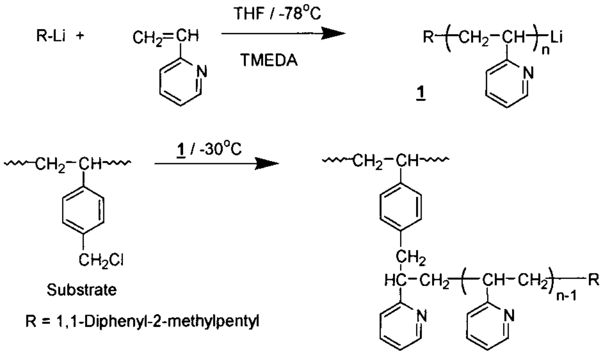


**Figure 1.** Preparation of sample G0PS-P2VP5: SEC traces for (a) chloromethylated G0 (comb) polystyrene substrate, (b) poly(2-vinylpyridine) side chains, (c) raw product from the grafting reaction, and (d) fractionated graft copolymer.

**Scheme 1**



polystyrene substrate and the molecular weight of the P2VP side chains used in the reaction.

The synthesis of an arborescent copolymer sample is illustrated in Figure 1 with a series of SEC traces corresponding to a chloromethylated polystyrene substrate (G0PS), P2VP side chains with $M_w \approx 5\ 000$, the raw grafting product, and the fractionated arborescent graft copolymer. Two peaks are present in the SEC trace for the raw grafting product (curve c). The leftmost (highest molecular weight) peak corresponds to the graft copolymer. The rightmost peak has the same elution volume as the side chain sample removed from the reactor prior to grafting (curve b) and corresponds to nongrafted side chains. These chains are presumably deactivated by residual protic impurities present in the chloromethylated polymer solution or else through side reactions. A comparison of curves a and c indicates that no excess grafting substrate is present in the raw product. This is a consequence of the colorimetric titration procedure used, which allows precise control over the stoichiometry of the grafting reaction. Curve d confirms complete removal of the nongrafted side chains by fractionation.

The fraction of P2VP side chains in the reaction mixture that becomes grafted onto the polystyrene substrate, defined as the grafting yield, can be determined from the SEC trace obtained for the raw product. The refractive index increments in THF for polystyrene ($dn/dc = 0.196$ at 514.5 nm) and poly(2-vinylpyridine) ($dn/dc = 0.180$ at 514.5 nm) are comparable, and therefore the response of the DRI detector can be assumed to be equivalent for each component. Furthermore, the overall composition of the graft copolymers is dominated by the P2VP component. Under these conditions, the ratio of the peak area for the graft copolymer to the total area for both peaks in the SEC trace yields the fraction of P2VP side chains grafted. For example, 89% of the P2VP side chains generated were grafted onto the G0PS substrate in the synthesis of sample G0PS-P2VP5 (Figure 1c). The grafting yield for each reaction can be compared to optimize the grafting conditions.

For the grafting reaction to proceed in high yield, the macroanions must remain "living" during the time required to complete the reaction, and coupling must be favored over side reactions leading to premature termination of the chain ends. This requires the macroanions to be stable, but nonetheless highly nucleophilic, which may be difficult to achieve when attempting to graft macroanions derived from polar monomers such as 2-vinylpyridine. The stability of the macroanions and the rate of the coupling reaction can be controlled to some extent using additives to modify the reactivity of the chain ends and by varying the temperature at which the grafting reaction is carried out. These parameters were systematically investigated to maximize the grafting yield. For each test reaction, a copolymer was prepared consisting of short ($M_w \approx 5\ 000$) P2VP side chains grafted onto a partially chloromethylated $M_w \approx 5\ 000$ linear polystyrene substrate.

**Effect of Additives.** The reactivity of P2VP anions may be increased or decreased, depending on the additive selected. The stability of the macroanions is expected to improve if the nucleophilic character is reduced; however, the rate of the coupling reaction should also decrease. Grafting was attempted at −78 °C in the absence of additives and in the presence of either lithium chloride or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). The results obtained in these experiments are summarized in Table 2.

The addition of excess lithium ions during the anionic polymerization of acrylates and methacrylates in polar solvents has been shown to prevent side reactions that lead to premature chain termination.[13] The presence of LiCl in the polymerization of 2-vinylpyridine has also been shown to have no detrimental effect on the living character of the anions and to facilitate the preparation of block copolymers incorporating poly(*tert*-butyl acrylate) end-blocks.[14] The reactivity of the chain ends is expected to decrease in the presence of excess lithium ions, thereby minimizing side reactions. Experimentally, the grafting yield decreases from 84% in the absence of additives to 77% when a 10-fold excess of lithium ions is present (Table 2). Different side reactions may occur during the anionic polymerization of 2-vinylpyridine: For example, proton transfer from the polymer backbone to the living macroanion results in chain termination,[15] and nucleophilic attack at the carbon α to the nitrogen atom within the pyridine ring can subsequently lead to chain cleavage or the formation of branched products.[16] On the basis of the grafting yield observed, it appears that the presence of excess lithium cations, while decreasing the reactivity of the macroanions, also reduces the rate of the coupling reaction even more than the rate of side reactions.

Considering the negative influence of an increased lithium ion concentration, an alternate method to perturb the dissociation equilibrium using TMEDA was

**Table 2. Effect of Additives and Reaction Temperature on the Grafting Yield**

| | | | side chains[a] | | | graft copolymer[a] | |
|---|---|---|---|---|---|---|---|
| additive | [A]/[LE][d] | temp/°C | $M_w^{app}$ | $M_w/M_n^{app}$ | grafting yield[e] | $M_w^{app}$ | $M_w/M_n^{app}$ |
| none | 0 | −78 | 4 800 | 1.08 | 0.84 | 31 900 | 1.15 |
| LiCl | 10 | −78 | 5 300 | 1.10 | 0.77 | 33 500 | 1.15 |
| TMEDA[b] | 10 | −78 | 5 270 | 1.09 | 0.92 | 33 000 | 1.11 |
| TMEDA[c] | 10 | −78 | 5 190 | 1.08 | 0.93 | 33 100 | 1.16 |
| TMEDA[c] | 10 | −30 | 5 760 | 1.08 | 0.92 | 34 100 | 1.11 |
| TMEDA[c] | 10 | 0 | 4 400 | 1.09 | 0.85 | 28 600 | 1.16 |

[a] Apparent values calculated by SEC analysis using a linear polystyrene standards calibration curve. [b] TMEDA added after complete polymerization of 2-vinylpyridine. [c] TMEDA added prior to the polymerization of 2-vinylpyridine. [d] Ratio of concentration of additive [A] to concentration of living ends [LE]. [e] Calculated from relative peaks areas in the SEC trace for the raw product.

**Table 3. Characterization Data for Arborescent Poly(2-vinylpyridine) Graft Copolymers**

| | side chains | | | graft copolymer | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| copolymer sample | $M_w^{app}$ (SEC)[a] | $M_w/M_n^{app}$ (SEC)[a] | grafting yield [b] | composition[c]/ mol % P2VP | $M_w^{app}$ (SEC)[a] | $M_w/M_n^{app}$ (SEC)[a] | $M_w$ (LS) | $f_w$ | coupling efficiency[d] |
| PS-P2VP5 | 5 200 | 1.08 | 0.92 | 86 | 33 100 | 1.15 | 81 500 | 14 | 100 |
| G0PS-P2VP5 | 5 820 | 1.08 | 0.89 | 90 | 105 300 | 1.11 | 718 000 | 112 | 80 |
| G1PS-P2VP5 | 5 050 | 1.06 | 0.81 | 86 | | | 5 730 000 | 991 | 72 |
| G2PS-P2VP5 | 5 200 | 1.12 | 0.76 | 81 | | | 25 200 000 | 3 880 | 50 |
| PS-P2VP30 | 27 200 | 1.07 | 0.80 | 97 | 165 200 | 1.09 | 415 000 | 14 | 100 |
| G0PS-P2VP30 | 28 600 | 1.08 | 0.65 | 97 | 385 700 | 1.06 | 3 240 000 | 111 | 79 |
| G1PS-P2VP30 | 32 400 | 1.09 | 0.56 | 96 | | | 26 900 000 | 808 | 58 |
| G1PS-P2VP30[e] | 34 400 | 1.09 | 0.26 | 96 | | | 26 800 000 | 758 | 55 |
| G2PS-P2VP30 | 31 200 | 1.10 | 0.40 | 92 | | | 67 100 000 | 1 990 | 26 |

[a] Apparent values based on a linear polystyrene standards calibration curve. [b] Calculated from relative peak areas in the SEC trace for the raw product. [c] Copolymer composition determined using $^1$H NMR spectroscopy. [d] Calculated from branching functionality, $f_w$, and potential grafting sites available. [e] Grafting reaction allowed to proceed for 6 h with 25 mol % excess of P2VP anions.

also investigated with the aim of reducing side reactions. It is known that TMEDA may act as a ligand for the lithium counterion.[17] Consequently, in the presence of excess TMEDA, the nucleophilic character of the P2VP macroanions may increase due to complexation of the lithium ions. For example, the addition of TMEDA prior to grafting polyisoprenyllithium onto partially chloromethylated polystyrenes was shown to enhance the coupling reaction and suppress side reactions.[18] Similarly, the addition of TMEDA was reported to disrupt the aggregation of living polymer chains, leading to increased reactivity for anions derived from ethylene, isoprene, and styrene.[19] The effect of adding TMEDA either prior to polymerization or immediately before grafting of the P2VP chains was examined. In both cases, the grafting yield was increased from 84% in the absence of additives to 92−93% at −78 °C with TMEDA (Table 2).

**Effect of Grafting Temperature.** It has been shown that the temperature at which the grafting reaction is carried out can influence the grafting yield in the preparation of arborescent polystyrenes.[2] This is a consequence of metal−halogen exchange competing with coupling. Capping the highly nucleophilic polystyryl anions with 1,1-diphenylethylene was shown to suppress metal−halogen exchange and increase the grafting yield. On the other hand, it has also been reported that the grafting yield for the reaction of P2VP anions with chloromethylated polystyrene proceeds in high yield, essentially independently of the reaction temperature, when potassium is used as a counterion.[7] Since the addition of TMEDA leads to increased grafting yields, the effect of temperature in the presence of TMEDA was examined in this study.

In the presence of TMEDA, the grafting yield is maximized in the low-temperature range (−78 to −30 °C, Table 2) and decreases slightly at 0 °C. Coupling of the chloromethylated substrate with the 2-vinylpyridine rings of the side chains by quaternization rather than according to Scheme 1 could be of concern, in particular at higher reaction temperatures (0 °C). However, the occurrence of such side reactions may be ruled out under the conditions used: Intermolecular quaternization reactions would lead to significant broadening of the molecular weight distribution, which is not observed in SEC analysis of the grafting products. Based on the results obtained, all coupling reactions discussed subsequently were carried out at −30 °C in the presence of TMEDA.

**Arborescent Polystyrene-*graft*-poly(2-vinylpyridine) Copolymers.** Two series of arborescent polystyrene-*graft*-poly(2-vinylpyridine) copolymers were synthesized by grafting either short ($M_w \approx 5000$, P2VP5) or long ($M_w \approx 30\,000$, P2VP30) poly(2-vinylpyridine) side chains onto partially chloromethylated polystyrene substrates of different generations (Table 1). Characterization data for the copolymers obtained are summarized in Table 3. The low apparent polydispersity index values obtained ($M_w/M_n \leq 1.12$) demonstrate that good control was maintained over the molecular weight distribution of the P2VP side chains under the conditions used.

When P2VP side chains are grafted onto randomly chloromethylated polystyrene substrates of different generations, the grafting yield (the fraction of available P2VP side chains that is grafted onto the substrate) ranges from 40% to 92% (Table 3). The grafting yield decreases in both the P2VP5 and P2VP30 series when the polystyrene substrates are more highly branched (G0, G1, and G2). Dependence of the grafting yield upon the length of the P2VP grafts is also observed: Comparison of the grafting yield for substrates of the same generation shows that the yield is always lower for the P2VP30 copolymers. This effect is most noticeable for the G2 polystyrene substrates for which the grafting yield decreases from 76% to 40% for samples G2PS-

P2VP5 and G2PS-P2VP30, respectively (Table 3). This large decrease is attributed to the lower concentration of living ends present when grafting P2VP30 side chains and a concomitant increased susceptibility to impurities.

Weight-average molecular weights in the ranges $M_w = 8.2 \times 10^4 - 2.5 \times 10^7$ and $4.2 \times 10^5 - 6.7 \times 10^7$ were obtained using static light scattering measurements for the P2VP5 and P2VP30 copolymer series, respectively. The corresponding branching functionalities ($f_w$, calculated using eq 1) range from 14 to 3880 for the P2VP5 series and from 14 to 1990 for the P2VP30 series. The coupling efficiency (Table 3), defined as the fraction of available chloromethyl sites consumed in the coupling reaction, is calculated by comparing $f_w$ and the number of available grafting sites on the substrate (Table 1). The trends observed for $f_w$ and the coupling efficiency are consistent with those obtained for the grafting yield: Both decrease for longer P2VP side chains and for higher polystyrene substrate generations. In the case of the linear polystyrene substrate, all available grafting sites are reacted.

Since the chloromethyl groups are presumably distributed randomly throughout the polystyrene substrate, all sites should have the same reactivity. On the other hand, when the substrate is more highly branched, the structure becomes more congested. As the grafting reaction proceeds, steric congestion leads to differential accessibility for the remaining chloromethyl sites, and the coupling efficiency decreases. The morphology of arborescent polystyrenes was probed using fluorescence quenching techniques to show that the inner portion of the molecule was less accessible to quencher molecules than chains in the outer layer.[20] The fraction of less accessible material was found to increase for higher generation polymers.

A grafting reaction, aimed at increasing the coupling efficiency, was allowed to proceed for 6 h with a 25% excess of poly(2-vinylpyridine) macroanions. The reaction of the G1PS substrate and $M_w \approx 30\,000$ P2VP side chains was used for this purpose. In contrast, the standard method consists of titrating the living P2VP anions solution with a solution of the chloromethylated substrate over approximately 1 h. In the presence of excess living ends, the deep red coloration of the solution persists over the course of the reaction. Residual anions are then terminated with degassed methanol to yield a clear solution. As expected, the grafting yield decreases from 56% to 26%, due to the excess of living ends present. However, the absolute molecular weight, branching functionality, and coupling efficiency obtained are virtually identical to those for a 1 h reaction time (Table 3). This confirms that the coupling efficiency is limited by the extent of steric congestion within the molecules and not by the experimental conditions used. On the basis of these results, grafting shorter P2VP side chains, grafting onto a less congested polystyrene substrate, or decreasing the chloromethylation level would be expected to increase the coupling efficiency.

Composition analysis indicates that the graft copolymers are dominated by the P2VP component, ranging from 81 to 90 mol % and 92 to 97 mol % for the P2VP5 and P2VP30 series, respectively (Table 3). This demonstrates that graft copolymers with a significant polystyrene component can be prepared if short P2VP (or alternately fewer) segments are grafted. The polystyrene content becomes negligible when longer P2VP segments are used. It is thus possible to control the composition of the copolymers, depending on the size and number of P2VP segments used.

**Table 4. Hydrodynamic Radii from Dynamic Light Scattering**[a]

| sample | $R_h$ (MeOH)/nm | $R_h$ (0.1 N HCl in MeOH)/nm |
|---|---|---|
| G0PS-P2VP5 | 12.8 ± 0.1 | 14.9 ± 0.1 |
| G1PS-P2VP5 | 25.1 ± 0.3 | 28.4 ± 0.2 |
| G2PS-P2VP5 | 34.4 ± 0.2 | 37.2 ± 0.2 |
| PS-P2VP30 | 12.6 ± 0.1 | 17.4 ± 0.1 |
| G0PS-P2VP30 | 26.8 ± 0.2 | 36.5 ± 0.2 |
| G1PS-P2VP30 | 38.9 ± 0.2 | 48.8 ± 0.2 |
| G2PS-P2VP30 | 44.5 ± 0.2 | 56.3 ± 0.3 |
| P2VP173 | 13.9 ± 0.1 | 14.7 ± 0.1 |
| P2VP370 | 18.4 ± 0.1 | 19.3 ± 0.1 |
| P2VP938 | 23.9 ± 0.1 | 25.4 ± 0.1 |

[a] The errors reported are standard deviations for a series of 10 measurements.

**Solution Properties.** Comparison of the absolute molecular weights obtained from light scattering measurements with the apparent values from size exclusion chromatography (SEC) shows that the graft copolymers have a very compact structure (Table 3). The copolymers based on the G1PS and G2PS substrates do not elute from the SEC column. The molecular weights are significantly underestimated using SEC, but the apparent molecular weight distribution remains narrow ($M_w/M_n \leq 1.15$) for all samples characterized. The hydrodynamic volumes of arborescent and linear P2VP can be compared on the basis of published intrinsic viscosity data for the linear polymers. Using the Mark–Houwink–Sakurada (MHS) constants $k = 0.0113$ mL/g and $\alpha = 0.73$ for linear P2VP in methanol at 25 °C,[21] the intrinsic viscosity $[\eta]$ and the hydrodynamic volume can be calculated for linear polymers. Keeping in mind that the literature MHS data were determined in a molecular weight range of $3-93 \times 10^4$, it is only possible to directly compare the hydrodynamic volumes for a linear polymer and for arborescent polymer sample G0PS-P2VP5 ($M_w = 7.18 \times 10^5$). The hydrodynamic radius determined in methanol for G0PS-P2VP5 is $R_h = 12.8$ nm (Table 4), for a hydrodynamic volume $V_h(\text{arb}) = 8780$ nm$^3$. The corresponding $V_h(\text{lin})$ for the linear polymer based on the MHS data is 101 000 nm$^3$. The arborescent polymer is therefore $V_h(\text{lin})/V_h(\text{arb}) = 11.5$ times more compact. Similar calculations for the higher generation arborescent polymers, while requiring extrapolation well outside of the molecular weight range used to establish the MHS correlation (and as such not valid), yield much larger hydrodynamic volume ratios [for example, $V_h(\text{lin})/V_h(\text{arb}) = 280$ for G2PS-P2VP5]. This result, while questionable in absolute terms, is at least indicative of the highly compact structure of the arborescent P2VP copolymers in solution.

The compact molecular structure of the copolymers should yield interesting solution properties. In particular, changes in the molecular dimensions upon partial ionization of the P2VP side chains were investigated in dilute solutions using dynamic light scattering (DLS) measurements.

All the copolymer samples synthesized are freely soluble in methanol and in dilute HCl solutions in methanol or water. Clear solutions are obtained for the copolymers based on linear, G0, and G1 polystyrene cores. Solutions of the copolymers based on the G2 polystyrene core are opalescent. To investigate molecular expansion upon ionization, the hydrodynamic radius of the arborescent copolymer molecules was

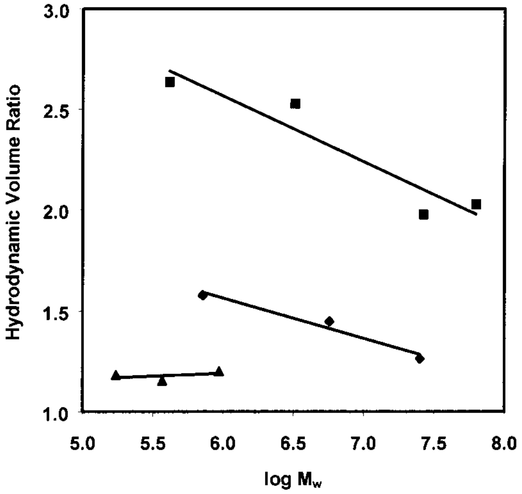


**Figure 2.** Molecular weight dependence of hydrodynamic volume expansion for linear P2VP (▲), P2VP5 (◆), and P2VP30 (■) arborescent copolymers. Volume expansion is expressed as the ratio of hydrodynamic volumes in acidic methanol (ionized) and in pure methanol (neutral).

determined using dynamic light scattering measurements in methanol and in methanol containing 0.1 N HCl (i.e., in excess of the number of equivalents of 2-vinylpyridine units in the copolymer). The diluted methanolic HCl solution was obtained by adding 1% v/v of a concentrated aqueous (10 M) HCl solution to methanol. To account for the presence of water in the acidified solutions, the same amount of water (1% v/v) was also added for the measurements in methanol. The hydrodynamic radius measurements for the neutral and ionized copolymers are compared in Table 4 and were reproducible to within 0.1–0.3 nm. The values obtained from first- and second-order cumulant analyses were in excellent agreement (±3–6%), as expected for molecules of uniform size. Furthermore, for the data reported in Table 4, the increase in hydrodynamic radius upon ionization is much less than would be expected in the presence of molecular aggregation. For sample PS-P2VP5, in contrast, the first- and second-order cumulant analysis data differed by ca. 40–50%, and successive runs yielded irreproducible results. This is presumably due to aggregation of the molecules.

The hydrodynamic radius increase upon protonation may alternately be expressed as the ratio of hydrodynamic volumes ($V_h = 4\pi R_h^3/3$) in acidic methanol (mostly ionized) and in pure methanol (neutral) based on the data reported in Table 4. The influence of structure on molecular expansion due to the polyelectrolyte effect can be explored by comparing the volume expansion factors for the graft copolymers to the hydrodynamic volume ratios determined for linear P2VP samples ($M_w = (1.73-9.38) \times 10^5$). The linear polymers were selected for their hydrodynamic radius that is comparable to some of the branched copolymers in the neutral state. The hydrodynamic volume expansion factors determined for the linear P2VP samples and for the two series of graft copolymers with $M_w \approx 5000$ (P2VP5) and $M_w \approx 30\ 000$ (P2VP30) P2VP side chains are compared in Figure 2. The increase in hydrodynamic volume upon protonation is much greater for the branched copolymers than for linear P2VP. This effect is attributed to increased charge density and electrostatic repulsions inside the branched copolymers, due to the very compact structure of the molecules. The volume expansion ratio is greatest for the copolymers with long, flexible P2VP30 side chains. Enhanced molecular expansion in these copolymers can be explained by further uncoiling of the long, flexible P2VP30 side chains (relative to the stiffer P2VP5 chains) under the influence of electrostatic repulsions, as shown in Figure 3.

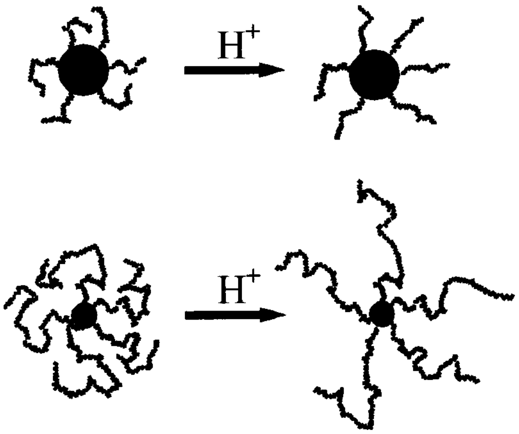


**Figure 3.** Comparison of the structure and the molecular expansion behavior of arborescent copolymers with short (top) and long (bottom) P2VP side chains due to the polyelectrolyte effect. The solid core represents the collapsed polystyrene substrate, and molecular expansion is purposely exaggerated to illustrate the effect.

Interestingly, within each series of arborescent copolymers, the hydrodynamic volume expansion ratio decreases for higher generations (Figure 2). Two factors may contribute to this trend, namely changes in the copolymer composition and in the structural rigidity of the molecules.

The arborescent copolymers with short ($M_w \approx 5000$) P2VP side chains have a significant polystyrene content (10–19 mol %) increasing for higher generations. The increased polystyrene content of the copolymers therefore correlates with the lower expansion factor observed for higher generation molecules. On the other hand, increased structural rigidity is also expected for higher generation copolymers with short P2VP side chains, due to their high branching functionality. A study of the solution properties of arborescent polystyrenes has indeed demonstrated that molecules with short ($M_w \approx 5000$) polystyrene side chains become more rigid for higher generations.[22] Under these conditions molecular expansion due to electrostatic repulsions is opposed by elastic forces linked to increased structural rigidity within the molecules.

The relative influence of composition vs. structural rigidity effects on molecular expansion may be clarified when considering the behavior of the P2VP30 series samples. The composition of the copolymers with long ($M_w \approx 30\ 000$) side chains is strongly dominated by the P2VP component (92–97 mol %), and solution properties consistent with P2VP homopolymers would be expected for these samples. The fact that a decrease in the expansion ratio is also observed for this sample series strongly suggests that increased structural rigidity for higher generation molecules is the dominant factor leading to decreasing molecular expansion.

## Conclusions

The results reported demonstrate that it is possible to prepare arborescent graft copolymers consisting of poly(2-vinylpyridine) side chains randomly grafted onto a partially chloromethylated arborescent polystyrene substrate. The efficiency of the coupling reaction between poly(2-vinylpyridine) anions and chloromethyl sites improves in the presence of TMEDA, presumably due to the increased reactivity of the anions. Dynamic light scattering measurements indicate that the arborescent poly(2-vinylpyridine) copolymers expand considerably more than linear homologous polymers when protonated with HCl. This effect is attributed to the higher charge density attained inside the highly branched copolymers.

The data obtained suggest that, by varying the structure of the copolymers, the physical properties of arborescent P2VP copolymers in solution can be controlled to a large extent. One way this can be achieved is by varying parameters such as the length and number of the P2VP segments and the size (generation) of the polystyrene substrate. Control over these parameters may enable the design of pH-sensitive reversible gels with controllable properties such as sol−gel transition point and gel modulus.

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