Anionic Synthesis of Graft Block Copolymers with Poly(2-vinylpyridine) Trunks: Effects of Trunk and Branch Molecular Weights

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Recently we synthesized polystyrene (PS)–poly(2-vinylpyridine) (PVP)–polybutadiene (PB) three-block polymers *via* coupling of living PB anions with PS–PVP–Cl diblock prepolymers having benzyl chloride groups at the PVP ends.[1] During the course of study, we found that the coupling was disturbed by a side reaction of bare PB anions with 2-vinylpyridine groups that proceeded quite likely *via* a mechanism reported by Tardi and Sigwalt[2] and Luxton et al.[3] (Scheme 1). This grafting reaction was efficiently suppressed by converting the living PB ends to less reactive diphenylethylenyl (DEP) anions, and this fact was utilized to successfully obtain the linear PS–PVP–PB block polymers.[1] This reaction, unfavorable for making linear block polymers, in turn provides an interesting and easy route to synthesize graft block copolymers having PVP chains as the trunk. From this point of view, we have examined features of the grafting reaction of polyisoprene (PI) and PS anions onto homo-PVP chains without any functionalized ends. (PI anions are chemically similar to PB anions.) We here present the results.

All reactions were carried out in high vacuum, and all chemical reagents used were purified with standard methods.[4,5] PVP anions were polymerized with DPE-Li^+ in tetrahydrofuran (THF) and terminated with a prescribed amount of methanol (≅4 times excess to the anions) diluted with THF. Both polymerization and termination steps were carried out at −78 °C. The resulting PVP chains were thoroughly dried (to remove excess methanol) and finally redissolved in pure THF. PS and PI living anions were synthesized with *sec*-butyllithium at room temperature in benzene and heptane, respectively. After polymerization was completed, the solvents were switched to THF *via in situ* vacuum distillation. Then, the PS or PI anions in THF were allowed to be grafted on the PVP chains at 0 °C. (For some cases, the grafting reaction was carried out also at 30 °C, but the product was the same.) The reaction was monitored on a gel permeation chromatograph (GPC; Tosoh HLC-8) having a combined refractive index (RI) and low-angle laser light scattering (LS) detector (Tosoh Model LS-8000) and an ultraviolet (UV) spectrometer (Tosoh UV-8000). The elution solvent was THF, and antiadsorption columns (Tosoh G-4000 H_{XL} and G-5000 H_{XL}) were used.

In the reaction mixtures, the PI or PS concentration C_{branch} was always ≅5 wt %. The amount of PVP chains was adjusted in such a way that the *molar* concentration of 2-vinylpyridine groups (not the PVP chains as a whole) was 5–10 times larger than that of PI or PS anion ends. Thus on the *weight* basis the anion/PVP ratio was much larger than unity. Under such conditions excess (unreacted) anions always remained after the reaction (cf. Figure 1).

As an example of GPC traces of prepolymers and reaction products, Figure 1 shows those obtained for a reaction of PVP and PI-Li^+ (with molecular weights 79.7K and 56.2K, respectively). Similar traces were obtained for all cases examined. In Figure 1, the solid, dashed, and dotted curves indicate the RI, UV, and LS signals, respectively. The signal sensitivities are reduced to be the same for all traces a–d. The RI increment per unit mass is roughly the same for PVP and PI, while the UV absorption (λ = 254 nm) per unit mass is very large for PVP but negligibly small for PI (cf. parts a and b). Thus, in Figure 1 the changes of PI/PVP composition due to the grafting reaction are seen as the changes of the RI/UV signal ratio. In addition, through the LS/RI signal ratio, we can examine changes of the molecular weight during the reaction.

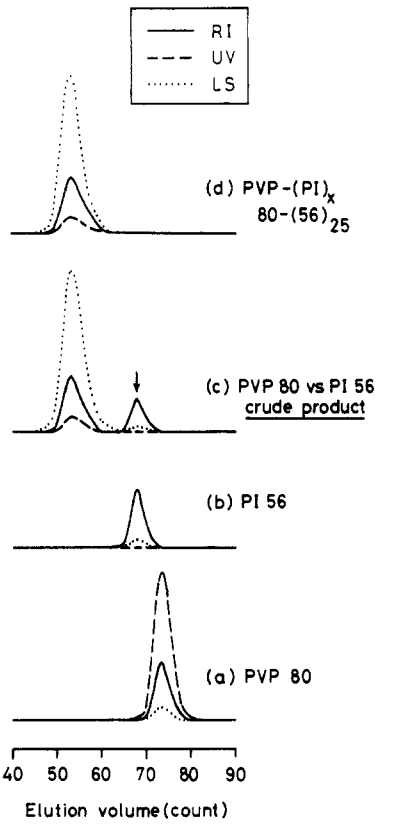

Figure 1. Changes of GPC traces during a course of synthesis of a PVP-(PI)$_x$ 80-(56)$_{25}$ graft block copolymer. The solid, dashed, and dotted curves indicate the RI, UV, and LS signals, respectively. The signal sensitivities are the same for all traces a–d. The arrow in part c indicates excess PI anions left in the reaction mixture.

As noted for traces a–c of Figure 1, the GPC peak of the PVP chains shifts to lower elution volume side on reaction with PI anions, and the RI/UV and LS/RI signal ratios drastically increase. These changes were accompanied with an almost immediate color change (from pale yellow to orange-red) and a drastic increase of the viscosity of the reaction mixture. Trace c clearly indicates that excess PI anions are left (cf. arrow). The amount of those PI anions remained the same when the reaction was conducted for 20 min at 0 °C and for 15 h at 30 °C. Thus, the reaction was rapidly completed, yielding graft block copolymers PVP-(PI)$_x$, with PVP trunks and PI branches, as in the case for PB anions (Scheme 1). We also confirmed that practically no grafting reaction took place when the PI ends were converted to DPE anions.[6] Finally, the crude product was fractionated from benzene/heptane/methanol mixtures to isolate the graft block copolymer (trace d). As seen from traces c and d, the copolymer has a relatively narrow molecular weight distribution. Thus the grafting points may be rather regularly spaced along the PVP trunk.

The prepolymers and graft block copolymers were characterized with GPC. For PI and PS prepolymers, the

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Scheme 1

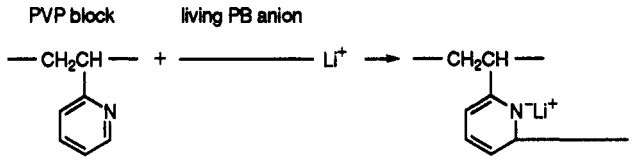

Table 1. Characteristics of PVP, PI, and PS Prepolymers

code[a]	$10^{-3}M_w$	M_w/M_n
PVP (Used as a Trunk)		
PVP-13	13.0	1.04
PVP-32	32.0	1.06
PVP-80	79.7	1.06
PVP-187	187	1.07
PI[b] (Used as a Branch)		
PI-14	13.7	1.04
PI-18	17.6	1.04
PI-35	34.8	1.05
PI-56	56.2	1.05
PS (Used as a Branch)		
PS-19	19.4	1.04
PS-31	30.9	1.05
PS-64	64.0	1.04

[a] Sample code indicates the molecular weight in units of 1000. [b] cis/trans/vinyl ≅ 75/20/5.

weight-average molecular weights M_w and heterogeneity indices M_w/M_n were determined from elution volume calibration for the RI signals. Previously made and characterized monodisperse PI's[7] and commercially available monodisperse PS's (Tosoh TSK's) were used as the elution standards. For PVP prepolymers, M_w were determined by LS. Using these M_w values, we made an elution volume calibration for the PVP prepolymers and determined their M_w/M_n ratios. The characteristics of all prepolymers are summarized in Table 1.

For the PVP–$(PI)_x$ and PVP–$(PS)_x$ graft block copolymers, the (apparent) M_w/M_n ratio was evaluated from the elution volume calibration made with standard PI and PS. The PVP content, ϕ_{PVP}, was determined from the UV and RI signal intensities, A_{RI} and A_{UV}, through a relationship valid for dilute copolymer solutions:

$$\frac{A_{RI}}{A_{UV}} = \frac{K_{RI}[\nu_J(1-\phi_{PVP}) + \nu_{PVP}\phi_{PVP}]}{K_{UV}[\epsilon_J(1-\phi_{PVP}) + \epsilon_{PVP}\phi_{PVP}]} \quad (J = \text{PI or PS}) \tag{1}$$

Here, ν_J and ϵ_J are the RI increment and UV absorption per unit mass of prepolymer J (J = PVP, PI, or PS), and K_{RI} and K_{UV} are the instrumental constants. The products $K_{RI}\nu_J$ and $K_{UV}\epsilon_J$ were determined from the data for the prepolymer J. Thus, applying eq 1 to the data for the prepolymers and graft block copolymers, we determined ϕ_{PVP} and calculated the copolymer molecular weight as $M_{g\text{-}b} = M_{PVP}/\phi_{PVP}$, with M_{PVP} being the molecular weight of the PVP prepolymer. The results are summarized in Table 2. ($M_{g\text{-}b}$ values were evaluated also from the LS and RI signals,[8] and the results agreed within 10% with those summarized in Table 2.)

From the $M_{g\text{-}b}$ values, we calculated the number of branches per trunk, $x = [M_{g\text{-}b} - M_{PVP}]/M_J$ (J = PS or PI), and further the average molecular weight for a *span* of the PVP trunk between neighboring branches, $M_{span} = M_{PVP}/x$. As seen in Table 2, M_{span} are much smaller than M_{PVP} of the trunk as a whole but are considerably larger than the monomeric molecular weight of 2-vinylpyridine (=105). Namely, the branches are densely grafted on the trunk but not on *all* 2-vinylpyridine groups. In this sense, the grafting reaction was imperfect. However, excess PI or PS anions were left in the reaction mixture (cf. arrow in part c of Figure 1), and the imperfect grafting is not due to a lack of anions. The origin of the imperfect grafting is further examined in Figure 2, where M_{span} is plotted against M_{trunk} (=M_{PVP} of the PVP chain) and M_{branch} (=M_{PI}, M_{PS}). As seen there, M_{span} is essentially independent of M_{trunk} unless M_{trunk} is very large (part a), and M_{span} increases with M_{branch} (part b). We also note that M_{span} is larger for PI branches (unfilled circles) than for PS branches (filled circles).

Table 2. Characteristics of Graft Block Copolymers

code[a]	$M_{g\text{-}b}$[b]	M_w/M_n	$10^{-3}M_{span}$[c]	prepolymer: trunk	prepolymer: branch
PVP–$(PI)_x$					
13-$(18)_6$	123	1.15	2.1	PVP-13	PI-18
32-$(18)_{13}$	262	1.15	2.5	PVP-32	PI-18
80-$(18)_{40}$	777	1.13	2.0	PVP-80	PI-18
187-$(18)_{46}$	995	1.12	4.1	PVP-187	PI-18
80-$(14)_{65}$	976	1.13	1.2	PVP-80	PI-14
80-$(35)_{28}$	1070	1.12	2.8	PVP-80	PI-35
80-$(56)_{25}$	1460	1.15	3.3	PVP-80	PI-56
PVP–$(PS)_x$					
13-$(19)_7$	148	1.08	1.9	PVP-13	PS-19
80-$(19)_{54}$	1130	1.08	1.5	PVP-80	PS-19
80-$(31)_{49}$	1590	1.16	1.6	PVP-80	PS-31
80-$(64)_{32}$	2110	1.07	2.5	PVP-80	PS-64

[a] Sample code indicates the molecular weight of prepolymers in units of 1000 and the number x of branches per trunk. [b] $M_{g\text{-}b}$ were determined from the UV and RI signal intensities (cf. eq 1).[8] [c] Average molecular weight of the PVP span between branches.

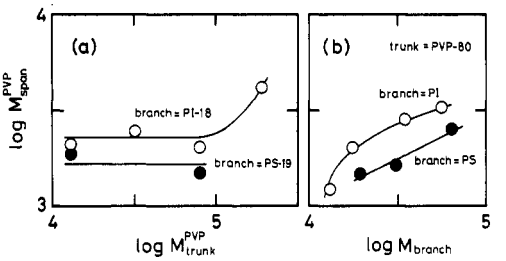

Figure 2. Plots of the molecular weight of the PVP span between branches against (a) the total molecular weight of the trunk and (b) the branch molecular weight. Unfilled and filled circles indicate the data obtained for PI and PS branches, respectively.

In the reaction mixture of $C_{branch} \cong 5$ wt %, segregation of the PVP trunk and PI or PS branches is enhanced for larger M_{trunk} and the grafting reaction tends to be suppressed. The increase of M_{span} seen for the highest M_{trunk} (part a of Figure 2) appears to be due to this segregation. However, for smaller M_{trunk}, M_{span} is essentially independent of M_{trunk} and effects of segregation are hardly observed. For such cases, the increase of M_{span} with M_{branch} seen in part b suggests that interactions between the branches determine M_{span}: When the branches are crowded on a trunk, they would not allow further grafting reaction to take place. From this point of view, it is interesting to compare the spatial size of the branches with that of the PVP span between the branches.

If the PI or PS branches are very long and dilute in the reaction mixture, their radius of gyration in THF (a good solvent), R_g, should be considerably larger than that in the unperturbed state, R_g^θ. However, the grafting reaction was carried out for rather short branches for which the excluded-volume effect is not significant.[9] In addition, the reaction mixture was moderately concentrated ($C_{branch} \cong 5$ wt %), and this effect should have been further screened. For such cases, R_g^θ is a good measure for the branch size in the reaction mixture. For the PVP span between neighboring branches, a fully stretched length

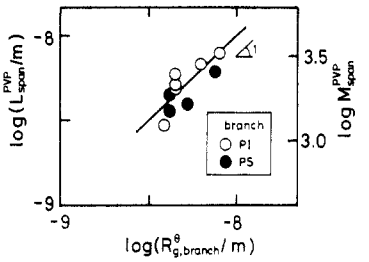

Figure 3. Plots of the fully stretched length L_{span} of the PVP span of molecular weight M_{span} against the unperturbed radius of gyration R_g^{θ} of the branches. L_{span} for the longest PVP trunk appears to be affected by segregation of the PVP and PI prepolymers in the reaction mixture (cf. Figure 2a) and is not involved in the plots.

L_{span} can be used as a measure for its size because the densely grafted branches would tend to stretch the trunk.[10] Thus, we evaluated R_g^{θ} values for the PI and PS branches from empirical equations reported in the literature[11,12] and compared them with $L_{span} = 2.4 \times 10^{-12} M_{span}$ (m). The results are shown in Figure 3. We note that the L_{span} vs R_g^{θ} plots are roughly the same for the PI and PS branches. The data points are collapsed around the solid line that indicates a relationship, $L_{span} = R_g^{\theta}$.

As the grafting reaction proceeds and the branches become crowded on the trunk, the trunk would be locally stretched to some extent so that the repulsion between the branches can relax. In other words, at earlier stages of the grafting reaction, the energy gain associated with the reaction would overwhelm the loss of conformational freedom of the trunk. However, when the reaction proceeds to some point where L_{span} is comparable to R_g^{θ} of the branches (cf. Figure 3), it would become difficult to further stretch the trunk and relax the repulsion between the grafted branches. Then, the branches crowded on a trunk would behave as an osmotic barrier for the PI or PS prepolymer anions left in the reaction mixture, and the grafting reaction would stop.

The grafting reaction involving nitranion formation (cf. Scheme 1) should be highly exothermic and thus irreversible. From this point of view, it seems reasonable to explain the imperfect grafting from a kinetic aspect, as we did above. However, it is also interesting to consider a thermodynamic aspect of the grafting reaction. Recently, Fredrickson[10] considered aggregation of surfactants (branches) on a polymer chain and calculated an equilibrium grafting density σ ($\propto 1/L_{span}$). He found that σ is essentially scaled as $M_{branch}^{-3/5}$ when the excluded-volume effect expands the branches. If this effect is very small (as for our systems), σ should be scaled as $M_{branch}^{-1/2}$, leading to the relationship $L_{span} \cong R_g^{\theta}$ found in Figure 3. Thus, this relationship is expected from both kinetic and thermodynamic aspects, although the kinetic aspect seems to be essential for the grafting reaction examined in this study.

In summary, we have found that graft block copolymers are easily obtained through the reaction of PVP trunks and bare anions of PI and/or PS branches. L_{span} are close to R_g^{θ} for both PI and PS branches, suggesting that the repulsion between the branches is an essential factor that determines L_{span} kinetically. Quantitative discussion on the relationship of L_{span} with R_g and C_{branch} of the reaction mixture requires detailed knowledge for the osmotic and elastic free energies of the branches, those of the trunk, and the energy of reaction. This discussion is considered as interesting future work.

References and Notes

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(6) Negligible grafting reaction of the PI-DPE-Li^+ and PVP prepolymers found in this study is consistent with our previous result that the reaction of PB-DPE-Li^+ and end-chlorinated PS-PVP-Cl prepolymers took place selectively at the chain ends to yield linear PS-PVP-PB three-block polymers.[1]
(7) Yoshida, H.; Watanabe, H.; Adachi, K.; Kotaka, T. *Macromolecules* **1991**, *24*, 2981.
(8) M_{g-b} of the graft block copolymers made in this study are much larger than M_{PVP} of the PVP trunks (cf. Table 2), and the LS and RI signals of those copolymers are mainly from the branches (PI or PS). For such cases, a standard LS equation valid for homopolymers can be used to estimate M_{g-b} from those signals. The results agreed within 10% with those of Table 2.
(9) R_g is not very different from R_g^{θ} for the branches used, and the reduced plots shown in Figure 3 hardly change even when R_g is used as the branch size.
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