Well-Defined Graft Copolymers Based on the Selective Living Anionic Polymerization of the Bifunctional Monomer 4-(Vinylphenyl)-1-butene

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ABSTRACT: The anionic copolymerization of the bifunctional monomer 4-(vinylphenyl)-1-butene (VSt) with styrene (St) was carried out in a mixture of toluene and tetrahydrofuran (THF), using *n*-BuLi as initiator, at −40 °C. During this process, the styrene type C═C bond of VSt was selectively polymerized, and the other one in its butenyl moiety remained unchanged. The molecular weight and the composition of the resulting copolymer could be well-controlled, and its molecular weight distribution was very narrow (M_w/M_n = 1.03−1.04). The unreacted butenyl groups of the VSt units were further reacted with chlorodimethylsilane, generating another functional copolymer with reactive chlorodimethylbutylsilyl side chains. This functional polymer was used as a backbone polymer and reacted with the anionic living polymers of St, isoprene (Is), or methyl methacrylate (MMA). This coupling reaction resulted in the formation of well-defined graft (co)polymers with a poly(St) backbone and either poly(St) or poly(Is) or poly(MMA) side chains.

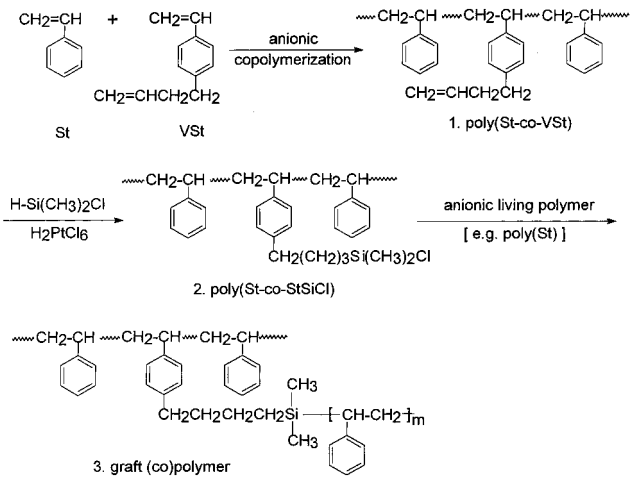
Introduction

The "grafting onto" method has been often employed for the preparation of graft (co)polymers by the anionic polymerization technique.[1] This method is based on the coupling reaction of the electrophilic groups attached to the backbone polymer and the propagating site of an anionic living polymer.[2] The key point of this method is to generate a backbone polymer that possesses suitable reactive groups. The scope of the present paper is to present a novel route to functional polymers with electrophilic groups and further to well-defined graft (co)polymers, based on the selective living anionic polymerization of a new bifunctional monomer.

Recently, we have investigated the anionic homopolymerization of the novel bifunctional monomer 4-(vinylphenyl)-1-butene (VSt) and its block copolymerization with styrene (St).[3] Under suitable conditions, the styrene type C═C bond of VSt could be selectively polymerized, generating a uniform-size functional polymer with a reactive butenyl group in each of its repeating units. The further reaction of the butenyl side chains of homopoly(VSt) or of the block copolymer poly(VSt-*b*-St) with 9-borabicyclo[3.3.1]nonane, followed by the addition of NaOH and H_2O_2, generated a new uniform-size hydrophilic functional polymer poly(4-hydroxybutylstyrene) or an amphiphilic block copolymer containing both poly(4-hydroxybutylstyrene) hydrophilic and poly(St) hydrophobic segments.

In the present paper, we will further demonstrate the advantages of the selective living polymerization of the novel bifunctional monomer by employing the resulting functional polymer in the preparation of well-defined graft (co)polymers. First, the anionic copolymerization of VSt and St was carried out (Scheme 1). Similar to the homo- and block copolymerizations, the resulting copolymer, poly(St-*co*-VSt) (1 in Scheme 1), possesses an unreacted C═C bond in each of its VSt units. Subsequently, this functional side chain was reacted with chlorodimethylsilane, producing another new functional copolymer, poly(St-*co*-StSiCl) (2 in Scheme 1), with reactive chlorosilyl side chains. The further coupling reaction of these side chains with the anionic living polymers of either St, or isoprene (Is), or methyl methacrylate (MMA) generated well-defined graft (co)polymers (3 in Scheme 1) with a poly(St) backbone and either poly(St) or poly(Is) or poly(MMA) side chains.

Scheme 1



Experimental Section

Materials. Tetrahydrofuran (THF) was dried with CaH_2 under reflux for more than 24 h, distilled, and distilled again from a solution of sodium naphthalenide just before use. Toluene and benzene were washed with concentrated sulfuric acid and then with water, dried with $MgSO_4$, distilled over CaH_2, and finally distilled from a *n*-BuLi solution. Hexane was first dried and distilled over CaH_2 and then distilled from a solution of *n*-BuLi. Vinylbenzyl chloride (VBC; Aldrich, 97%) was dried with CaH_2 and distilled under reduced pressure. Styrene (St; Aldrich, 99%) and isoprene (Is; Aldrich, 99%) were washed with 10 wt % aqueous NaOH solution and then with water, dried overnight with $MgSO_4$, distilled over CaH_2, and finally distilled in the presence of phenylmagnesium chloride prior to polymerization. Methyl methacrylate (MMA; Aldrich,

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99%) was washed and purified in a way similar to that used for St and Is, except the final distillation was carried out in the presence of triisobutylaluminum.[4] 1,1-Diphenylethylene (DPE; Aldrich, 97%) was distilled over CaH_2 and then distilled in the presence of 1,1-diphenylhexyllithium (DPHL) under reduced pressure. Lithium chloride (99.99%, Aldrich) was dried at 120 °C for 24 h and dissolved in purified THF.[5] Hydrogen hexachloroplatinate (Aldrich) was dissolved in propanol (5 wt %), and this solution was directly used. Chlorodimethylsilane (98%, Aldrich) was distilled under the protection of N_2 before use. *n*-BuLi (Aldrich, 1.6 M solution in hexane) was diluted with purified hexane. Allylmagnesium chloride (AMC; Aldrich, 2.0 M solution in THF) was used as received. The bifunctional monomer, 4-vinylphenyl-1-butene (VSt), was prepared via the coupling reaction between VBC and AMC[3] and distilled in the presence of phenylmagnesium chloride under reduced pressure prior to polymerization.

Preparation of the Backbone Copolymer of VSt and St [Poly(St-*co*-VSt)]. All the polymerizations were carried out in a round-bottom glass flask, under an overpressure of argon, with magnetic stirring, at selected temperatures. Poly(St-*co*-VSt) was prepared via the anionic copolymerization of VSt and St, which was performed in a mixture of toluene and THF (2:1 by volume), at −40 °C, using *n*-BuLi as initiator. After the solvents were added with dry syringes, the flask was placed in a bath kept at −40 °C, and the initiator solution (*n*-BuLi in hexane) was added. The polymerization was induced by introducing a prechilled mixture of VSt and St into the above initiator solution. After 50 min, the system was quenched by adding a small amount of methanol, and the copolymer was precipitated by pouring the polymerization solution into a large amount of methanol. The copolymer thus obtained was washed with methanol and vacuum-dried at 40 °C for more than 24 h.

Preparation of the Backbone Copolymer Containing Chlorosilyl Reactive Side Chains [Poly(St-*co*-StSiCl] by the Hydrosilylation of the C═C Functional Groups of VSt Units in Poly[St-*co*-VSt]. In a round-bottom flask, equipped with a condenser and a magnetic stirring bar and protected with nitrogen, a benzene solution of poly(St-*co*-VSt) and a trace amount of propanol solution of H_2PtCl_6 (5 wt %) were introduced. After the temperature was raised to 60 °C, chlorodimethylsilane was dropwise added carefully with a syringe in about 20 min. Then, this reaction was allowed to last more than 16 h at 80 °C. Subsequently, the benzene solution was freeze-dried for 12 h, followed by vacuum-drying at 60 °C for an additional 10 h. The copolymer thus obtained was dissolved in purified toluene, and the solution was employed in the next coupling reaction.

Preparation of Anionic Living Side Chain Polymers of St, Is, or MMA. The living poly(St), poly(Is), and poly(MMA) were prepared by the anionic living polymerizations of the corresponding monomers. The anionic polymerization of St was carried out under conditions similar to those for the preparation of poly(St-*co*-VSt). Upon the completion of polymerization, a small amount of solution (ca. 0.2 mL) was taken out for a GPC measurement. Without termination, this living polymer solution was used in the next coupling reaction step.

The anionic polymerization of Is was performed in benzene, at room temperature, using *n*-BuLi as initiator. To promote the dissociation of the initiator and/or the propagating site and to accelerate the polymerization reaction, a trace amount of polar solvent THF ($[THF]/[n\text{-BuLi}]_0 = 1.2-1.4$) was added. The polymerization was induced by adding the monomer to a mixture of benzene, THF, and initiator. After 70 min, the living poly(Is) solution was used for its coupling with poly(St-*co*-StSiCl).

The anionic polymerization of MMA was carried out using DPHL as initiator, in THF, at −78 °C, in the presence of LiCl ($[LiCl]/[DPHL]_0 = 1.2$). After THF, DPE, and a THF solution of LiCl were added with dry syringes, the flask was cooled to −40 °C, and *n*-BuLi (in hexane) was added. The deep red color of DPHL appeared at once, and the reaction between *n*-BuLi and DPE was allowed to continue for 15 min. The polymerization was started by the addition of the prechilled MMA to the above system, and the reaction was allowed to last 20 min. This THF solution of the living poly(MMA) was used for the preparation of the graft copolymer.

Preparation of the Graft (Co)polymer via the Coupling of Poly(St-*co*-StSiCl) with An Anionic Living Polymer of St, Is, or MMA. The graft (co)polymers were prepared through the coupling reaction between the chlorosilyl side chains of poly(St-*co*-StSiCl) and the anionic living polymer of St, Is, or MMA. After the anionic polymerization of a monomer, a toluene solution of poly(St-*co*-StSiCl) was introduced with a dry syringe into the living polymer solution. The reaction temperatures for living poly(St), poly(Is), and poly(MMA) were −40, 23, and −50 °C, respectively. After the reaction lasted 1.5 h, the polymer was precipitated by pouring the reaction mixture into a large amount of methanol, washed with methanol, and vacuum-dried at 40 °C for 24 h.

Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ on an INOVA-500 spectrometer. M_n and M_w/M_n of the polymer were determined by gel permeation chromatography (GPC), on the basis of a polystyrene calibration curve, and by vapor pressure osmometry (VPO). The VPO measurements were performed in toluene, at 45 °C, using an UIC SA 070 vapor pressure osmometer. The GPC measurements were carried out using THF as solvent, at 30 °C, at a 1.0 mL/min flow rate and a 1.0 cm/min chart speed. Three polystyrene gel columns (Waters, 7.8 × 300 mm; one HR 5E, part no. 44228, one Linear, part no. 10681 and one HR 4E, part no. 44240) were used, which were connected to a Waters 515 precision pump.

Results and Discussion

Preparation of the Backbone Copolymer, Poly(St-*co*-VSt), by the Anionic Copolymerization of VSt and St. As shown in Scheme 1, the functional units of the backbone copolymer, poly(VSt-*co*-St), will be turned into grafting points after hydrosilylation. If the copolymerization of VSt and St can proceed smoothly in a living manner, the grafting number can be controlled by the feed amount ratio of the two monomers.

In a previous paper,[3] the effects of the initiator, temperature, and the solvent on the selective anionic polymerization of VSt were investigated and the optimum conditions determined. Using *n*-BuLi as initiator, in a mixture of toluene and THF (5:1−2:1 by volume), at −40 °C, VSt could undergo anionic polymerization in a living manner without cross-linking or any other side reaction. The polymer thus obtained possesses a controlled molecular weight and a very narrow molecular weight distribution ($M_w/M_n = 1.03-1.05$). The quantitative presence of the unreacted 1-butene type C═C double bond was verified by ^{1}H NMR and FT-IR. The block copolymerization of VSt and St could also proceed smoothly either in the polymerization sequence VSt followed by St, or vice versa, generating a well-defined block copolymer with a controlled molecular weight and composition and a very narrow molecular weight distribution ($M_w/M_n = 1.03-1.07$). The above results indicate that the living site of VSt or St can initiate quickly the living anionic polymerization of the other monomer. Therefore, the copolymerization of these two monomers can be also expected to proceed smoothly.

The copolymerization of VSt and St was carried out under conditions similar to those for the homopolymerization of VSt and its block copolymerization with St (see Experimental Section), except the two monomers were added simultaneously to the initiator solution. As shown in Table 1, the monomer conversion is quantitative in every case, the molecular weight determined by GPC is in good agreement with that calculated, and the MWD of the copolymer is very narrow ($M_w/M_n = 1.03-$

Table 1. Anionic Copolymerizaiton of VSt and St[a]

no.	$[n\text{-BuLi}]_0$, mM	$[VSt]_0$, M	$[St]_0$, M	$10^{-3}M_n$ (calcd)	$10^{-3}M_n$[b] (obsd)	M_w/M_n[b]
SVS-1	18.8	0.441	0.685	7.53	8.08	1.04
SVS-2	7.8	0.160	0.739	13.2	13.9	1.03
SVS-3	6.5	0.168	1.09	21.6	22.9	1.03

[a] The anionic copolymerization was carried out in a mixture of toluene and THF (2:1 by volume) at −40 °C for 50 min. The polymer yield was 100% in each case. [b] Determined by GPC on the basis of a standard poly(St) calibration curve.

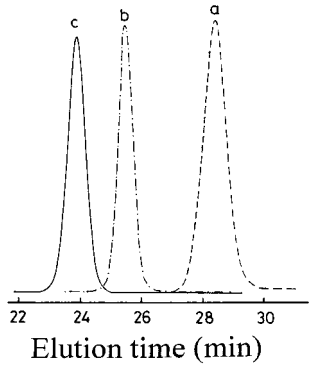


Figure 1. GPC traces of the graft copolymer (c; GP-5 in Table 4, $M_{n(GPC)} = 3.23 \times 10^4$, $M_{n(VPO)} = 4.01 \times 10^4$, $M_w/M_n = 1.05$) and its precursors: a, poly(Is) (PIs-1 in Table 3, $M_n = 1060$, $M_w/M_n = 1.11$); b, poly(St-*co*-VSt) (SVS-2 in Table 1, $M_n = 1.39 \times 10^4$, $M_w/M_n = 1.03$).

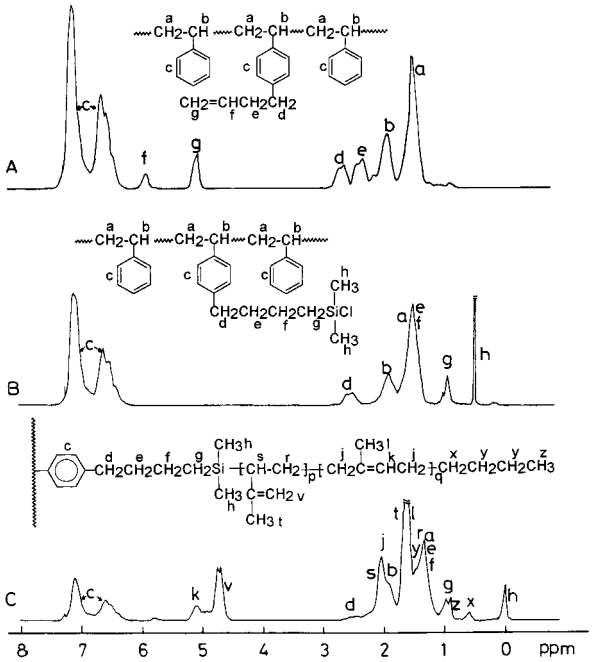


Figure 2. ^{1}H NMR spectra of poly(St-*co*-VSt) (A; SVS-2 in Table 1), its hydrosilylation product (B; SVSiCl-2 in Table 2), and the graft copolymer (C; GP-5 in Table 4) prepared by the coupling reaction between B and the living poly(Is) (PIs-1 in Table 3).

1.04). As illustrated in Figure 1b (SVS-2 in Table 1, $M_n = 1.39 \times 10^4$, $M_w/M_n = 1.03$), the GPC chromatogram exhibits a very sharp and symmetrical peak. The above results indicate that the anionic copolymerization of VSt and St proceeded in a living manner and that a uniform-size copolymer, poly(St-*co*-VSt), was obtained.

Figure 2A depicts the ^{1}H NMR spectrum of the copolymer, SVS-2 (Table 1). The absorptions corresponding to the $-CH{=}CH_2$ groups of VSt units are

Table 2. Hydrosilylation of the C=C Functional Side Chains of Poly(St-*co*-VSt)[a]

no.	poly(St-*co*-VSt), wt %[b]	C=C,[c] mmol	$(CH_3)_2SiHCl$, mmol	*t*, h	functionality,[d] %
SVSiCl-1	SVS-1 5.5	11.1	18.0	24	100
SVSiCl-2	SVS-2 6.4	5.38	16.0	16	100

[a] The reaction was started at 60 °C by carefully adding chlorodimethylsilane to a benzene solution of poly(St-*co*-VSt) and of a trace amount of H_2PtCl_6 (0.1 mL 5.0 wt % propanol solution). Then, this reaction was allowed to last more than 16 h at 80 °C. [b] Benzene solution. [c] Molar amount of C=C bonds in poly(St-*co*-VSt). [d] Determined by ^{1}H NMR.

quantitatively detectable (peak g, $=CH_2$; peak f, $-CH=$). The weight content (25.6%) of VSt units based on the intensities of $=CH_2$ and of the phenyl groups of St units is close to its feed amount (24.7%). Furthermore, the resulting copolymer is soluble in common organic solvents, such as benzene, chloroform, THF, 1,4-dioxane, etc. Therefore, one can conclude that the composition of the copolymer was well-controlled, that no cross-linking reaction occurred during the copolymerization, and that the C=C functional side chains of VSt units remained unreacted.

Hydrosilylation of the C=C Functional Groups of Poly(St-*co*-VSt). Chlorosilyl groups possess high reactivity with nucleophilic reagents, including the anionic living polymers.[6] On the other hand, the reaction of chlorodimethylsilane with C=C bond in the presence of Pt-based catalyst has been frequently used in the preparation of compounds containing reactive chlorosilyl groups.[7] In the present paper, this hydrosilylation reaction is employed for the preparation of a new functional copolymer containing reactive chlorosilyl side chains, which is further used as the backbone polymer for the preparation of graft (co)polymers.

For an easy purification of the resulting polymer by freeze-drying after hydrosilylation, the purified benzene was selected as solvent. The reaction was carried out using an excess molar amount of chlorodimethylsilane compared to the C=C bonds, at 80 °C, for more than 16 h (see Table 2 and Experimental Section). As soon as the chlorodimethylsilane was dropwise added to the benzene solution of poly(St-*co*-VSt) and of the catalyst H_2PtCl_6, the system started to boil vigorously and to darken gradually, indicating that the addition reaction between C=C and Si−H occurred. Because of the proton sensitivity of the chlorosilyl group, the resulting copolymer could not be purified by the common method, namely, the precipitation in methanol. Instead, the reaction mixture was directly freeze-dried, followed by the vacuum-drying at 60 °C. After a small amount of sample was taken out under the protection of nitrogen for a NMR measurement, this product was dissolved in purified toluene, and the solution was used in the next coupling reaction step.

Figure 2B presents the ^{1}H NMR spectrum of the hydrosilylation product, poly(St-*co*-StSiCl) (SVSiCl-2 in Table 2). Comparing this spectrum with that of its precursor poly(St-*co*-VSt), the absorptions due to $-CH{=}CH_2$ (peaks g and f in Figure 2A) disappeared completely, and the peaks corresponding to the chlorodimethylsilyl groups (peak h in Figure 2B) emerged quantitatively. Therefore, the butenyl side chains of VSt units of poly(St-*co*-VSt) were completely changed to chlorodimethyl butylsilyl groups.

Preparation of the Graft (Co)polymers with Poly(St) or Poly(Is) Side Chains. The graft (co)-

Table 3. Preparation of the Anionic Living Side Chain Polymers[a]

no.	initiator, mM	$[M]_0$, M	solvent	additive	temp, °C	time, h	M_n (calcd)	M_n (obsd)[b]	M_w/M_n[b]
PSt-1	*n*-BuLi 52.7	0.456	toluene	[THF] = 2.1 M	−40	50	960	920	1.12
PSt-2	*n*-BuLi 26.4	0.456	toluene	[THF] = 2.1 M	−40	60	1850	1880	1.08
PSt-3	*n*-BuLi 52.7	0.456	toluene	[THF] = 2.1 M	−40	50	960	960	1.11
PSt-4	*n*-BuLi 52.7	0.628	toluene	[THF] = 2.1 M	−40	60	1300	1260	1.10
PIs-1	*n*-BuLi 52.7	0.735	benzene	[THF] = 63 mM	23	70	1000	1060	1.11
PIs-2	*n*-BuLi 52.7	1.27	benzene	[THF] = 79 mM	23	70	1700	1760	1.11
PIs-3	*n*-BuLi 37.4	1.21	benzene	[THF] = 52 mM	23	70	2260	2340	1.12
PMMA-1	DPHL[c] 52.7	0.600	THF	[LiCl] = 63 mM	−78	20	1200	1290	1.10
PMMA-2	DPHL[c] 33.3	0.513	THF	[LiCl] = 40 mM	−78	20	1600	1740	1.11

[a] The polymerization was started by adding the monomer to the mixture of solvent, additive, and initiator. [b] Determined by GPC. [c] 1,1-Diphenylhexyllithium (DPHL) was prepared in situ, before the monomer addition, by the reaction between *n*-BuLi and 1,1-diphenylethylene, at −40 °C, for about 15 min.

Table 4. Preparation of the Graft Copolymers (GP)[a]

					graft copolymer			
no.	backbone[b]	$-Si(CH_3)_2Cl$, mmol[c]	living polymer,[d] mmol	$10^{-4}M_n$ (calcd)	$10^{-4}M_{n(VPO)}$[e]	$10^{-4}M_{n(GPC)}$[f]	M_w/M_n[f]	peak no.
GP-1	SVSiCl-1	1.06	PSt-1 1.58	3.14		2.22[g]	1.13[g]	double[h]
GP-2	SVSiCl-1	1.06	PSt-2 0.84	4.57	4.74	3.19	1.08	single
GP-3	SVSiCl-2	1.10	PSt-3 1.06	3.48	3.80	2.51	1.08	single
GP-4	SVSiCl-2	1.10	PSt-4 1.06	4.10	3.98	3.07	1.06	single
GP-5	SVSiCl-2	1.10	PIs-1 1.10	3.78	4.01	3.23	1.05	single
GP-6	SVSiCl-2	1.10	PIs-2 0.94	5.03	4.86	3.49	1.09	single
GP-7	SVSiCl-2	0.88	PIs-3 0.67	5.28	5.11	4.02	1.12	single
GP-8	SVSiCl-1	1.06	PMMA-1 1.58	4.08		2.83[g]	1.15[g]	double[h]
GP-9	SVSiCl-1	1.06	PMMA-2 1.06	5.23		3.16	1.10	single

[a] The coupling reaction was carried out by introducing a toluene solution of poly(St-*co*-StSiCl) into a living anionic polymer solution of St, Is, or MMA, and the reaction was allowed to last 1.5 h. [b] See Tables 1 and 2. [c] Molar amount of the chlorosilyl groups of the backbone copolymer. [d] Molar amount of the living side chain polymer, which is equal to that of the initiator (see Table 3 and the Experimental Section). [e] Determined by VPO. [f] Determined byGPC. [g] The results only correspond to the graft polymer, not including the excess of side chain polymers. [h] Double peaks because of excess side chain polymers.

polymers were prepared through a two-step process. A living side chain polymer was first prepared, followed by its coupling with the chlorosilyl groups of poly(St-*co*-StSiCl). The anionic polymerization of St was carried out in a mixture of toluene and THF ([THF] = 2.1 M) at −40 °C, and that of Is was performed in benzene in the presence of a trace amount of THF ($[THF]/[n\text{-BuLi}]_0$ = 1.2−1.4) at room temperature (see Experimental Section). As shown in Table 3, the living poly(St) or poly(Is) thus prepared possesses a controlled molecular weight and a narrow MWD (M_w/M_n = 1.08−1.12). To a living polymer solution of St or Is, a toluene solution of poly(St-*co*-StSiCl) was added, and the coupling reaction was allowed to last 1.5 h at the corresponding polymerization temperature of St or Is.

As illustrated in Figure 1, a very sharp and single peak due to the graft copolymer emerges after the coupling reaction, in the short elution time region (peak c, GP-5 in Table 4), with a higher molecular weight ($M_{n(GPC)} = 3.23 \times 10^4$, $M_{n(VPO)} = 4.01 \times 10^4$, M_w/M_n = 1.05) than those of its precursor polymers, namely, the side chain poly(Is) (peak a, PIs-1 in Table 3, M_n = 1060, M_w/M_n = 1.11) and the backbone polymer SVS-2 (Table 1, $M_n = 1.39 \times 10^4$, M_w/M_n = 1.03). In addition, it is clear from the GPC chromatograms (Figure 1) that the graft copolymer obtained was free of its precursor polymers. As shown in Figure 2C, besides the absorptions (a to h) corresponding to the backbone polymer (see Figure 2B), the peaks due to poly(Is) side chains (peaks j, k, l, r, s, t, v, x, y, and z) are also present. All the above results indicate that a pure graft copolymer with a narrow MWD and designed backbone and side chain lengths was obtained.

To obtain a pure graft copolymer that is free of its precursors, it is important to control the mole ratio of the chlorosilyl group of the backbone and the anionic living polymer. As shown in Table 4, if the amount of the latter is larger than that of the former, the excess side chain polymer will remain in the reaction system. For instance, when an excess living poly(St) was employed (GP-1 in Table 4), its red color was maintained during the whole polymerization process, and the GPC chromatogram exhibited double peaks belonging to the produced graft polymer and the excess side chain poly(St), respectively. When the amount of living polymer was less than that of the chlorosilyl group (GP-2 to GP-7), the color of the living polymer disappeared at once upon the introduction of the toluene solution of the backbone into the reaction system, and each of the graft (co)polymers thus obtained exhibited a single, symmetrical peak. In addition, the molecular weights of the graft (co)polymers determined by VPO are close to those calculated, but much larger than those determined by GPC, because the graft (co)polymers possess smaller hydrodynamic volumes compared to the corresponding linear polymers.

Preparation of the Graft Copolymer with Poly(MMA) Side Chains. A graft copolymer with poly(MMA) side chains was prepared using a procedure similar to that for the graft (co)polymers with poly(St) or poly(Is) side chains. The anionic polymerization of MMA was carried out using the bulky initiator DPHL, in a polar solvent THF, at a low temperature −78 °C. To stabilize the propagating site and to avoid side reactions, LiCl ($[LiCl]/[DPHL]_0 = 1.2$) was employed as additive.[5] After the polymerization lasted 20 min, the temperature was raised to −50 °C, and the coupling reaction was started by introducing a toluene solution of poly(St-*co*-StSiCl) into the above system. Before quenching, a small amount of solution was taken out for a GPC measurement. As shown in Figure 3, the formation of the graft copolymer (GP-8 in Table 4) is

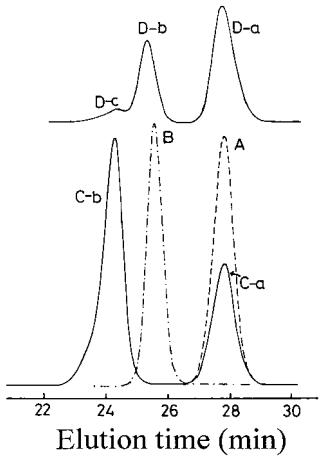
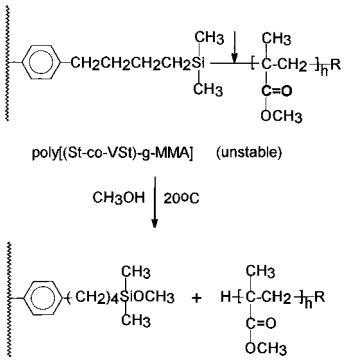


Figure 3. GPC traces of the graft copolymer (C-b; GP-8 in Table 4) containing poly(MMA) side chains, its precursors (A and B), and its decomposed product (D). A: Living poly(MMA) (PMMA-1 in Table 3, $M_n = 1290$, $M_w/M_n = 1.10$). B: Poly(St-*co*-VSt) (SVS-1 in Table 1, $M_n = 8080$, $M_w/M_n = 1.04$). C-b: Graft copolymer ($M_{n(GPC)} = 2.83 \times 10^4$, $M_w/M_n = 1.15$) prepared by the coupling reaction between A and the hydrosilylation product of B (SVSiCl-1 in Table 2). This graft copolymer is accompanied by the excess of poly(MMA) (C-a). D-a and D-b: Decomposed products from the graft copolymer (D-c).

confirmed by the emergence of a new peak (C-b), with a larger molecular weight ($M_{n(GPC)} = 2.83 \times 10^4$, $M_w/M_n = 1.15$) than its precursor polymers, namely, the side chain poly(MMA) (A; PMMA-1 in Table 3, $M_n = 1290$, $M_w/M_n = 1.10$) and the backbone polymer (B; SVS-1 in Table 1, $M_n = 8080$, $M_w/M_n = 1.04$). The graft copolymer (peak C-b) is accompanied by the excess of poly(MMA) side chain (peak C-a). In contrast to the graft (co)-polymers with poly(St) or poly(Is) side chains, this graft copolymer is unstable in proton-containing media, such as methanol or water. Upon the coupling reaction, the product was precipitated in methanol and kept in methanol for about 12 h. As well-known, this constitutes a general purification method for the common polymers, particularly for poly(St)-based (co)polymers. Surprisingly, the GPC result of the polymer thus treated was different from those of the graft copolymers involving poly(St) or poly(Is) side chains. As shown in Figure 3D, the graft copolymer (D-c) almost completely decomposed back to its precursor polymers (D-a and D-b). To examine this decomposition, the THF solution of the graft copolymer with poly(MMA) side chains (GP-9 in Table 4) was poured into either water or a dilute HCl aqueous solution. The decomposition took place in both media, and particularly when the acidic solution was used, the decomposition completed almost instantaneously. Therefore, the graft copolymer with poly(MMA) side chains is stable in organic solvents, such as THF, toluene, etc., but decomposes in the polar solvents containing an active proton, such as alcohol, water, etc. For comparison, the graft copolymers with poly(St) or poly(Is) side chains were also subjected to the same treatment, but no change in the molecular structures was detected even in an acidic environment. As shown in Scheme 2, the presence of the strong electron-withdrawing carbonyl group of the last MMA unit makes the Si−C linkage (indicated by an arrow) very weak, and for this reason, it is easily fractured in proton-containing media.

Scheme 2



Conclusions

Using *n*-BuLi as initiator, in a mixture of toluene and THF (2:1), at −40 °C, the anionic copolymerization of the bifunctional monomer 4-(vinylphenyl)-1-butene (VSt) and styrene (St) could proceed smoothly, generating a copolymer with controlled molecular weight and composition, and very narrow molecular weight distribution ($M_w/M_n = 1.03-1.04$). The butenyl type C═C double bonds of VSt remained unreacted during the copolymerization process and could be further reacted with chlorodimethylsilane in the presence of the catalyst H_2PtCl_6, generating another new functional copolymer with a reactive chlorosilyl group in each of its VSt units. Subsequently, graft copolymers with poly(St), poly(isoprene), or poly(methyl methacrylate) side chains were prepared by the coupling reactions between the chlorosilyl groups of the above copolymer and the anionic living polymers of St, Is, or MMA, respectively. The graft copolymer thus obtained was free of its precursor polymers and possessed a very narrow dispersity ($M_w/M_n = 1.05-1.15$). The molecular weights of both its backbone and side chains, and hence the total molecular weight of the graft (co)polymer as well as its composition, could be well controlled. In addition, the stability of the graft copolymer with poly(MMA) side chains was different from those of the graft (co)polymers with poly(St) or poly(Is) side chains. The former graft copolymer could be easily decomposed by alcoholysis or hydrolysis at room temperature.

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