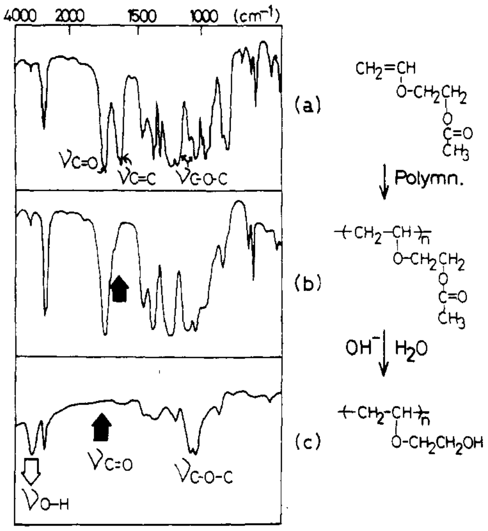

Figure 8. Hydrolysis of poly(AcOVE) monitored by IR spectroscopy: (a) AcOVE monomer; (b) poly(AcOVE) ($\bar{M}_w = 11.0 \times 10^4$) prepared with BF_3OEt_2; (c) hydrolysis product [poly(HOVE)] from sample b.

spectra expected for poly(HOVE): ^{1}H NMR (D_2O) δ 3.9 (m, 5 H, $CHOCH_2CH_2O$), 2.0 (m, 2 H, CCH_2C); ^{13}C NMR (D_2O) δ 74.8 (CH), 70.2 (CH_2OH), 61.6 (OCH_2), 40.7 and 39.1 (CCH_2C). The spectral analysis shows the quantitative removal of acetoxyl groups from the precursor and the formation of a new polyalcohol **3**, having both ether and alcohol units in the pendant.

Similarly, hydrolysis of poly(AcOVE) obtained with HI/I_2 gave poly(HOVE) in a quantitative yield. Because no evidence for main-chain degradation during the hydrolysis was obtained, the resulting polyalcohol should inherit the narrow MWD of the precursor.

In Table II, the solubility characteristics of poly(HOVE) are compared with those of poly(AcOVE) and related polymeric alcohols.[12] Poly(HOVE) completely differed in solubility from poly(AcOVE), i.e., insoluble in good solvents for poly(AcOVE) [ethers (dioxane and THF) and aromatic (toluene) or chlorinated (CH_2Cl_2) hydrocarbons] while soluble (in water) and swelling (in methanol) in nonsolvents of poly(AcOVE) at room temperature. Although the apparent hydrophilicity of poly(HOVE), indicated by the carbon/oxygen (C/O) and carbon/hydroxy (C/OH) ratios (Table II), lies intermediate between those of poly(vinyl alcohol) (**5**, soluble in water) and poly(2-hydroxy-3-butene) (**6**, soluble in methanol but not in water), polyalcohol **3** was in fact more soluble in cold water than poly(vinyl alcohol).

Registry No. **1**, 6026-79-5; **2**, 31742-55-9; CEVE, 110-75-8; sodium acetate, 127-09-3; hydrogen iodide, 10034-85-2; iodine, 7553-56-2.

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(9) In the following part of this paper, the term "living" means that, because of the absence or suppression of termination and chain transfer, the propagating species has a very long lifetime to give polymers whose $\bar{M}_n$ is directly proportional to monomer conversion. In view of the successful sequential polymerizations under our conditions (monomer-addition experiments and block copolymerizations) and the resulting increase in polymer molecular weight, there is no doubt that almost all polymer chains carry an active propagating end. It has recently been pointed out, however, that such a proportionality of $\bar{M}_n$ does not necessarily prove the "complete absence" of termination and chain transfer required for "perfectly living" polymerization if the observed $\bar{M}_n$'s are less than 10000.[10]
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Polymerization of Monomers Containing Functional Silyl Groups. 1. Anionic Living Polymerization of (4-Vinylphenyl)dimethyl-2-propoxysilane

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ABSTRACT: Anionic polymerization of (4-vinylphenyl)dimethyl-2-propoxysilane (**4**) was investigated under various conditions: at −78, 0, and +30 °C in THF with lithium and potassium as the countercation. **4** has been readily polymerized by either oligo(α-methylstyryl)lithium or -potassium to form polymers of any desired molecular weight with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.04–1.1). The propagating active end of the polymer with potassium cation is found to be stable at −78 °C for 24 h. The glass transition temperature and solubility of the resulting polymer were measured. Cross-linking of the polymer through hydrolysis of pendant alkoxysilyl groups was examined.

Introduction

A variety of applications of organic–inorganic composite materials have been developed in recent years. Polymers having alkoxysilyl functions have attracted special interest in this regard because they may be used for the purpose of grafting polymers onto inorganic solid surfaces like silica and metal oxides as well as for cross-linking between polymer chains through hydrolysis of alkoxysilyl groups

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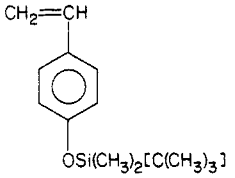
and consequent condensation of silanols.

Extensive studies of the radical-initiated homo- and copolymerization of vinylalkoxysilanes and acrylates and methacrylates containing alkoxysilyl groups have appeared, mainly in patents. These monomers are currently available as silane coupling reagents. It was also reported that vinylalkoxysilanes were polymerized by γ-ray irradiation.[1] Walton and co-workers prepared 4-(dimethylalkoxysilyl)styrenes and polymerized them by radical initiator, and the hydrolysis of the resulting polymers was preliminarily examined.[2] In contrast to references on radical initiation, no reports exist on the anionic polymerization of monomers containing alkoxysilyl groups.

In previous studies,[3,4] we found that by protecting the hydroxy groups with suitable trialkylsilyl functions, anionic living polymerization of (4-vinylphenoxy)dimethyl-*tert*-butylsilane (**1**) and (2-(4-vinylphenyl)ethoxy)trimethylsilane (**2**) could be achieved and that the resulting polymers of predicted molecular weights and narrow molecular weight distributions were obtained in quantitative yields. Throughout these studies we observed that the silicon–oxygen–carbon bonds were proved to be nearly inactive toward highly reactive anionic initiators and propagating anions at −78 °C.



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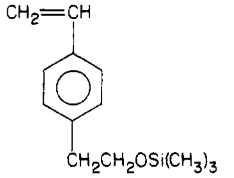


2

We now report the anionic polymerization of a styrene para substituted with a dimethyl-2-propoxysilyl group with hydrolytic potential, and we present some information regarding whether the anionic living polymerization of this monomer occurs.

Experimental Section

Materials. 4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co., Ltd. It was distilled at 52–54 °C (5 mm) over calcium hydride. α-Methylstyrene, dimethyldichlorosilane, dimethyldimethoxysilane, and 2-propanol were purified from the commercial products by distillation over calcium hydride. *n*-Pentane was refluxed over phosphorus pentoxide for 5 h and distilled at 36 °C. Tetrahydrofuran (THF) was used as the solvent in all polymerization experiments. It was refluxed over sodium wire for 5 h and distilled from sodium naphthalide solution. Naphthalene was purified from the commercial product by sublimation. The oligomeric (α-methylstyryl)lithium and -potassium were freshly prepared just prior to polymerization from the corresponding metal naphthalides and a 2–4 molar quantity of α-methylstyrene at 30 °C for 1 min and then at −78 °C for 5 min. The concentration of metal naphthalide was determined by previous titration with standard 1-octanol in a sealed reactor through breakseals under vacuum.

2-Propoxydimethylchlorosilane. To a stirred solution of dimethyldichlorosilane (22.7 g, 0.176 mol) in *n*-pentane (150 mL) were slowly added 2-propanol (10.6 g, 0.176 mol) and triethylamine (16.7 g, 0.165 mol) in *n*-pentane (150 mL) over a 1-h period at 0 °C under an atmosphere of nitrogen. After the mixture was stirred for 5 h at room temperature, it was filtered and the white solid was washed with *n*-pentane. From the combined *n*-pentane solution, the product was fractionally distilled at 52–54 °C (110 mm) to give 9.2 g (34%) of colorless liquid 2-propoxydimethylchlorosilane: 60-MHz ^{1}H NMR (CCl_4) δ 4.17 (1 H, m, methine CH), 1.2 (6 H, d, CCH_3), 0.4 (6 H, s, $SiCH_3$).

(4-Vinylphenyl)dimethyl-2-propoxysilane. A solution of 2-propoxydimethylchlorosilane (10.4 g, 68.3 mmol) in dry THF (50 mL) was added dropwise over a 1-h period to a solution of (4-vinylphenyl)magnesium chloride (70 mmol, prepared from 4-vinylphenyl chloride (9.7 g, 70 mmol) and magnesium (2.43 g, 100 mmol) in dry THF (100 mL)). The temperature was maintained at 10 °C during the addition. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. The crude product was obtained by direct distillation. It was purified by fractional distillation at 75–78 °C (1 mm) to give 12.0 g (54.5 mmol, 80%) of colorless, liquid (4-vinylphenyl)dimethyl-2-propoxysilane (lit.[2] bp 86 °C (0.8 mm)): 60-MHz ^{1}H NMR (CCl_4) δ 7.60–7.13 (4 H, m, phenyl), 6.65 (1 H, 2 d, vinyl CH), 5.65–5.17 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 4.30–3.57 (1 H, m, methine CH), 1.08 (6 H, d, CCH_3), 0.30 (6 H, s, $SiCH_3$).

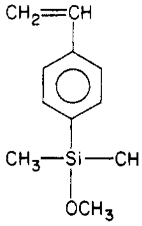
(4-Vinylphenyl)dimethylmethoxysilane. A reaction similar to the one above was run with dimethoxydimethylsilane (8.4 g, 70 mmol) and (4-vinylphenyl)magnesium chloride (75 mmol) in THF (150 mL). After the reaction was complete, the product was distilled at 64–65 °C (1 mm) (lit.[2] bp 70–72 °C (1 mm)) to give 9.6 g (50 mmol, 71%) of colorless, liquid (4-vinylphenyl)dimethylmethoxysilane: 60-MHz ^{1}H NMR δ 7.57–7.20 (4 H, m, phenyl), 6.68 (1 H, 2 d, vinyl CH), 5.69–5.19 (2 H, 2 d, J = 11, 18 Hz, vinyl CH_2), 3.37 (3 H, s, OCH_3), 0.33 (6 H, s, $SiCH_3$).

Polymerization Procedure. All the operations were carried out at −78 °C under high-vacuum conditions ($\approx 10^{-6}$ mm) in an all-glass apparatus equipped with breakseals, as previously reported by Morton and co-workers.[5] All the polymerizations were carried out at −78 °C with shaking. The polymerization of **4** was usually completed within less than 1 min and was terminated with methanol or 1-octanol after 2–10 min. The polymers were collected, after adding large excess of methanol, by precipitation. They were redissolved in THF, precipitated into methanol two additional times, and freeze-dried.

Instruments for Measurements. IR spectra were run with a Jasco IR-G spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL JNM-PMX 60 instrument. Gel permeation chromatograms (GPC) were obtained with a Toyo Soda HLC-802 instrument with UV or refractive index detection, THF being the elution solvent. Vapor-pressure osmometry (VPO) measurements for the number-average molecular weight determination were made with a Corona 117 instrument in benzene solution. The glass transition temperature (T_g) of the polymer was evaluated from the differential scanning calorimetry (DSC) diagrams recorded on a Perkin-Elmer DSC-2 instrument with a 10 °C/min heating rate.

Results and Discussion

Anionic Polymerization of (4-Vinylphenyl)dimethyl-2-propoxysilane. Two monomers having alkoxysilyl groups (**3** and **4**) were prepared by the reactions of (4-vinylphenyl)magnesium chloride with dimethyldimethoxysilane and dimethyl-2-propoxychlorosilane in THF, respectively. The yields of **3** and **4** were usually in the range 60–80%. They are relatively stable and resistant to hydrolysis under neutral conditions.



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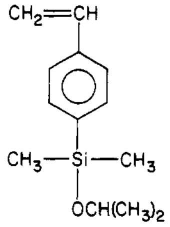


4

Anionic polymerization of **3** with oligo(α-methylstyryl)lithium as an initiator was first carried out in THF at −78 °C. When **3** was mixed into an initiator solution, an immediate color change from dark red to brownish orange occurred with an increase in the viscosity of the system. However, the color faded gradually and almost disappeared after 30 min. A polymer soluble in THF was obtained in 78% yield by addition of a large amount of methanol to precipitate the polymer. No insoluble portion was found at all. The GPC curve shows that the polymer possesses a very broad molecular weight distribution.

Table I
Anionic Polymerization of 4 with Oligo(α-methylstyryl)lithium in THF at -78 °C[a]

monomer 4, mmol	lithium naphthalide, mmol	α-methylstyrene, mmol	$\bar{M}_n$ calcd	$\bar{M}_n$ obsd[b]	$\bar{M}_w/\bar{M}_n$
0.77	0.0890	0.600	5400	5500	1.06
1.98	0.0896	0.330	12000	15000	1.08
4.56	0.118	0.970	19000	17000	1.16
3.14	0.101	0.353	20000	20000	1.14
7.53	0.0924	0.322	37000	43000	1.09
10.90	0.0898	0.435	55000	64000	1.19

[a] Yields of polymers were 80–100%. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution.

Table II
Anionic Polymerization of 4 with Oligo(α-methylstyryl)potassium in THF at -78 °C[a]

monomer 4, mmol	potassium naphthalide, mmol	α-methylstyrene, mmol	$\bar{M}_n$ calcd	$\bar{M}_n$ obsd[b]	$\bar{M}_w/\bar{M}_n$
5.78	0.188	0.472	14000	14000	1.05
5.67	0.131	0.349	19000	20000	1.04
6.10	0.0970	0.273	28000	26000	1.06
6.11	0.0902	0.255	31000	28000	1.08
7.14	0.0911	0.246	35000	33000	1.06
6.85	0.0747	0.255	41000	45000	1.10
11.40	0.0486	0.225	100000	81000	1.07

[a] Yields of polymers were 95–100%. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution.

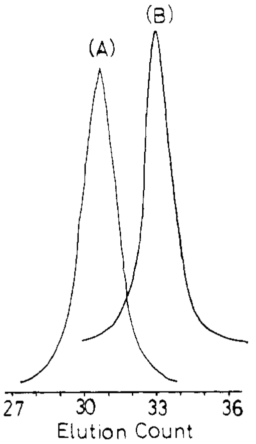


Figure 1. GPC curves for poly[(4-vinylphenyl)dimethyl-2-propoxysilane]. peak A: $\bar{M}_n$(obsd) = 43000, $\bar{M}_w/\bar{M}_n$ = 1.09. peak B: $\bar{M}_n$(obsd) = 15000, $\bar{M}_w/\bar{M}_n$ = 1.08.

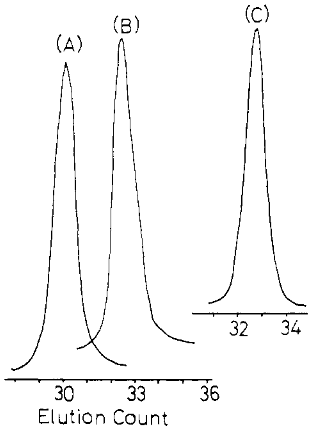


Figure 2. GPC curves for poly[(4-vinylphenyl)dimethyl-2-propoxysilane] (A and B) and for polystyrene standard sample (C). Peak A: $\bar{M}_n$(obsd) = 33000, $\bar{M}_w/\bar{M}_n$ = 1.06. Peak B: $\bar{M}_n$(obsd) = 14000, $\bar{M}_w/\bar{M}_n$ = 1.05. Peak C: $\bar{M}_n$(obsd) = 10000, $\bar{M}_w/\bar{M}_n$ = 1.02.

Apparently, serious side reactions such as transfer and termination reactions compete with the propagation reaction, suggesting the lability of the methoxysilyl group toward the carbanion, presumably because there is less steric hindrance.

Next, we tried to carry out the anionic polymerization of 4, which bears the bulkier 2-propoxysilyl group in place of the methoxysilyl group. Rapid initiation of 4 and oligo(α-methylstyryl)lithium took place at −78 °C as evidenced by the same color change from dark red to brownish orange as in the case of 3. In this case, however, the color seemed to remain unchanged at −78 °C for several hours. Termination was accomplished by quenching with a few drops of methanol, and the characteristic brownish orange color immediately disappeared. The polymer was then precipitated by addition of a large amount of methanol. The results are summarized in Table I. It can be seen that there is good agreement between the measured and predicted molecular weights based on the molar ratio of monomer to initiator. The GPC curves in Figure 1 show that all the polymers possess single peaks with relatively narrow molecular weight distributions. The $\bar{M}_w/\bar{M}_n$ ratios calculated from these curves were found to be around 1.1.[6] When oligo(α-methylstyryl)potassium was used as an initiator, a dark red coloration was observed in the polymerization mixture. Yields of the polymers were always found to be quantitative. These results are summarized in Table II. It can be seen that a comparison of the measured and calculated values of molecular weights also shows good agreement, and very narrow molecular weight distributions with $\bar{M}_w/\bar{M}_n$ in the range 1.04–1.10 have been obtained. Figure 2 shows examples of the GPC of the polymers thus prepared, which have been found to be virtually identical with that of the commercially available polystyrene standard sample. These results clearly indicate that anionic polymerization of 4 with either oligo(α-methylstyryl)lithium or -potassium proceeds without chain-transfer and chain-termination reactions. Furthermore, rapid initiation in these systems may be evidenced by the fact that the polymers have narrow molecular weight distributions. Thus, the bulkier isopropyl group compared with the methyl group can efficiently

Table III
Conditions and Results of Stability of Carbanions Derived from 4 and (α-Methylstyryl)lithium in THF

conditions: temp, °C	conditions: time, h	(α-methylstyryl)lithium, mmol	carbanion from 4 and (α-methylstyryl)lithium, mmol	% loss of active anion[a]
−78	0.5	0.118	0.117	>1
−78	24	0.0970	0.0758	22
0	0.5	0.121	0.0480	60
30	0.5	0.0764	0.0136	82

[a] Loss of active anion was calculated from the equation loss of active anion = {[(α-methylstyryl)lithium] − [carbanion from 4]}/[(α-methylstyryl)lithium] × 100.

Table IV
Conditions and Results of Stability of Carbanions Derived from 4 and (α-Methylstyryl)potassium in THF

conditions				
temp, °C	time, h	(α-methylstyryl)potassium, mmol	carbanion from 4 and (α-methylstyryl)potassium, mmol	% loss of active anion[a]
-78	0.5	0.0767	0.0748	2
-78	24	0.0976	0.0998	~0
30	0.5	0.130	0.117	10

[a] Loss of active anion was calculated from the equation loss of active anion = {[(α-methylstyryl)potassium] − [carbanion from 4]}/[(α-methylstyryl)potassium] × 100.

Table V
Conditions and Results of Stability of Carbanions Derived from Styrene and (α-Methylstyryl)lithium in THF

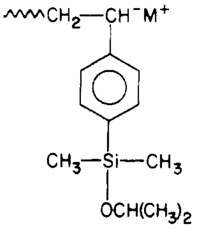
conditions				
temp, °C	time, h	(α-methylstyryl)lithium, mmol	carbanion from styrene and (α-methylstyryl)lithium, mmol	% loss of active anion[a]
-78	0.5	0.127	0.133	~0
-78	24	0.135	0.142	~0
30	0.5	0.100	0.102	~0

[a] Loss of active anion was calculated from the equation loss of active anion = {[(α-methylstyryl)lithium] − [carbanion from styrene]}/[(α-methylstyryl)lithium] × 100.

protect the silicon–oxygen bond from attack of carbanions at the polymer ends.

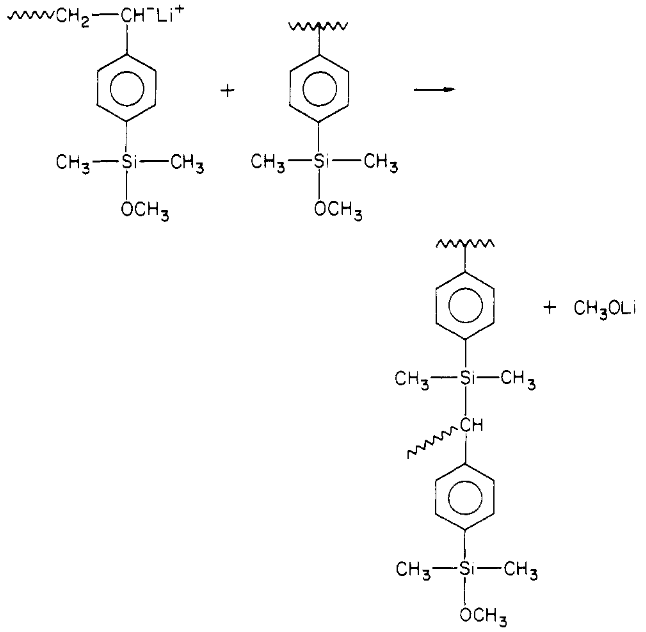
Estimation of Stability of Active Anions Derived from 4. Morton and co-workers developed previously a colorimetric titration technique by which the actual concentration of living polystyryl anion could be determined.[7] This was accomplished by direct titration of the characteristically colored polystyryl anion in a sealed glass reactor in vacuo to a colorless end point by a standard 1-butanol solution. In this way, it is possible to estimate the actual concentration of carbanions in the polymerization system and hence to discuss quantitatively the stability of carbanion.

Since 4-(dimethyl-2-propoxysilyl)styryl anion **5** is a carbanion of novel type and includes alkoxysilyl functionality, which may be susceptible to nucleophilic attack with its own carbanion, it is important to evaluate to what extent **5** may be stable under various conditions. By the application of the colorimetric titration method to our system, the actual concentration of **5** in the polymerization system has been determined. To minimize the influence of impurity in **4** these titration experiments were taken at the ratio [**4**]:[initiator] $\simeq 10$. The results are summarized in Tables III and IV. As can be seen, **5** with lithium cation as the countercation was stable at -78 °C for 30 min but appeared to be destroyed gradually at that temperature because 22% of the active carbanion disappeared after 24 h. At these initiator levels, 60% and 75% losses were observed after 30 min at 0 and 30 °C, respectively. On the other hand, **5** with potassium cation as the countercation was found to show an outstanding stability. No loss of carbanion could be detected within experimental error at -78 °C even after 24 h. Surprisingly, more than 90% of the initial carbanion remained at 30 °C for 30 min. Thus, the effect of countercation seems to be very critical.



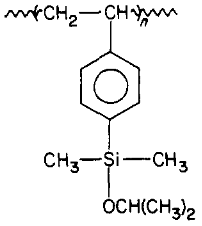
5 (M=Li, K)

As control experiments, the same colorimetric titrations for polystyryllithium were carried out. The results are summarized in Table V, where it can be seen that no loss of living ends of the polymers is indicated at -78 °C after 24 h and at 30 °C after 30 min. Thus, styryl anions are found to be stable under these conditions. Accordingly, the most likely explanation for decomposition reactions of the carbanion of **5** would be attack by the carbanion upon the silicon atom on the polymer chain, which is a very well-known substitution reaction of alkoxysilanes with organolithium reagents.[8] During the course of and/or after the conclusion of polymerization, it would result in a chain-termination reaction with the introduction of branch points, although this is not clear. As a result, polymers of very broad molecular weight distribution and/or intermolecularly cross-linked insoluble polymers would be obtained. The polymerization of **3** may be such a case as outlined in the following equation:



On the other hand, in the case of the polymerization of **4** with either oligo(α-methylstyryl)lithium or -potassium at -78 °C, it can be seen from GPC charts that the prepared polymers still had narrow molecular weight distributions and that broadening of the distribution was not observed in all cases. In practice there is no problem concerning the influence of such reactions on the polymerization of **4**. Since the anionic polymerization of **4** appears to occur almost instantaneously at −78 °C and the decomposition reactions are completely suppressed even after 30 min, as shown in Table III and IV.

Some Properties of Poly[(4-vinylphenyl)dimethyl-2-propoxysilane] (6). Polymer **6** is a white solid and soluble in benzene, toluene, *n*-hexane, cyclohexane, tetrahydrofuran, 1,4-dioxane, diethyl ether, carbon tetrachloride, chloroform, dichloromethane, acetone, methyl ethyl ketone, methyl isobutyl ketone, *n*-butyl alcohol, and *N*,*N*-dimethylformamide but insoluble in water, methanol, and ethanol. The solubility of **6** resembles very closely that of polystyrene, except for *n*-hexane in which the latter is insoluble.



6

6 can be cast from THF solutions to give a transparent, colorless, and brittle film.

Polymer **6** has a glass transition temperature of 180 °C, which was determined by differential scanning calorimetry. This value is about 80 °C higher than that of polystyrene, probably due to the steric bulkiness of **6** arising from the presence of the dimethyl-2-propoxysilyl substituent.

As expected, **6** is readily cross-linked by hydrolysis of the alkoxysilyl groups and subsequent condensation between the two resulting silanol groups. For example, when **6** was dissolved in THF and the solution treated at room temperature with a little aqueous 6 N hydrochloric acid, irreversible precipitation of the polymer occurred. Similarly, it is possible to cross-link **6** in film form by treatment with gaseous hydrochloric acid. The resulting polymers are highly cross-linked materials and hence insoluble in organic solvents and water. Applications of **6** are currently under study.

Registry No. **3**, 17983-64-1; **3** (homopolymer), 98542-13-3; **4**, 58556-56-2; **4** (homopolymer), 98542-14-4; **5**·Li, 98611-50-8; **5**·K, 98611-49-5; 2-propoxydimethylchlorosilane, 1825-71-4; 4-vinylphenyl chloride, 1073-67-2; dimethyldichlorosilane, 75-78-5; 2-propanol, 67-63-0; dimethoxydimethylsilane, 1112-39-6.

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Reactive Site and Mechanism of Graft Copolymerization onto Poly(ether urethane) with Ceric Ion as Initiator

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ABSTRACT: The reaction mechanism of graft copolymerization of acrylamide onto poly(ether urethane) (PEU) initiated by ceric ion was investigated. A series of organic compounds were used as the model compounds for the functional groups and different segments of PEU, and the graft copolymerization onto PEUs having different compositions was carried out. It was found that the phenyl carbamate group (1,4-C_6H_4NHCOO–) in the hard segment is highly reactive. The reaction mechanism was then proposed for the first time to involve the complex formation between a ceric ion and a carbamate group as the first step, followed by its decomposition into free radical on the N atom as the main site of grafting. Therefore, the main reactive site of graft copolymerization initiated by ceric ion would take place predominately at the hard segments of PEU.

Introduction

Although successful graft copolymerizations of acrylamide onto poly(ether urethane) (PEU) films[1,2] were performed by using ceric salt as an initiator, the reaction mechanism as well as the grafting site of initiation were never reported. We used a series of organic compounds as the models for the functional groups and the different segments of PEU and compared their reaction activities in the rate of vinyl polymerization. Then we examined the influence of the hard and soft segments of PEU on the graft reaction and also the relationship between the PEU structures and the grafting reactivities from which the reactive site and the reaction mechanism of graft copolymerization is then proposed.

Experimental Section

Materials. Acrylamide (AAM) was recrystallized from acetone three times, mp 84 °C. Ammonium ceric nitrate and solvents were used as reagent-grade chemicals. *N*-Methylacetanilide was prepared by the reaction of acetic anhydride with *N*-methylaniline. *p*-Substituted acetanilides were synthesized from acetic anhydride and corresponding para-substituted anilines. Poly(tetramethylene ether) glycol (PTMG) was obtained from Du Pont. Poly(ether

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