Synthesis of Poly(silyl ester)s via AB Monomer Systems

Min Wang, Jennifer M. Weinberg,† and Karen L. Wooley*

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received September 8, 1999; Revised Manuscript Received December 7, 1999

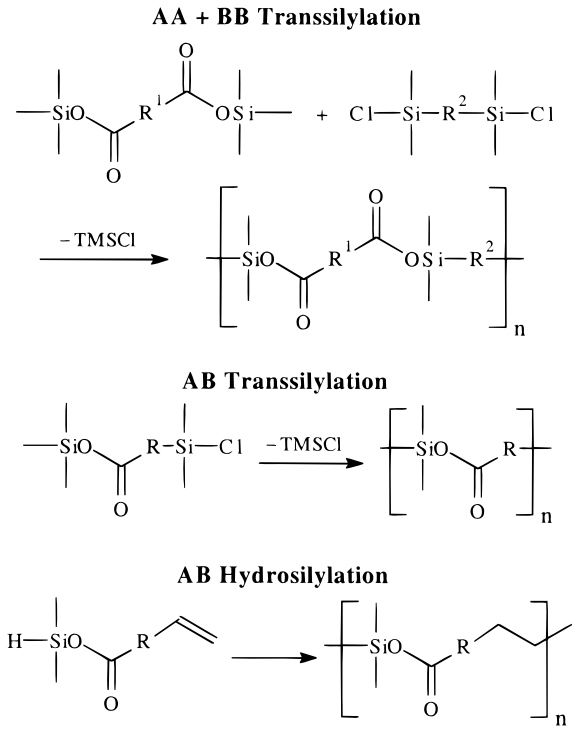
ABSTRACT: The polymerization of AB-type monomers was investigated for the preparation of hydrolytically labile poly(silyl ester)s. AB-type polymerizations were based upon either transsilylation or hydrosilylation reactions, and each case gave polymers of higher molecular weight in shorter polymerization times than the previously studied transsilylation polymerizations of AA/BB monomer systems. The transsilylation reaction between the chlorosilane and trimethylsilyl ester functional groups of trimethylsilyl 5-(chlorodimethylsilyl)pentanoate as a neat sample in the presence of DMF catalyst and heated to 100 °C under argon for 8 days gave poly(5-dimethylsilyl pentanoate) (M_w = 12 400, M_w/M_n = 3.8). The strategy using hydrosilylation chemistry has the additional advantage of elimination of monomer preparation difficulties and polymerization at lower reaction temperatures. Polymerization of (dimethylsilyl) 4-pentenoate, (dimethylsilyl) 4-vinyl benzoate, and (dimethylsilyl) 4-pentynoate as 10 M solutions in dry tetrahydrofuran afforded poly(5-dimethylsilyl pentanoate), poly(*p*-dimethylsilylethyl benzoate), and poly(dimethylsilyl 4-pentenoate) respectively, by hydrosilylation in the presence of 0.5 mol % dichloro(1,5-cyclooctadiene)platinum(II) catalyst. The temperature was optimized for each polymerization, to yield the poly(silyl ester)s having degrees of polymerization of approximately 100 in 120 min. The characterization of each polymer included infrared (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Comparisons were made between the degradative properties of polymer materials based upon different backbone compositions. It was found that the incorporation of a phenyl moiety α to the carbonyl and the attachment of a vinyl group to the silicon atoms increased the susceptibility of the silyl ester linkage toward nucleophilic attack and thereby decreased the hydrolytic stabilities of the poly(silyl ester)s. In addition, several small molecule model studies were performed to help understand the degradation behavior of the polymer materials.

Introduction

Nearly since the first synthetic polymer was prepared, issues regarding its degradation properties have been considered.[1] The design of degradable polymers[2−17] that exhibit complex degradation profiles under specific conditions has received increasing attention as a means to tailor materials for a number of intended applications, for example, as recyclable materials,[18] gene delivery carriers,[19] matrices for drug delivery and biodegradable surgical devices,[20] etc. Poly(silyl ester)s have recently been reported as a new type of degradable material with rapid and attunable degradative properties.[21−24] The control over the degradative properties comes from the substituents attached to the silicon atoms and carbonyl groups of the silyl ester linkages, whereby sufficiently sterically bulky groups or substituents of differing electronic character can alter the extent of attack by nucleophilic agents at the silicon vs the carbonyl[25,26]—the first step in the breakdown of the silyl ester bond. Synthetic methods that allow for the convenient preparation of silyl ester polymers of differing compositions and at sufficient degrees of polymerization are required to further investigate their properties and potential applications.

In our previous work, the basic methodology for the synthesis of poly(silyl ester)s was based upon the condensation reaction of AA/BB monomer systems (Scheme 1), involving a transsilylation ester interchange reaction between trimethylsilyl ester and chlorosilane functional groups with the elimination of trimethylsilyl chloride ((TMS)Cl) as the driving force.[22−24] The primary drawback to the use of an AA/BB monomer system is the requirement of exact precision of measurement to

Scheme 1



* To whom correspondence should be addressed: Department of Chemistry, Washington University, One Brookings Drive, St. Louis, MO 63130-4899. Telephone: (314) 935-7136. Fax: (314) 935-4481. E-mail: klwooley@artsci.wustl.edu.

† Current address: Bayer Corporation, 100 Bayer Road, Pittsburgh, PA 15205-9741.

10.1021/ma991530m CCC: $19.00
Published on Web 01/13/2000

Table 1. Comparison of the Different Methods for the Preparation of Poly(silyl ester)s: (a) Polymerization through AA/BB Monomers;[22−24] (b) Polymerization by Transsilylation through AB Monomers; (c) Polymerization by Hydrosilylation through AB Monomers

	a	b	c
stoichiometric balance of starting materials	required	not necessary	not necessary
reaction temp (°C)	100	100	25
reaction time	2 weeks	1 week	2 h
degree of polym	≤50	50−100	100−200
applicability	a large variety of monomers	currently limited to dimethylsilyl esters	

ensure equimolar amounts of each monomer. If an excess of either monomer is present, the formation of high molecular weight polymer will be prevented by the termination of growing chains by the excess functionality. The technical difficulties in reaching an equimolar stoichiometry can be additionally challenging for highly reactive and moisture sensitive reagents. The use of an AB monomer system alleviates these problems, since stoichiometric equivalence of reactive functional groups is achieved within a single molecule, thus avoiding the difficulties of controlling the measurement and potential quenching of reactive groups. The development of such a system requires that the AB monomer contains functional groups that are stable and unreactive toward each other at conditions that allow for purification and characterization of the monomer, yet they must be sufficiently reactive with each other under the appropriate polymerization conditions to form high molecular weight polymers. Comparison of AB and AA/BB monomer systems have been reported for various polymers including, but not limited to: poly(ester)s,[27] poly(amide)s,[28] poly(imide)s,[29] poly(quinoline)s[30] and poly(carbonate)s.[31]

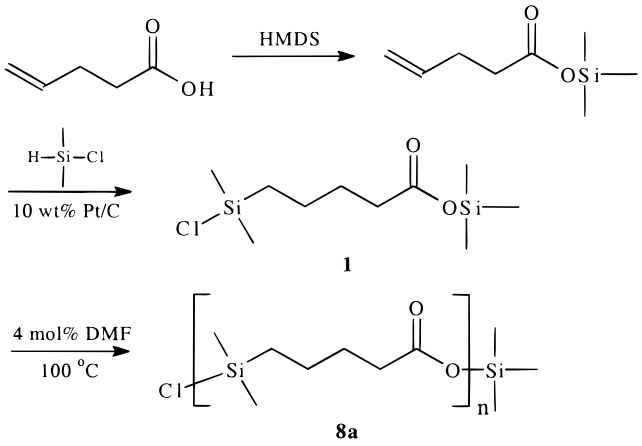
Two methodologies for the preparation of poly(silyl ester)s through polymerization of AB monomer systems are introduced here (Scheme 1). In the first case, the silyl ester bonds along the polymer backbone are formed via transsilylation ester interchange reactions of trimethylsilyl ester and chlorosilane functionalities during the polymerization. This approach is an extension of previous bifunctional comonomer polymerizations involving transsilylation.[22−24] A second method is then developed, in which hydridosilyl ester and terminal unsaturated carbon−carbon bond functionalities are both present within the monomer units and the polymerization is accomplished via hydrosilylation.[32] The features of each of these methods (Table 1) and the properties of poly(silyl ester)s thus prepared are described and compared.

Results and Discussion

The transsilylation transesterification reaction has already proven useful for the preparation of poly(silyl ester)s through reaction of bis(trimethylsilyl) ester and bis(chloro) silane monomers.[22−24] An important finding is that trialkylsilyl chlorides and trimethylsilyl esters do not undergo reaction in the absence of a nucleophilic catalyst (e.g., *N*,*N*-dimethylformamide (DMF)).[33] The inertness of the two functional groups toward each other without catalysis and the ability to initiate the transsilylation polymerization provide an opportunity for the AB-type polymerization to be performed once the AB monomer, containing a chlorosilane and a trimethylsilyl ester functionality, has been synthesized and purified.

The desired AB monomer, **1**, was synthesized by silylation of the acid group of 4-pentenoic acid with

Scheme 2



hexamethyldisilazane (HMDS) to convert the carboxylic acid functionality to a trimethylsilyl ester, followed by hydrosilylation of the terminal vinyl group by reaction with chlorodimethylsilane. Attempts at the hydrosilylation using carbonylchlorobis(triphenylphosphine)rhodium(I) $\{[(C_6H_5)_3P]_2Rh(CO)Cl\}$,[36] hydrogen hexachloroplatinate(IV) (H_2PtCl_6),[37] bis(divinyltetramethylsiloxane)dichloroplatinum(II) $\{[(CH_3)_4(CH_2{=}CH)_2Si_2O]_2PtCl_2\}$,[38] or *cis*-bis(benzonitrile)dichloroplatinum(II)[39] $[(C_6H_5CN)_2PtCl_2]$ as catalysts proved unsuccessful. Instead, a transsilylation reaction between the trimethylsilyl ester and chlorodimethylsilane occurred, which was noted by the reduction of ^{29}Si NMR signal intensity of the resonance for the trimethylsilyl ester at 24 ppm and the appearance of resonances for (TMS)Cl and dimethylsilyl ester at 31 and 7 ppm, respectively. Adjusting the reaction temperature from room temperature to reflux and changing solvents (benzene and tetrahydrofuran (THF)) did not prevent the transsilylation in the presence of the hydrosilylation catalysts. However, hydrosilylation in the presence of platinum on carbon as a mild hydrosilylation catalyst allowed for preparation of the AB monomer without significant contamination by transsilylation products. This two-step route is a slight modification from the procedure reported by Kazuma et al.[34,35] Formation of the trimethylsilyl ester by reaction with HMDS, isolation of the intermediate silyl ester, and limitation of transsilylation reactions through controlled heating and careful catalyst selection afforded **1** in 60% yield.

The purified AB monomer **1** was then polymerized in the presence of 4 mol % DMF by heating at 100 °C under an argon flow for 8 days (Scheme 2). As expected, polymerization of **1** proceeded to higher molecular weight in shorter polymerization time than similar polymerizations with AA/BB monomer systems. After 3 days, the M_w had reached 5580, and another 5 days of heating produced a polymer with molecular weight over 12 000 (Table 2). In comparison, the AA/BB poly-

Table 2. Characterization Data for the Poly(silyl ester)s

polymer	M_w[a]	PDI	DP_w	T_g (°C)	^{29}Si NMR (δ (ppm))	$t_{1/2}$ in solution[b] (h)	$t_{1/2}$ in bulk[c] (h)
8a	12 400	3.8	78	−65	23.0[d]	4	1
8b	27 800	5.6	176	−63	22.0, 22.4[e] (α, β)	4	1
9	23 000	25	111	17	23.1, 23.3[e] (α, β)	0.4	-
11	12 800	12	82	−48	9.3, 9.5[e] (α, β trans)	1	0.4

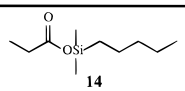
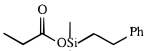
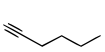
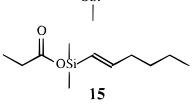
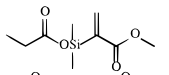
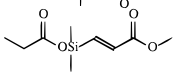
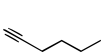
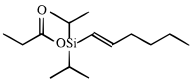
[a] M_w values were obtained from SEC and are based upon calibration with polystyrene standards. [b] $t_{1/2}$ in solution values are the half-lives of the polymers dissolved in THF and exposed to the laboratory environment (ca. 20 °C and 40% humidity). The $t_{1/2}$ value was taken as the time at which the polymer molecular weight (M_w) had reduced to half of the original M_w. [c] $t_{1/2}$ in bulk values are the half-lives of the polymers as neat samples in the solid state and exposed to the laboratory environment (ca. 20 °C and 40% humidity). The $t_{1/2}$ value was taken as the time at which the polymer molecular weight (M_w) had reduced to half of the original M_w. [d] In $CDCl_3$. [e] In THF-d_8.

merization of bis(trimethylsilyl)adipate and bis(dimethylchlorosilyl)ethane gave a poly(silyl ester) with an aliphatic backbone having M_w of 3360 after 2 weeks of heating under similar conditions.[23] Although the molecular weight increase is a significant improvement, the transsilylation chemistry still requires several days of heating to obtain poly(silyl ester)s. Therefore, alternative polymerization chemistries were investigated.

Hydrosilylation reactions have been employed for polymer formation and have allowed for broadly differing monomer compositions.[40−42] To employ hydrosilylation chemistry toward the preparation of poly(silyl ester)s, the silyl ester bond was preformed in the monomers and the polymer backbone was established via Si−C bond formation (Scheme 1). The monomers designed in this methodology contained a dimethylsilyl ester group and a terminal unsaturated carbon−carbon bond; these functionalities are stable in the presence of each other until a hydrosilylation catalyst is added. Moreover, while high temperatures and lengthy reaction times are required for the transsilylation polymerizations to proceed to high molecular weight polymers, the hydrosilylation route can be accomplished at room temperature within a few hours with the addition of a small amount of an appropriate catalyst.

The study of poly(silyl ester) formation through hydrosilylation began with a series of monofunctional small molecule model reactions monitored by ^{1}H and ^{29}Si NMR (Table 3). Dimethylsilyl propionate (**12**) and diisopropylsilyl propionate (**13**) were selected as models of the hydridosilyl ester functionality of the monomers and growing polymer chain ends having different degrees of steric bulk around the silicon atoms. The model dimethylsilyl propionate was prepared by heating propionic acid with excess tetramethyldisilazane (TMDS) in THF at reflux. The model diisopropylsilyl propionate was synthesized through the reaction of propionic acid with chlorodiisopropylsilane at room temperature in the presence of excess imidazole in DMF.[43,44] The reactions of the two silyl propionates with a variety of olefins and alkynes were monitored by ^{1}H NMR and ^{29}Si NMR, and the results provided valuable information on the feasibility of the hydrosilylation addition reaction toward polymer formation.[40−42] Hydrosilylation has been successfully carried out by a multitude of transition metal catalysts.[45,46] A number of these catalysts were screened

Table 3. Model Hydrosilylation Reactions Performed Neat under Argon at Room Temperature for 2 h with 0.3 mol % $Pt(COD)Cl_2$ Added as Catalyst

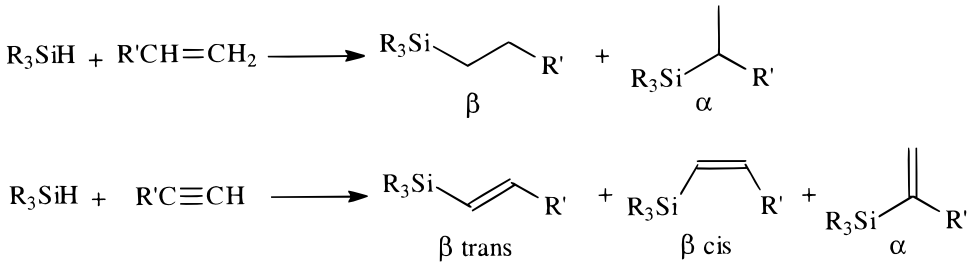
Silyl Ester	Unsaturated Cmpd.	Overall Yield[a] (%)	Main Product	Ratio (%)	^{29}Si NMR (ppm)
12		100	 **14**	99	23.2
12		100		97	22.8
12		100	 **15**	95	9.8
12		100		70	8.8
				30	9.9
13		-	No Reaction	-	-
13		-	No Reaction	-	-
13		86		100	9.7
13		-	No Reaction	-	-

[a] Overall yields were determined by direct ^{1}H NMR and ^{29}Si NMR INEPT analysis.

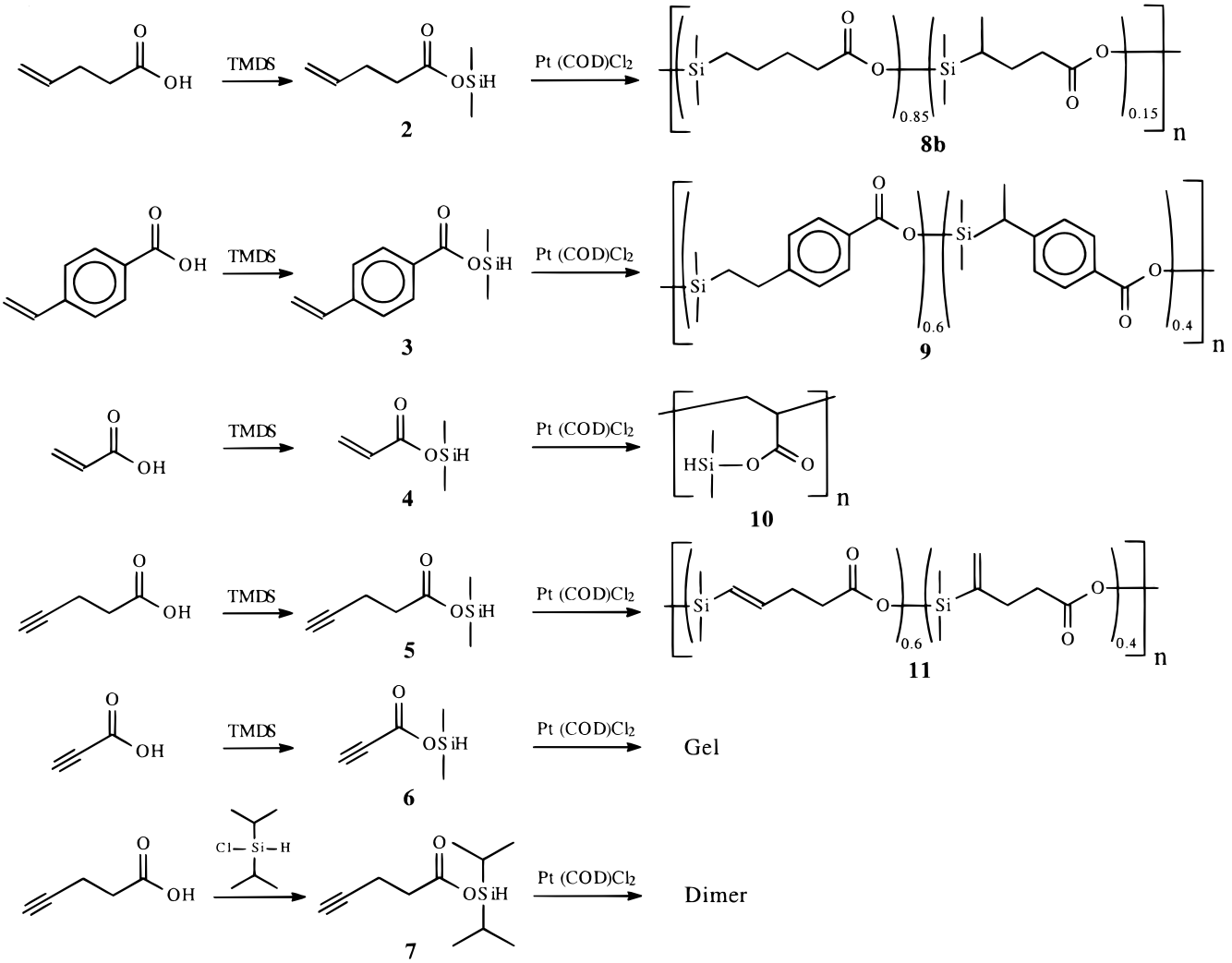
in this study, including $[(C_6H_5)_3P]_2Rh(CO)Cl$,[36] H_2PtCl_6,[37] platinum,[35] dichloro(1,5-cyclooctadiene)platinum(II) [$Pt(COD)Cl_2$],[47−49] and $(C_6H_5CN)_2PtCl_2$.[39] Of these catalysts, $Pt(COD)Cl_2$, which has been used for intramolecular hydrosilylations of β,γ-unsaturated silyl esters at high dilution,[49] was found to be superior for the intermolecular hydrosilylation of silyl esters at increased concentrations, giving the fastest reaction rate and cleanest products. The results from reactions of **12** and **13** with olefins and alkynes using $Pt(COD)Cl_2$ as catalyst are listed in Table 3. **12** underwent smooth reaction with olefins with high regioselectivity,[47] giving >99% β-addition product for the reaction with 1-pentene, and ca. 97% β-addition product for the reaction with styrene. The addition of **12** to alkynes proceeded at higher rates with lower regioselectivity than the olefin hydrosilylations and gave >95% β-trans-addition product for addition to hexyne and 30% β-trans-addition and 70% α-addition products for addition to methyl propiolate (Scheme 3). These results were consistent with the rates and regioselectivities exhibited in the addition of hydridotrialkylsilane compounds to olefins and alkynes.[50] Due to the presence of sterically bulky isopropyl substituents attached to the silicon atoms **13** could only react with hexyne to give a β-trans-hydrosilylation product.

Polymers synthesized through the hydrosilylation chemistry were then produced in two steps, when the starting unsaturated carboxylic acids were readily available: silylation of the acid groups to convert the carboxylic acid functionality into a hydridosilyl ester, followed by polymerization of the purified AB monomers through the hydrosilylation reactions between the hy-

Scheme 3



Scheme 4



dridosilyl ester and the terminal unsaturated carbon−carbon bond (Scheme 4). The desired AB monomers (**2**−**6**) were synthesized by silylation of the acid groups with TMDS to form dimethylsilyl esters. To eliminate the autopolymerization of styrenyl group, purification of **3** required the use of a Kugelrohr apparatus for distillation (ca. 100 °C/0.2 mmHg). A control study involving the polymerization of **2** allowed for the amount of catalyst, reaction temperature, reaction time, solvent, and the concentration of reagents to be optimized to produce poly(silyl ester)s with high molecular weight with little or no introduction of addition polymerization products. Size exclusion chromatography (SEC) and NMR were employed to monitor the reactions. An addition of 0.5 mol % catalyst was found to effectively produce polymers with relatively high molecular weight (Figure 1). The dramatic increase in the viscosity at the late stage of the polymerization retarded further chain propagation. However, dilution by THF to form a 10 M solution lowered the viscosity and increased the chain mobility to yield higher degrees of polymerization (Table 4). Further dilution led to the formation of polymers with decreased molecular weight. The molecular weight continued to increase for the first 2 h of polymerization time (Figure 1). With the addition of THF to form a 10 M solution and 0.5 mol % $Pt(COD)Cl_2$ as the catalyst into the freshly distilled monomer, the polymerization occurred instantly, accompanied by the release of a large amount of heat. The disappearance of the resonance for the hydridosilyl ester functionality of the monomer and the appearance of the corresponding resonance for the new trialkylsilyl ester linkages along the polymer backbone were observed in ^{29}Si NMR.

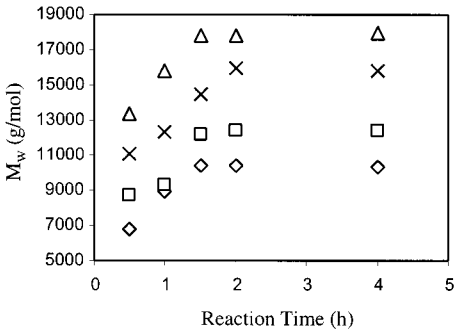


Figure 1. M_w of polymer as a function of catalyst concentration and reaction time: (◇) 0.2 mol %; (□) 0.3 mol %; (△) 0.5 mol %; (×) 0.7 mol %. The data are for the bulk polymerization of **2** at room temperature.

Table 4. Evaluation of the Effects of Polymerization Temperature and Monomer Concentration upon the Polymerizattion of 2, As Determined by Measurement of M_w by SEC[a]

	M_w for polymerization temperatures		
concentration of **2**	0 °C	25 °C	50 °C
1 M in THF		4080	
5 M in THF		14 200	
10 M in THF	17 000	19 400	23 800
15 M in THF	14 900	17 200	21 700
neat	9080	15 700	21 850

[a] The M_w values were measured after polymerization of **2** in THF at concentrations of 1, 5, 10, and 15 M and neat and temperatures of 0, 25, and 50 °C for 2 h in the presence of 0.5 mol % catalyst ($Pt(COD)Cl_2$).

The polymerization of **2** to form **8b** proceeded with relatively high regioselectivity, leading to the formation of polymer with 85% β-addition and 15% α-addition linkages along its backbone. The hydrosilylation of **3** and **5** exhibited less regioselectivity: the backbone of polymer **9** contained 60% β-addition product and 40% α-addition product; and the backbone of polymer **11** contained 60% β-trans-and 40% α-addition products. In general, the regioselectivities exhibited in the polymerization were lower than those exhibited in the model studies. These differences are believed to be the result of the exothermal chain reaction character of the polymer formation. Although in model reactions **12** underwent hydrosilylation with all of the olefins and alkynes, attempts to polymerize **4** and **6** failed to obtain the desired silyl ester polymers. The polymerization of **4** yielded linear-addition polymerization product **10** with a polyethylene backbone, instead of the hydrosilylation product with the condensation silyl ester functionality along its backbone. This was confirmed by the persistence of the resonance for hydrogen atoms attached to the silicons in ^{1}H NMR and the resonance for dimethylhydridosilyl ester in ^{29}Si NMR. Hydrolysis of this polymer monitored by SEC also revealed no degradation of the polymer backbone. Polymerization of **6** yielded a cross-linked "gel" after a vigorous exothermic reaction. Lowering the reaction temperature to 0 °C and further dilution with THF did not overcome this problem. Attempts to polymerize **7** also failed; heating to as high as 100 °C yielded only oligomer (mainly dimer). It is possible that the two sterically bulky isopropyl groups attached to the silicon atoms limited the reactivity of hydridosilyl ester toward hydrosilylation and thereby inhibited the polymerization. In comparison with the synthesis of poly(silyl ester)s through AA/BB monomer systems, which gave typical monomer conversions of 85−90%,[22−24] the synthesis through AB monomer systems increased the monomer conversion to 95% for the strategy using the transsilylation route and 97% for the hydrosilylation route.

The characterization of each polymer included infrared (IR), ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR INEPT spectroscopies, SEC, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The IR spectra of polymers contained absorbances at frequencies corresponding to a Si−O stretch between 1000 and 1100 cm^{-1}, a Si−CH_3 stretch at ca. 1250 cm^{-1}, a C−O stretch at 1250−1350 cm^{-1}, a strong C═O absorption at ca. 1700 cm^{-1}, and C−H stretches between 2800 and 3000 cm^{-1}. The absorbance for aromatic C−H stretches (>3000 cm^{-1}) was observed for **9**, and the absorbance for C═C stretching vibrations (1650−1680 cm^{-1}) was observed for **11**.

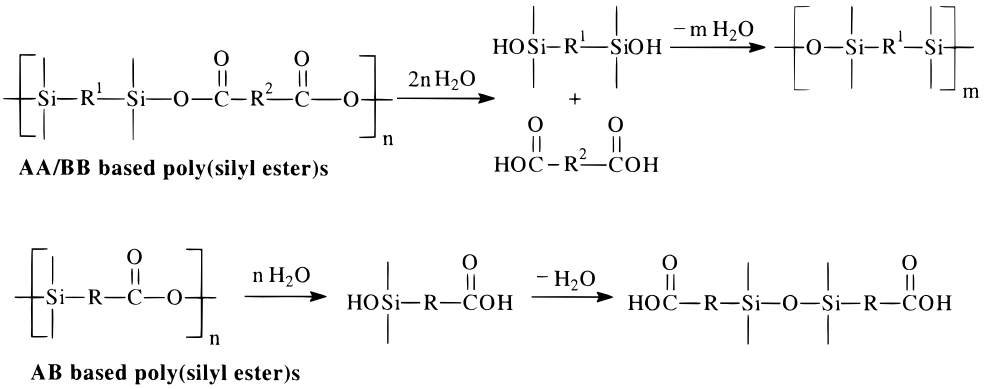
Glass transition temperatures (T_g's) of the poly(silyl ester)s were measured by DSC under nitrogen, and the data are presented in Table 2. Each of the poly(silyl ester)s exhibited a T_g correlating well with its chemical structure. The T_g of **9** (17 °C) is much higher than those of other poly(silyl ester)s, which can be explained by the increased chain rigidity brought about by the high density of aromatic rings along the polymer backbone. The thermal stabilities of the poly(silyl ester)s were evaluated by TGA from 25 to 500 °C in air. Each of the four poly(silyl ester)s (**8a**, **8b**, **9**, and **11**) exhibited no mass loss up to 180 °C.

The degradation studies by hydrolysis were performed upon the poly(silyl ester)s as neat samples, as well as in THF solutions exposed to the lab environment (ca. 20 °C and 40% humidity). The decreasing molecular weights of the polymers over time were observed by SEC. The half-life of each poly(silyl ester) is listed in Table 2. Although the AB polymerizations proceeded very nicely from readily synthesized monomers, the polymers formed were extremely hydrolytically labile. This was expected since the silyl ester linkages in the polymer backbones have only methyl side groups attached to the silicon atoms. Poly(5-dimethylsilyl pentanoate)s synthesized from transsilylation (**8a**) and hydrosilylation chemistry (**8b**) exhibited similar stabilities toward nucleophilic attack, which is reasonable because the polymers have the same chemical structure, although their origins of preparation were different, and this suggests that the remaining catalysts do not affect the polymer degradation. The degradation rates of **8a** and **8b** were also comparable with those of the methyl-substituted polymers synthesized through AA/BB monomers.[23,24]

Although the degradation of poly(silyl ester)s synthesized from AA/BB monomer systems gave degradation products containing silanol groups at both ends that self-condensed to form poly(siloxane)s,[23,24] the hydrolysis of poly(silyl ester)s synthesized through AB monomer systems gave degradation products that contain silanol and carboxylic acid terminal groups. Therefore, the degradation products from the present poly(silyl ester)s had no opportunity to form another polymer and were limited to the dimerization of two molecules through the condensation of silanol functionalities (Scheme 5).

The degradation rates in their solid states were faster than those observed for the hydrolysis of the polymers in solution. It is uncertain whether this behavior was due to an autoacceleration effect in the solid state as the hydrophilicity and polarity increased with increas-

Scheme 5



ing formation of hydrolysis products. This phenomenon is being further evaluated by analysis of surface erosion processes by atomic force microscopy.[51]

The backbone compositions of the poly(silyl ester)s substantially affected the susceptibility of the polymer materials toward nucleophilic attack. Polymer **9** was found to be less stable toward nucleophilic attack than **8a** and **8b**. A mechanistic study was performed using trimethylsilyl acetate and trimethylsilyl benzoate as small molecule models. Hydrolysis of trimethylsilyl benzoate upon nucleophilic attack by excess methanol in THF was found to be about one hundred times faster than the hydrolysis of trimethylsilyl acetate under the same conditions. As revealed by ^{29}Si NMR analysis, attack by methanol on both silyl esters occurred entirely on the silicon atoms of the silyl ester linkages to form the silyl ether and corresponding carboxylic acids as hydrolysis products. Because the benzoate anion is a better leaving group than the aliphatic carboxylic anion, the attack by nucleophiles should occur more readily for trialkylsilyl benzoate than for trialkylsilyl acetate. This also supports the relatively lower stability of **9**, compared to **8a** and **8b**. Polymer **11** was also found to be more hydrolytically labile than polymers **8a** and **8b**. The only difference between these polymers (**11**, **8a**, and **8b**) is the backbone unit attached to the silicon atoms: alkyl vs vinyl. Theoretically, the π-orbital of the C=C bonds adjacent to the silicon atoms overlaps with the antibonding σ-orbital of Si−O bonds, thereby lowering the bond order of the Si−O bonds and causing lower stability for Si−O bonds with vinyl substituents than those for Si−O bonds with alkyl substituents. Experimentally, two small molecule silyl esters, dimethylpentylsilyl propionate (**14**) and (butylvinyl)dimethylsilyl propionate (**15**), were synthesized to model the alkyl and vinyl silyl ester functionalities along the polymer backbones (Table 3). Upon reaction with methanol in THF, 13% of **14** was hydrolyzed into propionic acid and corresponding silyl ether in 10 min, whereas 76% of **15** was hydrolyzed in 3 min. This demonstrated that the vinyl attachment increased the electrophilicity of the silicon atoms, and therefore decreased the stability of silyl ester linkages toward nucleophilic attack.

Experimental Section

General Directions. All manipulations of reagents and reactions were performed under argon on a double manifold and all glassware was flame-dried under vacuum. ^{1}H NMR spectra were recorded on a Varian Unity-plus (300 MHz) spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75 MHz on a Varian Unity-plus spectrometer with the solvent carbon signal as standard. ^{29}Si NMR spectra were recorded using standard INEPT (insensitive nuclei enhanced by polarization transfer) experiments on a Varian Unity-plus spectrometer at 59.6 MHz and were referenced externally to tetramethylsilane at 0 ppm. IR spectra were obtained on a Mattson polaris spectrometer as thin films between NaCl disks. Size exclusion chromatography was conducted with a Hewlett-Packard series 1050 HPLC, and detection was by a Hewlett-Packard 1047A refractive index detector; data analysis was performed with Trisec SEC Software, version 3.00 (Viscotek Corporation, Houston, TX). Two 5 μm Polymer Laboratories PL$_{gel}$ columns (300 × 7.7 mm) connected in series in order of increasing pore size were used with THF distilled from calcium hydride as the eluent. Molecular weights were based on polystyrene standards (Polymer Laboratories Ltd., Amherst, MA). Glass transition temperatures (T_g's) were measured by differential scanning calorimetry under N_2 or He, on a Perkin-Elmer DSC-4 differential scanning calorimeter. Heating rates were 10 °C/min up to 150 °C. T_g was taken as the midpoint of the inflection tangent. Thermogravimetric analyses were done in air, on a Perkin-Elmer TGS-2 Thermogravimetric analyzer. For both DSC and TGA, the Perkin-Elmer instruments were upgraded with Instrument Specialists, Inc. (Antioch, IL) temperature program interface-PE, and data were acquired and analyzed using TA-PC software version 2.11a (Instrument Specialists, Inc.).

Materials. *N*,*N*-Dimethylformamide (DMF) was purchased from Aldrich Co. and distilled under reduced pressure from CaO. Tetrahydrofuran (THF) (omnisolv grade) was purchased from EM Science and distilled from sodium/benzophenone. Benzene was purchased from EM Science, dried over sodium and distilled. Silicon compounds were purchased from United Chemical Technologies and distilled immediately prior to use. All the other chemicals were purchased from Aldrich and used as received. *p*-Vinylbenzoic acid was prepared according to the literature procedure.[52,53]

Trimethylsilyl 5-(Chlorodimethylsilyl)pentanoate (1). A sample of 10 wt % platinum on activated carbon (5 mg) and trimethylsilyl pentenoate (4.77 g, 27.7 mmol) (distilled from the reaction of pentenoic acid and hexamethyl disilazane) were stirred under an argon atmosphere and chlorodimethylsilane (6.0 mL, 54 mmol) was added slowly via syringe. The reaction mixture was allowed to stir at 30 °C for 2 h. The product was isolated by distillation (93 °C/3 mmHg) as a colorless liquid (3.76 g, 14.1 mmol): yield 51%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 9H, −COOSi(C***H***$_3$)$_3$), 0.33 (s, 6H, −Si(C***H***$_3$)$_2$Cl), 0.77 (t, J = 7 Hz, 2H, −C***H***$_2$CH$_2$CH$_2$CH$_2$COO−), 1.39 (overlapping tt, J = 7 Hz, 2H, −CH$_2$C***H***$_2$CH$_2$CH$_2$COO−), 1.60 (overlapping tt, J = 7 Hz, 2H, −CH$_2$CH$_2$C***H***$_2$CH$_2$COO−), 2.25 (t, J = 7 Hz, 2H, −CH$_2$CH$_2$CH$_2$C***H***$_2$COO−) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.37 (−COOSi(***C***H$_3$)$_3$), 1.48 (−Si(***C***H$_3$)$_2$Cl), 18.58 (−***C***H$_2$CH$_2$CH$_2$CH$_2$COO−), 22.40 (−CH$_2$***C***H$_2$CH$_2$CH$_2$COO−), 27.98 (−CH$_2$CH$_2$***C***H$_2$CH$_2$COO−), 35.35 (−CH$_2$CH$_2$CH$_2$***C***H$_2$-COO−), 173.95 (carbonyl***C***) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 23.1 (−COO***Si***(CH$_3$)$_3$), 31.5 (−***Si***(CH$_3$)$_2$Cl) ppm.

Poly(5-dimethylsilyl pentanoate) by Transsilylation (8a). To a 10 mL reaction flask equipped with a Teflon stopcock

were added **1** (1.56 g, 5.86 mmol) and DMF (0.02 mL, 0.26 mmol). The reaction mixture was allowed to stir under an argon atmosphere at 100 °C for 8 days. Because of the hydrolytic sensitivities of the polymer, no further purification techniques were performed. IR (NaCl): 2900, 2850, 1712, 1254, 1198, 1170, 1044, 850, 840, 831, 824, 794 cm^{-1}. $T_g = -65$ °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 6H, $-Si(CH_3)_2$-), 0.75 (t, $J = 7$ Hz, 2H, $-CH_2CH_2CH_2CH_2COO-$), 1.39 (m, 2H, $-CH_2CH_2CH_2CH_2COO-$), 1.61 (m, 2H, $-CH_2CH_2CH_2CH_2COO-$), 2.28 (t, $J = 7$ Hz, 2H, $-CH_2CH_2CH_2CH_2COO-$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −1.85 ($-Si(CH_3)_2-$), 15.79 ($-CH_2CH_2CH_2CH_2COO-$), 22.42 ($-CH_2CH_2CH_2CH_2COO-$), 28.34 ($-CH_2CH_2CH_2CH_2COO-$), 35.53 ($-CH_2CH_2CH_2CH_2COO-$), 174.81 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 23.0 ppm. $M_w = 12\,400$; $M_w/M_n = 3.8$, based upon SEC with polystyrene standards.

(Dimethylsilyl) 4-Pentenoate (2). To a solution of 4-pentenoic acid (3.92 g, 39.2 mmol) in THF (25 mL) was added slowly via syringe 1,1,3,3-tetramethyl disilazane (TMDS) (4.0 mL, 23 mmol) with stirring under an argon atmosphere. The reaction was heated at reflux for 4 h. The solvent and excess TMDS were removed under reduced pressure, and the product was isolated by distillation (58−59 °C, 10 mmHg) as a colorless liquid (6.02 g, 38.0 mmol): yield 97%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.30 (d, $J = 3$ Hz, 6H, $-Si(CH_3)_2H$), 2.36 (t, $J = 6$ Hz, 2H, $-COCH_2CH_2-$), 2.41 (quartet, $J = 6$ Hz, 2H, $-COCH_2CH_2-$), 4.78 (septet, $J = 3$ Hz, 1H, $-Si(CH_3)_2H$), 4.99 (dd, $J_1 = 10$ Hz, $J_2 = 1$ Hz, 1H, $-CH_2CH=CHH$), 5.05 (dd, $J_1 = 17$ Hz, $J_2 = 1$ Hz, 1H, $-CH_2CH=CHH$), 5.80 (m, 1H, $-CH_2CH=CHH$ ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.15 ($-Si(CH_3)_2H$), 16.44 ($-COCH_2CH_2-$), 34.74 ($-COCH_2CH_2-$), 115.35 ($-CH_2CH=CH_2$), 136.56 ($-CH_2CH=CH_2$), 173.74 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 6.3 ppm.

(Dimethylsilyl) 4-vinyl benzoate (3). To a solution of 4-vinylbenzoic acid[52,53] (1.17 g, 7.90 mmol) in THF (25 mL) was added slowly via syringe TMDS (2.0 mL, 11 mmol) with stirring under an argon atmosphere in an ice−water bath. The reaction was allowed to warm to room temprature and stirred for another 6 h. The solvent and excess TMDS were removed under reduced pressure and the product was distilled on a Büchi distillation apparatus (100 °C/0.1 mmHg) as a colorless liquid (0.84 g, 4.1 mmol): yield 52%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.50 (d, $J = 3$ Hz, 6H, $-Si(CH_3)_2H$), 4.98 (septet, $J = 3$ Hz, 1H, $-Si(CH_3)_2H$), 5.42 (dd, $J_1 = 11$ Hz, $J_2 = 1$ Hz, 1H, $-CH=CHH$), 5.89 (dd, $J_1 = 18$ Hz, $J_2 = 1$ Hz, 1H, $-CH=CHH$), 6.78 (dd, $J_1 = 11$ Hz, $J_2 = 18$ Hz, 1H, $-CH=CH_2$), 7.49 (d, $J = 8$ Hz, 2H, Ar), 8.00 (d, $J = 8$ Hz, 2H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −1.95 ($-Si(CH_3)_2H$), 116.51 ($-CH=CH_2$), 126.65 (Ar**C**), 129.94 (ipso Ar**C**), 130.50 (Ar**C**), 136.00 ($-CH=CH_2$), 142.12 (ipso Ar**C**), 166.45 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 7.7 ppm.

(Dimethylsilyl) Acrylate (4). To a solution of acrylic acid (4.06 g, 56.3 mmol) in THF (25 mL) was added slowly via syringe TMDS (7.0 mL, 39 mmol) with stirring under an argon atmosphere in an ice−water bath. The reaction was allowed to warm to room temprature and stirred for another 6 h. The solvent and excess TMDS were removed under reduced pressure, and the product was isolated by distillation (38−39 °C, 32 mmHg) as a colorless liquid (6.60 g, 50.7 mmol): yield 90%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.40 (d, $J = 3$ Hz, 6H, $-Si(CH_3)_2H$), 4.80 (septet, $J = 3$ Hz, 1H, $-Si(CH_3)_2H$), 5.83 (dd, $J_1 = 10$ Hz, $J_2 = 1$ Hz, 1H, $-CH=CHH$), 6.06 (dd, $J_1 = 17$ Hz, $J_2 = 1$ Hz, 1H, $-CH=CHH$), 6.36 (dd, $J_1 = 17$ Hz, $J_2 = 10$ Hz, 1H, $-CH=CHH$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 7.1 ppm.

(Dimethylsilyl) 4-Pentynoate (5). To a solution of 4-pentynoic acid (1.60 g, 16.3 mmol) in THF (25 mL) was added slowly via syringe TMDS (2.0 mL, 11 mmol) with stirring under an argon atmosphere. The reaction was heated at reflux for 4 h. The solvent and excess TMDS were removed under reduced pressure, and the product was isolated by distillation (59−60 °C, 4 mmHg) as a colorless liquid (2.44 g, 15.6 mol): yield 96%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.33 (d, $J = 3$ Hz, 6H, $-Si(CH_3)_2H$), 1.93 (s, 1H, $-CH_2C\equiv CH$) 2.42 (t, $J = 6$ Hz, 2H, $-COCH_2CH_2-$), 2.51 (t, $J = 6$ Hz, 2H, $-COCH_2CH_2-$), 4.75 (septet, $J = 3$ Hz, 1H, $-Si(CH_3)_2H$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.23 ($-Si(CH_3)_2H$), 14.24 ($-COCH_2CH_2-$), 34.48 ($-COCH_2CH_2-$), 68.92 ($-CH_2C\equiv CH$), 82.32 ($-CH_2C\equiv CH$), 173.27 (carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 7.0 ppm.

(Dimethylsilyl) Propiolate (6). To a solution of propiolic acid (2.85 g, 40.7 mmol) in THF (25 mL) was added slowly *via* syringe TMDS (4.0 mL, 22 mmol) with stirring under an argon atmosphere in ice−water bath. The reaction was allowed to warm to room temprature and stirred for another 6 h. The solvent and excess TMDS were removed under reduced pressure, and the product was isolated by distillation (45−46 °C, 21 mmHg) as a colorless liquid (3.96 g, 30.9 mmol): yield 76%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.41 (d, $J = 3$ Hz, 6H, $-Si(CH_3)_2H$), 2.93 (s, 1H, $-C\equiv CH$), 4.86 (septet, $J = 3$ Hz, 1H, $-Si(CH_3)_2H$) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 10.4 ppm.

(Diisopropylsilyl) 4-Pentynoate (7). To a DMF solution containing chlorodiisopropylsilane (3.0 mL, 17.4 mmol) and imidazole (2.30 g, 33.8 mmol) was added slowly via additional funnel 4-pentynoic acid (1.60 g, 16.3 mmol) with stirring at 35 °C for 10 h under an argon atmosphere. The product was isolated by distillation (82−83 °C, 0.3 mmHg) as a colorless liquid (2.59 g, 12.2 mmol): yield 75%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.00 (d, $J = 7$ Hz, 12H, $-CH(CH_3)_2$), 1.08 (m, 2H, $-CH(CH_3)_2$), 1.90 (s, 1H, $-CH_2C\equiv CH$), 2.44 (t, $J = 6$ Hz, 2H, $-COCH_2CH_2-$), 2.55 (t, $J = 6$ Hz, 2H, $-COCH_2CH_2-$), 4.35 (t, $J = 3$ Hz, 1H, $-Si(C_3H_7)_2H$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 14.7 ppm.

General Procedure for the Synthesis of Poly(silyl ester)s through Hydrosilylation. The appropriate dimethylsilyl ester was distilled into a flame-dried reaction tube. To the reaction tube was then added THF to form a 10 M solution of monomer in solvent, and 0.5 mol % of $Pt(COD)Cl_2$ as the catalyst. The reaction was typically allowed to proceed with stirring under an argon atmosphere for 2 h. The THF solvent was then removed in vacuo. Because of the hydrolytic instabilities of the polymers, purification was not performed. However, removal of catalyst via filtration was done prior to SEC analysis.

Poly(5-dimethylsilyl pentanoate) (8b). This was prepared from **2** at 50 °C. $T_g = -63$ °C. IR (NaCl): 2960−2860, 1717, 1368, 1255, 1198, 1170, 1044, 848, 832 cm^{-1}. ^1H NMR (300 MHz, THF-d_8): δ 0.24 (s, 6H, $-Si(CH_3)_2-$), 0.53 (m, 1H, 15% $-CH(CH_3)CH_2CH_2COO-$), 0.77 (t, $J = 7$ Hz, 2H, 85% $-CH_2CH_2CH_2CH_2COO-$), 1.40 (d, $J = 7$ Hz, 3H, 15% $-CH(CH_3)CH_2CH_2COO-$), 1.42 (m, 2H, 85% $-CH_2CH_2CH_2CH_2COO-$), 1.60 (m, 2H, $-CH_2CH_2COO-$), 2.28 (t, $J = 7$ Hz, 2H, $-CH_2CH_2COO-$) ppm. ^{13}C NMR (75 MHz, THF-d_8): δ −1.74 (15% $-Si(CH_3)_2-$), −1.64 (85% $-Si(CH_3)_2-$), 16.02 (15% $-CH(CH_3)CH_2CH_2COO-$), 16.62 (85% $-CH_2CH_2CH_2CH_2COO-$), 18.75 (15% $-CH(CH_3)CH_2CH_2COO-$), 23.25 (85% $-CH_2CH_2CH_2CH_2COO-$), 29.26 (15% $-CH_2CH_2CH_2CH_2COO-$), 29.46 (85% $-CH_2CH_2CH_2CH_2COO-$), 36.01 (15% $-CH_2CH_2CH_2CH_2COO-$), 36.11 (85% $-CH_2CH_2CH_2CH_2COO-$), 173.80 (15% carbonyl**C**), 173.93 (85% carbonyl**C**) ppm. ^{29}Si NMR (59.6 MHz, THF-d_8) δ 22.0 (α product), 22.4 (β product) ppm. $M_w = 27800$; $M_w/M_n = 5.6$, based upon SEC with polystyrene standards.

Poly(dimethylsilylethyl benzoate) (9). This was prepared from **3** at room temperature. $T_g = 17$ °C. IR (NaCl): 3100−3000, 2950−2850, 1684, 1653, 1609, 1575, 1425, 1315, 1293, 1252, 1176, 1126, 1086, 1017, 835, 800 cm^{-1}. ^1H NMR (300 MHz, THF-d_8): δ 0.32 (s, 6H, $-Si(CH_3)_2-$), 1.22 (br m, 3H, 40% $-Si(CH_3)_2CH(CH_3)-$), 1.34 (br m, 2H, 60% $-Si(CH_3)_2CH_2CH_2-$), 2.78 (br m, 1H, 40% $-Si(CH_3)_2CH(CH_3)-$), 2.84 (br m, 2H, 60% $-Si(CH_3)_2CH_2CH_2-$), 7.06 (br m, 2H, Ar) ppm, 7.28 (br m, 2H, Ar) ppm, 7.32 (br m, 2H, Ar) ppm, 7.88 (br m, 2H, Ar) ppm. ^{13}C NMR (75 MHz, THF-d_8): δ 0.44 (40% $-Si(CH_3)_2-$), −1.54 (60% $-Si(CH_3)_2-$), 16.13 (40% $-SiCH_3)_2-CH(CH_3)-$), 20.81 (60% $-Si(CH_3)_2CH_2CH_2-$), 30.29 (60% $-Si(CH_3)_2CH_2CH_2-$), 30.56 (40% $-Si(CH_3)_2CH(CH_3)-$), 128.42 (Ar**C**), 128.52 (Ar**C**), 128.77 (ipso Ar**C**), 129.38 (ipso Ar**C**), 130.62 (Ar**C**), 130.94 (Ar**C**), 148.30 (ipso Ar**C**), 150.95 (ipso Ar**C**), 167.45 (carbonyl**C**), 167.55 (carbonyl**C**) ppm. ^{29}Si NMR

(59.6 MHz, THF-d_8): δ 23.1 (α product), 23.3 (β product) ppm. $M_w = 23\,000$; $M_w/M_n = 25$, based upon SEC with polystyrene standards.

Poly(dimethylsilyl acrylate) (10). This was prepared from **4** at room temperature. ^{1}H NMR (300 MHz, THF-d_8): δ 0.30 (d, $J = 3$ Hz, 6H, $-$Si(C***H***$_3$)$_2$H), 4.80 (br m, 1H, $-$Si(CH$_3$)$_2$***H***), 1.13 (br m, 1H, $-$C***H***HCH(COOSiC$_2$H$_7$)$-$), 1.49 (br m, 1H, $-$CH***H***C***H***(COOSiC$_2$H$_7$)$-$), 2.39 (br m, 1H, $-$CH$_2$C***H***-(COOSiC$_2$H$_7$)$-$) ppm. ^{29}Si NMR (59.6 MHz, THF-d_8): δ 6.0 ppm. $M_w = 9000$; $M_w/M_n = 2.6$, based upon SEC with polystyrene standards.

Poly(dimethylsilyl 4-pentenoate) (11). This was prepared from **5** at room temperature. $T_g = -48$ °C. IR (NaCl): 2970−2910, 1739, 1733, 1717, 1705, 1700, 1684, 1652, 1617, 1350, 1259, 1065, 668 cm^{-1}. ^{1}H NMR (300 MHz, THF-d_8): δ 0.28 (s, 6H, $-$Si(C***H***$_3$)$_2-$), 2.40 (br m, 4H, $-$C***H***$_2$C***H***$_2-$), 5.70 (br m, 1H, 60% $-$Si(CH$_3$)$_2$C***H***=CHCH$_2-$), 5.78 (d, $J = 1$ Hz, 1H, 40% $-$Si(CH$_3$)$_2$(C=C***H***H)CH$_2$CH$_2-$), 6.15 (br m, 1H, 60% $-$Si(CH$_3$)$_2$CH=C***H***CH$_2-$), 6.21 (d, $J = 1$ Hz, 1H, 40% $-$Si(CH$_3$)$_2$C(=CH***H***)CH$_2$CH$_2-$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ −1.88 (40% $-$Si(***C***H$_3$)$_2-$), −1.78 (60% $-$Si(***C***H$_3$)$_2-$), 31.12 (40% $-$***C***H$_2$CH$_2$CO$-$), 31.31 (60% $-$***C***H$_2$CH$_2$CO$-$), 34.06 (40% $-$CH$_2$***C***H$_2$CO$-$), 34.34 (60% $-$CH$_2$***C***H$_2$CO$-$), 123.50 (40% $-$Si(CH$_3$)$_2$C(=***C***H$_2$)CH$_2$CH$_2-$), 126.35 (60% $-$Si(CH$_3$)$_2$***C***H=CHCH$_2-$), 148.03 (40% $-$Si(CH$_3$)$_2$***C***(=CH$_2$)CH$_2$CH$_2-$), 148.39 (60% $-$Si(CH$_3$)$_2$CH = ***C***HCH$_2-$), 173.20 (40% carbonyl***C***), 173.30 (60% carbonyl***C***) ppm. ^{29}Si NMR (59.6 MHz, THF-d_8): δ 9.3 (α product), 9.5 (β trans product) ppm. $M_w = 12\,800$; $M_w/M_n = 12$, based upon SEC with polystyrene standards.

Pentyldimethylsilyl Propionate (14). A catalytic amount of Pt(COD)Cl$_2$ and pentene (1.0 mL, 9.1 mmol) were stirred under an argon atmosphere at room temperature for 30 min after which time **12** (0.90 g, 6.8 mmol) (distilled from the reaction of pentenoic acid and TMDS) was added. The reactants were stirred for 4 h. The product was isolated by distillation (38−39 °C/0.2 mmHg) as a colorless liquid (1.11 g, 5.5 mmol): yield 81%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.24 (s, 6H, $-$COOSi(C***H***$_3$)$_2-$), 0.72 (t, $J = 7$ Hz, 2H, $-$C***H***$_2$CH$_2$CH$_2$-CH$_2$CH$_3$), 0.86 (t, $J = 7$ Hz,3H, $-$CH$_2$CH$_2$CH$_2$CH$_2$C***H***$_3$), 1.08 (t, $J = 7$ Hz, 3H, $-$COCH$_2$C***H***$_3$), 1.20−1.45 (br m, 6H, $-$CH$_2$C***H***$_2$C***H***$_2$C***H***$_2$CH$_3$), 2.30 (quart, $J = 7$ Hz, 2H, $-$COC***H***$_2$-CH$_3$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ −2.01 ($-$COOSi-(***C***H$_3$)$_2-$), 8.98 ($-$COCH$_2$***C***H$_3$), 13.71 ($-$***C***H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 15.74 ($-$CH$_2$CH$_2$CH$_2$CH$_2$***C***H$_3$), 22.10 ($-$CH$_2$CH$_2$CH$_2$***C***H$_2$CH$_3$), 22.30 ($-$CH$_2$***C***H$_2$CH$_2$CH$_2$CH$_3$), 28.96 ($-$CO***C***H$_2$CH$_3$), 35.18 ($-$CH$_2$CH$_2$***C***H$_2$CH$_2$CH$_3$), 174.78 (carbonyl***C***) ppm. ^{29}Si NMR (59.6 MHz, CDCl$_3$): δ 23.2 ppm.

(Butylvinyl)dimethylsilyl Propionate (15). A catalytic amount of Pt(COD)Cl$_2$ and hexyne (1.0 mL, 8.7 mmol) were stirred under an argon atmosphere at room temperature for 30 min after which time **12** (0.90 g, 6.8 mmol) (distilled from the reaction of pentenoic acid and TMDS) was added. The reactants were stirred for 4 h. The product was isolated by distillation (69−70 °C/0.2 mmHg) as a colorless liquid (1.16 g, 5.4 mmol): yield 80%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.33 (s, 6H, $-$COOSi(C***H***$_3$)$_2-$), 0.90 (t, $J = 7$ Hz, 3H, $-$CH$_2$CH$_2$-CH$_2$C***H***$_3$), 1.10 (t, $J = 7$ Hz, 3H, $-$COCH$_2$C***H***$_3$), 1.24−1.48 (br m, 4H, $-$CH$_2$C***H***$_2$C***H***$_2$CH$_3$), 2.15 (quart, $J = 7$ Hz, 2H, $-$C***H***$_2$-CH$_2$CH$_2$CH$_3$), 2.32 (quart, $J = 7$ Hz, 2H, $-$COC***H***$_2$CH$_3$), 5.73 (d, $J = 18$ Hz, 1H, $-$C***H***=CHC$_4$H$_9$), 6.25 (dt, $J_1 = 18$ Hz, $J_2 = 7$ Hz, 1H, $-$CH=C***H***C$_4$H$_9$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ −1.85 ($-$COOSi(***C***H$_3$)$_2-$), 8.94 ($-$COCH$_2$***C***H$_3$), 13.75 ($-$CH$_2$-CH$_2$CH$_2$***C***H$_3$), 22.08 ($-$CH$_2$CH$_2$***C***H$_2$CH$_3$), 28.96 ($-$CO***C***H$_2$CH$_3$), 30.37 ($-$CH$_2$***C***H$_2$CH$_2$CH$_3$), 36.07 ($-$***C***H$_2$CH$_2$CH$_2$CH$_3$), 125.24 ($-$***C***H=CHC$_4$H$_9$), 150.88 ($-$CH=***C***HC$_4$H$_9$), 174.79 (carbonyl***C***) ppm. ^{29}Si NMR (59.6 MHz, CDCl$_3$): δ 9.8 ppm.

Degradation of Polymers in Solution. Approximately 10 mg of polymer was dissolved in 2 mL of THF. Exposure to the laboratory atmosphere (ca. 20 °C, 40% humidity) provided for degradation by water. At the appropriate times (5 min, 0.5 h, 1 h, 2 h, 4 h, 8 h, 1 d, and 2 d), 0.1 mL of the polymer solution was injected into the SEC and the resulting chromatogram was analyzed.

Degradation of Polymers as Solid Samples in Air. Samples of ca. 10 mg each of the polymer were placed into individual glass vials. The vials were open to the laboratory environment (ca. 20 °C and 40% humidity). At the appropriate times (5 min, 0.5 h, 1 h, 2 h, 4 h, 8 h, 1 d, and 2 d), the polymer samples were dissolved in THF and the SEC chromatograms were obtained.

Conclusions

In this work, the syntheses of poly(silyl ester)s based on AB monomer systems through transsilylation and hydrosilylation routes were designed and accomplished. In comparison to the polymerizations through AA/BB systems, relatively faster propagation rates and higher degrees of polymerization were achieved. Furthermore, polymerizations through the hydrosilylation route reduced the monomer preparation difficulties, lowered the reaction temperatures to ambient temperature, and substantially shortened the reaction times. Because of difficulties for silyl compounds with sterically bulky substituents to undergo hydrosilylation using the current catalyst system, the polymerizations through AB monomer systems are still limited to the synthesis of poly(silyl ester)s with methyl side chain substituents. To improve the stability toward nucleophilic attack, this limitation will have to be overcome.

Acknowledgment. Financial support for this work by a DuPont Young Professor Grant is gratefully acknowledged.

References and Notes

(1) Nakagawa, K. *Shitsuryo Bunseki* **1961**, *9*, 110.
(2) Allcock, H. R.; Pucher, S. R.; Scopelianos, A. G. *Macromolecules* **1994**, *27*, 1.
(3) Batycky, R. P.; Hanes, J.; Langer, R.; Edwards, D. A. *J. Pharm. Sci.* **1997**, *86*, 1464.
(4) Davies, M.; Lynn, R.; Watts, J.; Paul, A.; Vickerman, J.; Heller, J. *Macromolecules* **1991**, *24*, 5508.
(5) Domb, A.; Langer, R. *Macromolecules* **1989**, *22*, 2117.
(6) Duguet, E.; Schappacher, M.; Soum, A. *Macromolecules* **1992**, *25*, 4835.
(7) Gilding, D. K.; Reed, A. M. *Polymer* **1979**, *20*, 1459.
(8) Hanes, J.; Chiba, M.; Langer, R. *Macromolecules* **1996**, *29*, 5279.
(9) Hrkach, J.; Ou, J.; Lotan, N.; Langer, R. In *Hydrogels and Biodegradable Polymers for Bioapplications*; Ottenbrite, R. M., Huang, S. J., Park, K., Ed.; American Chemical Society: Washington DC, 1996; p 93.
(10) Mader, K.; Bacic, G.; Domb, A.; Elmalak, O.; Langer, R.; Swartz, H. M. *J. Pharm. Sci.* **1997**, *86*, 126.
(11) Mathiowitz, E.; Jacob, J.; Pekarek, K.; Chickering, D., III. *Macromolecules* **1993**, *26*, 6756.
(12) Ng, S.; Vandamme, T.; Taylor, M.; Heller, J. *Macromolecules* **1997**, *30*, 770.
(13) Penco, M.; Marcioni, S.; Ferruti, P.; D'Antone, S.; Deghenghi, R. *Biomaterials* **1996**, *17*, 1583.
(14) Peppas, N. A.; Langer, R. *Science* **1994**, *263*, 1715.
(15) Staubli, A.; Ron, E.; Langer, R. *J. Am. Chem. Soc.* **1990**, *112*, 4419.
(16) Uhrich, K. E.; Gupta, A.; Thomas, T. T.; Laurencin, C. T.; Langer, R. *Macromolecules* **1995**, *28*, 2184.
(17) Vert, M.; Li, S.; Garreau, H. *Macromol. Symp.* **1995**, *98*, 663.
(18) Swift, G. *Acc. Chem. Res.* **1993**, *26*, 105.
(19) Lim, Y.; Choi, Y. H.; Park, J. *J. Am. Chem. Soc.* **1999**, *121*, 5633.
(20) Langer, R. *Acc. Chem. Res.* **1993**, *26*, 537.
(21) Shirai, M.; Miwa, T.; Tsunooka, M. *Chem. Mater.* **1995**, *7*, 642.
(22) Gitto, S. P.; Wooley, K. L. *Macromolecules* **1995**, *28*, 8887.
(23) Weinberg, J. M.; Gitto, S. P.; Wooley, K. L. *Macromolecules* **1998**, *31*, 15.
(24) Wang, M.; Weinberg, J. M.; Wooley, K. L. *Macromolecules* **1998**, *31*, 7606.
(25) Sommer, L. H. *Sterochemistry, Mechansim and Silicon*; McGraw-Hill: New York, 1965.
(26) Hudrlik, P. F.; Feasley, R. *Tetrahedron Lett* **1972**, *18*, 1781.

(27) Stevens, M. P. *Polymer Chemisty: An Introduction*; Oxford University Press: New York, 1990; p 392.
(28) Stevens, M. P. *Polymer Chemisty: An Introduction*; Oxford University Press: New York, 1990; p 424.
(29) Wang, Z. Y.; Qui, Y.; Bender, T. P.; Gao, J. P. *Macromolecules* **1997**, *30*, 764.
(30) Harris, R. M.; Stille, J. K. *Macromolecules* **1981**, *14*, 1584.
(31) Bolton, D. H.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1133.
(32) *Comprehensive Handbook On Hydrosilylation*; Marciniec, Bogdan, Ed.; Pergamon: New York, 1992.
(33) Weinberg, J. M.; Wooley, K. L. *J. Organomet. Chem.* **1997**, *542*, 235.
(34) Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225.
(35) Kazama, H.; Tezuka, Y.; Imai, K. *Macromolecules* **1991**, *24*, 122.
(36) Lukevics, E. *Russ. Chem. Rev.* **1977**, *46*, 264.
(37) Steinmetz, M. G.; Udayakumar, B. S. *J. Organomet. Chem.* **1989**, *378*, 1.
(38) Karstedt, B. D. Platinum Complexes of Unsaturated Siloxanes and Platinum Containing Organopolysiloxanes; US 3775452, 1973.
(39) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1989**, *366*, 275.
(40) Lorenz, K.; Frey, H.; Stuhn, B.; Mulhaupt, R. *Macromolecules* **1997**, *30*, 6860.
(41) Lorenz, K.; Mulhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. J. *Macromolecules* **1995**, *28*, 6657.
(42) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1992**, *25*, 3247.
(43) Corey, E. J.; Venkateswariu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(44) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797.
(45) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.
(46) Ojima, I. In *The Chemistry of Organic Silcon Compounds*; Patai, S., Rappoport, Z., Ed.; John Wiley & Sons: Ltd.: New York, 1989.
(47) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.
(48) Albinati, A.; Caseri, W. R.; Pregosin, P. S. *Organometallics* **1987**, *6*, 788.
(49) Sibi, M. P.; Christensen, J. W. *Tetrahedron Lett.* **1995**, *36*, 6213.
(50) Lewis, L. N.; Sy, K. G.; Garold, L. B.; J.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.
(51) Chen, X.; McGurk, S. L.; Davies, M. C.; Roberts, C. J.; Shakesheff, K. M.; Tendler, S. J. B.; Williams, P. M.; Davies, J.; Dawkes, A. C.; Domb, A. *Macromolecules* **1998**, *31*, 2278.
(52) Broos, R.; Travenier, D.; Anteunis, M. *J. Chem. Soc.* **1978**, *55*, 813.
(53) Hess, B. A., Jr.; Tuleen, D. L. *J. Chem. Educ.* **1971**, *48*, 476.

MA991530M