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(26) This is supported by the observation that mixtures of natural-origin PHB and P([*R*]-BML)[13,14] form incompatable blends from studies by DSC carried out in our laboratory.
(27) See: Bluhm, T. L.; et al. in ref 18.

Chain Propagation/Step Propagation Polymerization. 4. A DSC Study of Phase Separation in Regular Poly(oxyethylene)-*block*-Poly(pivalolactone) Telechelomers

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ABSTRACT: Anionic chain polymerization coupled with step polymerization is being used to prepare segmented copolymers containing soft poly(oxyethylene) (POE) and hard poly(pivalolactone) (PPVL) segments each having narrow molecular weight distributions (MWD). The chain polymerization results in formation of a telechelomer (a high molecular weight monomer capable of self-polymerization via a step propagation mechanism) wherein the telechelomer contains one POE segment and one PPVL segment. The phase separation of four telechelomers containing 17, 33, 37, and 54 wt % poly(pivalolactone) was investigated by using differential scanning calorimetry (DSC). The crystalline melting temperature (T_m) of the segments was used as a criterion for phase separation, and the approach used was first to adjust the T_m's to take into account such variables as molecular weight, end groups, and copolymerization and then to observe the variation of T_m's with increasing poly(pivalolactone) content. It was found that both segments are phase mixed to some extent.

Introduction

The field of multiphase segmented copolymers, although some 30-years old, remains quite active[1,2] in part due to the possibility of obtaining a variety of useful meterials ranging from impact-resistant plastics to elastomers. Poly(urethane ethers) and particularly poly(ester ethers) lend themselves to melt extrusion such that these polymers can be shaped easily, an extremely valuable feature. As true elastomers, however, these copolymers lack the physical properties that are demanded in many applications, particularly when they are melt processed.[3] Specifically, the elastic properties that are deficient in melt-extruded segmented copolymers are stress and recovery related, like immediate elastic recovery (often less than 95%), stress decay (often greater than 15%), and compression set (more than 10%). These properties are direct manifestations of the inefficiency of the physical cross-links in the copolymer, which in turn is a function of how well the phase separation in the copolymer is achieved.

Phase mixing can be attributed partly to the irregularity of the copolymer chain. In the case of poly(ester ether) copolymers, synthesized by normal step polymerization reactions, the hard segment has a polydispersity ratio approaching 2, and this distribution of chain lengths within the hard segment adversely affects phase separation.[4] Droescher and co-workers support the hypothesis that high regularity within segments, i.e., monodispersity within each segment, leads to enhanced phase separation and crystallization phenomena.[5] Their investigations involved monodisperse aromatic poly(ester ether) copolymers synthesized in a multistep scheme of nucleophilic substitution reactions.[5] Inoue and co-workers,[6] also have prepared low molecular weight versions of poly(ester ether) block copolymers having monodisperse segments using porphyrin catalysts. The molecular weights of these polymers are about 5000.

Our goal is to synthesize highly regular poly(ester ether) segmented copolymers, to investigate their phase separation behavior, and to see how the phase separation behavior affects mechanical and surface properties. Our strategy involves synthesizing a highly regular telechelomer[7] and then converting it to high molecular weight polymer. In order to obtain narrow molecular weight distributions for both segments, the telechelomer has been prepared by anionic polymerization; the telechelomer then can be converted to high molecular weight copolymer by step polymerization. Figure 1 shows this strategy applied to the synthesis of poly(oxyethylene-*co*-pivalolactone) segmented copolymers. Since the soft poly(oxyethylene) (POE) segment is incompatible with the hard poly(pivalolactone) (PPVL) segment, these regular copolymers will exhibit enhanced phase separation. A high molecular weight poly(pivalolactone-*b*-dimethylsiloxane) diblock copolymer has been prepared, and its phase separation behavior has been investigated in the past.[8]

Differential scanning calorimetry (DSC) has been used to study phase separation in a number of multiphase polymer systems.[9] A few excellent quantitative DSC investigations appeared in the literature,[10,11] and many other qualitative investigations[12] were quite adequate to determine the presence of phase mixing. In the qualitative studies, the phase mixing was determined by monitoring the glass transition temperature (T_g) of the soft segment (which was completely amorphous) and the crystalline melting point (T_m) of the hard segment. An increase in T_g of the soft segment and a decrease in T_m of the hard segment, with increasing hard segment content in the copolymer, indicated phase mixing. When the soft segment

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Table I
Compositions and DSC Data of Telechelomers[a]

	PPVL		T_m(POE),[c] °C		T_m(PPVL), °C	T_g(POE), °C	
	wt %	$\bar{M}_n$[b]	calcd[c]	obsd[f]	calcd	obsd[f]	obsd
T1	17	(200)	28.4–37.4	34.1	97.0–132.1	104.4	
T2	33	(500)	18.1–37.4	38.4	154.2–173.8	121.6	-52.2
T3	37	(600)	14.9–37.4	22.1	172.7–179.0	140.5	-54.5
T4	54	(1100)			180.4–190.7	147.0	-54.2
PPVL1	100	(200)				132.1	
PPVL2	100	(500)				173.8	
PPVL4	100	(1000)				190.7	

[a] The samples (11–14 mg) were heated to 180 °C, kept at this temperature for 1 min, and cooled to room temperature before obtaining the DSC scan. [b] Calculated by using 300-MHz ^{1}H NMR. [c] $\bar{M}_n$ = 1012, by 300 MHz ^{1}H NMR. [d] Calculated by using eq 1. [f] The T_m's reported are peak values. When the samples showed multiple endotherms, the highest peak temperatures were reported.

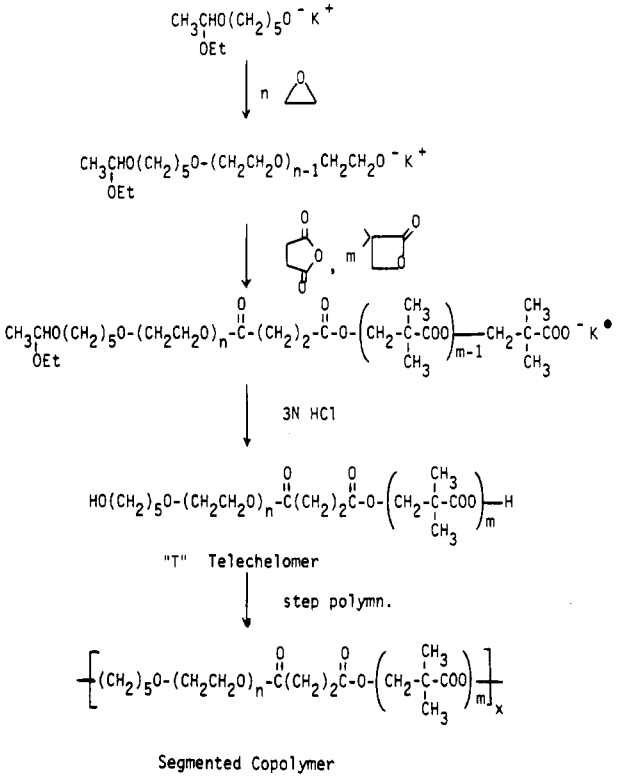

Figure 1. Chain propagation/step propagation polymerization for preparing poly(oxyethylene-*co*-pivalolactone) segmented copolymer.

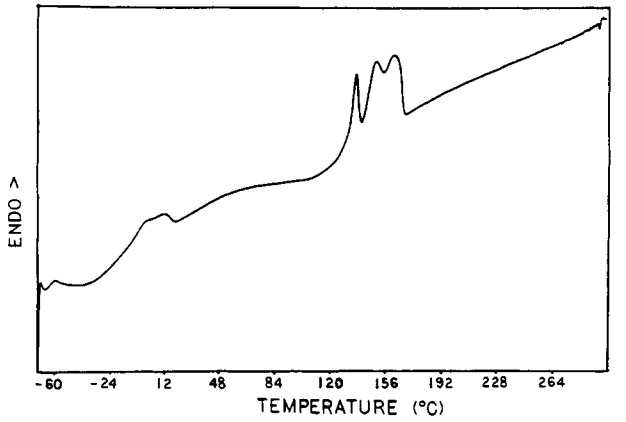

Figure 2. Thermogram for T4 telechelomer quenched to -163 °C from melt (180 °C) prior to the scan.

is also crystalline, the T_g is affected by the soft segment crystallinity too,[13] and as such T_g is not a good measure of phase mixing.

We plan to investigate phase separation in the poly(oxyethylene-*co*-pivalolactone) segmented copolymers by DSC, and the "T" telechelomers (Figure 1) are excellent models to develop a method, because they contain only one soft segment and one hard segment. Our approach is to first adjust T_m's of both segments to take into account such variables as molecular weight, crystallinity, nonequilibrium DSC conditions, etc., and then to observe their variation with increasing hard segment percent.

Experimental Section

The preparation and characterization of the "T4" telechelomer were reported earlier.[14,15] This telechelomer had a narrow molecular weight distribution as shown by gel permeation chromatography.[15] The other telechelomers were also prepared in a similar manner. These compounds were purified rigorously, and they were kept at 40 °C under vacuum for a day to remove any remaining solvent and moisture. The homopoly(pivalolactones) were prepared using tetrabutylammonium salt of pivalic acid as the initiator. The conditions used were the same as those used to prepare telechelomers.[14,15] The initiator was prepared by mixing equimolar quantities of tetrabutylammonium hydroxide (Aldrich) and pivalic acid (Aldrich) in methanol. The resulting salt was dried at 45 °C under vacuum.

DSC data were obtained with a Perkin-Elmer 7 Series thermal analysis system equipped with a data station. For subambient operations, the instrument was calibrated by a two-point method using *n*-decane and indium. For operations above room temperature, it was calibrated with indium. The purge gas was dry helium in subambient operations and dry nitrogen in operations above 200 °C. A scan rate of 20 °C/min was used in all runs.

The quenched sample that was run from -80 to 280 °C was prepared by dropping the molten sample (in a sample pan at 240 °C) into liquid nitrogen (-163 °C). Other samples were prepared by melting them in a sample pan to 180 °C and allowing them to cool to room temperature in air. Sample sizes ranged from 25 to 30 mg in the case of T_g investigations and from 11 to 14 mg in the case of T_m investigations. The samples for annealing studies were held at 250 °C for 1 min, cooled at 10 °C/min to the prescribed annealing temperature, left at this temperature for a prescribed time, and then quenched to -163 °C.

Results and Discussion

Table I shows the compositions of the telechelomers used in this study. The number-average molecular weight ($\bar{M}_n$) and the weight percents of PPVL segment were calculated by using 300-MHz ^{1}H NMR. The $HO(CH_2)_5O$ end group and the connecting succinic anhydride moiety were excluded in percentage calculations. The number-average molecular weight, $\bar{M}_n$, of the POE segment was 1012 (by ^{1}H NMR).

Figure 2 shows a DSC curve obtained for the telechelomer T4, quenched to -163 °C from melt (200 °C). Three transition regions are apparent: from -80 to -24 °C showing the T_g of the POE segment, from -24 to 40 °C showing the T_m of the POE segment, and from 100 to 190 °C showing the T_m of the PPVL segment. The PPVL segment does not show a T_g, because it is low in molecular

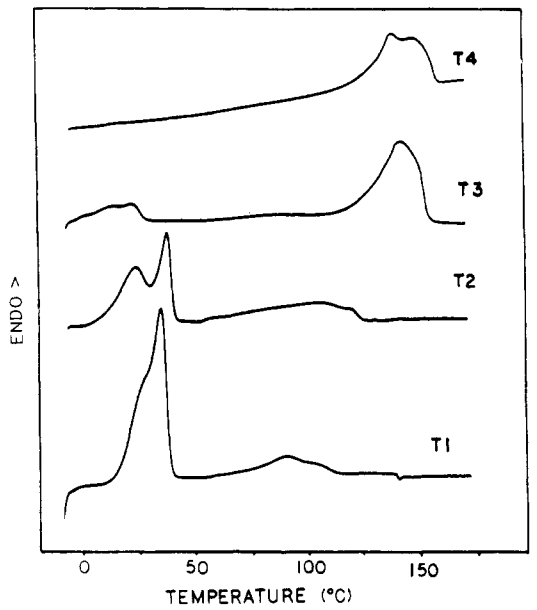

Figure 3. Melting endotherms of telechelomers as a function of hard poly(pivalolactone) segment content. The samples (11–14 mg) were heated in the sample pan to 180 °C, kept at this temperature for 1 min, and cooled to room temperature prior to the scans.

weight, and it crystallizes very fast. Polyesters which do not show a T_g due to similar reasons have been reported.[16] Considering the low T_g and the high T_m of the telechelomer, it is apparent that the high molecular weight segmented copolymer will have a very broad service temperature range.

T_m(POE). Figure 3 shows the transitions due to melting of the POE segment in the telechelomers, and Table I shows T_m's calculated by using the computer. Even though the equilibrium T_m of high molecular weight POE is 69.1 °C,[17] that of low molecular weight POE is quite lower.[18] A T_m of 38.4 °C was observed by Fraser et al.[18] for POE fractions of molecular weight 1000 having hydroxyl end groups. A further lowering of T_m by 1 °C was noted when the hydroxyl end groups were changed to methoxy groups. Considering the low molecular weight of the POE segment (i.e., 1012) and the presence of two end groups, namely the $HO(CH_2)_5O$ group and the succinic anhydride group, it is reasonable to assume a theoretical value of 37.4 °C for the T_m of the POE segment.

Copolymerization will decrease T_m further, and the decrease could be calculated by using eq 1.[19] This equation has been used to calculate the decrease in T_m of the poly(hexamethylene sebacate) segment due to block copolymerization with poly(dimethylsiloxane) segment[16,20]

$$1/T_m = 1/T^\circ_m - (R/\Delta H) \ln p \qquad (1)$$

where T_m is the melting point of the crystalline segment in the copolymer, $T^\circ_m = T_m$ in the crystalline homopolymer, ΔH is the heat of fusion (per mole of repeat unit) of the crystalline segment, and p is the crystalline sequence propagation probability.

In view of the assumptions used in applying eq 1 to the T telechelomers, exact theoretical values for T_m's could not be calculated; instead ranges were calculated (Table I). For instance, in the case of block-type copolymers, characterized by crystallizable units occurring is very long sequences, $p \gg X_c$, where X_c is the mole fraction of crystallizable units.[19] The upper limit in the T_m range (Table I) was calculated assuming that $p = 1$; i.e., there was no T_m depression due to block copolymerization. The lower limit was calculated assuming that $p = X_c$. A value of 37.4 °C was used for T°_m and a value of 1980 cal/mol of repeat unit was used for ΔH.[21] X_c was calculated excluding the $HO(CH_2)_5O$ group and the succinic anhydride moiety. It is also worthwhile noting that the telechelomer does not have very long crystallizable units and that both the segments in the telechelomer are crystalline. Equation 1 was derived for copolymers in which only one type of unit was capable for crystallizing.

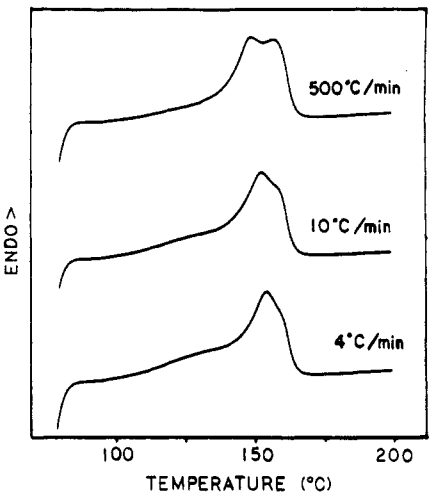

Figure 4. Poly(pivalolactone) melting endotherms of T4 telechelomer as a function of cooling rate. The samples (11–14 mg) were heated in the sample pan to 180 °C, kept at this temperature for 1 min, and cooled to room temperature. They were then heated to 250 °C in the instrument under nitrogen, kept at 250 °C for 1 min, and cooled at different rates.

These values could further change by varying the sample thermal history and nonequilibrium instrument conditions, but these factors were kept constant in order to compare the four telechelomers. Comparison of the calculated values with the observed values (Table I) shows that, except for T2, all telechelomers have lower T_m(POE)'s than the theoretically possible highest values, indicating that the POE segments are mixed with PPVL segments.

T_m(PPVL). Melting of the PPVL segment is seen as a broad transition with multiple endotherms (Figure 3). In the case of Tl, which contains only two units of PPVL, the endotherms start as low as 60 °C. Similar multiple melting endotherms have been observed for segmented poly(ether urethanes),[9] and their morphological origins have been identified using thermal annealing and cooling experiments. Borri et al.[22] used annealing and cooling experiments to investigate melting of homopoly(pivalolactone) and reported that two endotherms were present, and their positions and sizes depended on annealing temperature, annealing time, and cooling rate. Later Meille et al.[23] identified these endotherms and attributed the high temperature endotherm to α crystallites and the low temperature endotherm to γ crystallites. These two types of crystallites were differentiated easily by changing the cooling rate from melt prior to scanning experiments. At a slower cooling rate, particularly when the polymer is quenched from the melt, the γ form was formed substantially.[22,23]

The multiple endotherms observed for the telechelomers could be identified on the basis of the above information. Figure 2 shows three endotherms for the PPVL segment in T4 telechelomer quenched to −163 °C from melt. These occur around 133, 150, and 159 °C. The lowest temperature endotherm is not so sharp when the cooling rates from melt are much slower (Figure 4). Thus, the lowest temperature endotherm in the telechelomer is attributed to γ crystallites. Changing the cooling rate (Figure 4) or

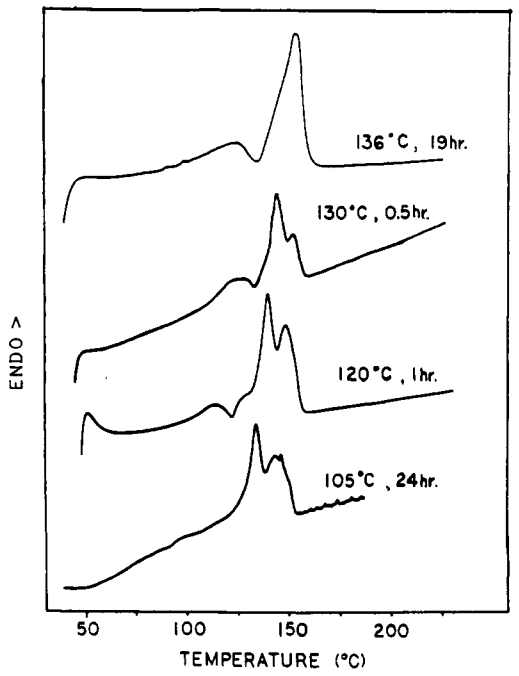

Figure 5. Poly(pivalolactone) melting endotherms of T4 telechelomer as a function of annealing conditions. Prior to taking the scans, the following operations were carried out. The samples (11–14 mg) were heated in the sample pan to 180 °C, kept at this temperature for 1 min, and cooled to room temperature. They were then heated to 250 °C in the instrument under nitrogen, kept at 250 °C for 1 min, and cooled at 10 °C/min to the prescribed annealing temperature. After the samples were left at the annealing temperature for a prescribed time, they were quenched to −163 °C.

changing annealing conditions (Figure 5) varies the sizes and positions of the endotherms. Annealing the sample at 136 °C for 19 h causes the two high temperature endotherms to merge (Figure 5), indicating that different sizes of crystallites are present. The maximum T_m attainable in the case of T4 was 159.5 °C which was obtained by annealing the sample for 19 h at 136 °C (Figure 5).

When the thermal history and the nonequilibrium DSC conditions are kept constant, the variation of T_m(PPVL) with increasing PPVL content can be due to (a) the molecular weight of the PPVL segment, (b) the effect of copolymerization with POE segment, and (c) phase mixing. The effects of a and b have to be taken into account before the effects of c are considered.

Table I shows T_m's observed for homopoly(pivalolactones) having molecular weights comparable to those of PPVL segments in telechelomers. The T_m's are quite lower compared to those of high molecular weight polymers (i.e., 240 °C), and they show a decrease when the molecular weight is decreased from 1000 to 200. A similar decrease was observed by Thamm and Buck.[24] Copolymerization decreases these values further, and the new T_m's were calculated by using eq 1 (assumptions used in the calculation of T_m(POE) were also used in this calculation). The T_m of the homopolymer having the same molecular weight as the PPVL segment was used as T^o_m, and a value of 3550 cal/mol of repeat unit[22] was used for ΔH.

The calculated ranges and the observed values for T_m(PPVL)'s indicate that the PPVL segments in all the telechelomers are phase mixed (Table I). Based on the upper limits of the calculated values, the T_m(PPVL) depressions are in the range of 28–52 °C. These are higher than the T_m(PPVL) depressions (16–31 °C) observed for poly(dimethylsiloxane–pivalolactone) diblock copolymers containing very long segments[8] (poly(dimethylsiloxane) and

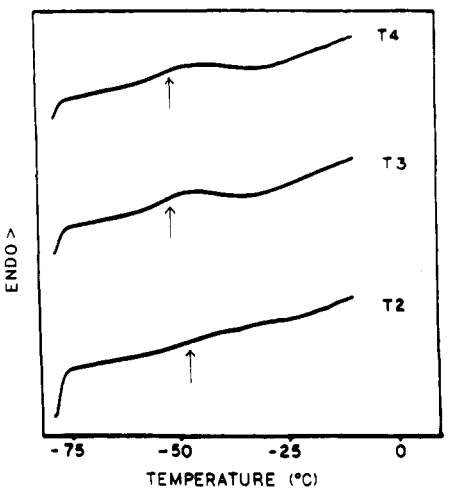

Figure 6. Glass transition of poly(oxyethylene) segments as a function of hard poly(pivalolactone) segment content. Prior to the scan, the samples (25–30 mg) were heated in the sample pan to 180 °C, kept at this temperature for 1 min, and dropped into liquid nitrogen (−163 °C).

PPVL segment $\bar{M}_n$'s were more than 12 500 and 5000, respectively). Considering the T_m depressions in both segments, the highest phase separation was observed in the T1 telechelomer. We plan to further investigate these telechelomers using a direct method such as small-angle X-ray scattering, SAXS.

T_g(POE). Figure 6 shows the glass transitions observed for the POE segments. The T_g's calculated by using the computer are given in Table I. However, the T_g's cannot be used as a measure of phase mixing, because the POE segments are also crystalline.[12]

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Registry No. (Ethylene oxide)(pivalolactone) (block copolymer), 107558-01-0; "T" telechelomer, 115203-92-4.

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Stereoregularity in Ziegler–Natta and Anionic Polymerization of 2-[(Trimethylsilyl)methyl]-1,3-butadiene. Protodesilation of *cis*-1,4-Poly[2-[(trimethylsilyl)methyl]-1,3-butadiene]

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ABSTRACT: Ziegler–Natta polymerization of 2-[(trimethylsilyl)methyl]-1,3-butadiene (I) catalyzed by triethylaluminum and titanium tetrachloride yields a polymer whose microstructure, as established by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, is predominantly comprised of cis-1,4 units. On the other hand, anionic polymerization of I yields a polymer whose microstructure is made up of cis-1,4-, trans-1,4-, and 3,4-units. Protodesilation of *cis*-1,4-poly[2-[(trimethylsilyl)methyl]-1,3-butadiene] with iodine in D_2O yields poly(3-deuterio-2-methylenebutane). The mechanism of this reaction is discussed.

Introduction

There is considerable interest both in stereoregular polymerization of 1,3-diene monomers and in chemical modification of intact polymers.[1,2] Anionic polymerization of isoprene initiated by alkyllithium reagents in hydrocarbon solvents such as cyclohexane yields polyisoprene of narrow molecular weight distribution whose microstructure has been shown by IR,[3,4] ^1H NMR,[5] and ^{13}C NMR[6] to be predominantly *cis*-1,4-polyisoprene (80%). However, appreciable amounts of trans-1,4- (15%) and 3,4-units (5%) are also present. Thus the anionic polymerization of isoprene is neither completely regio- nor stereoselective. By comparison, Ziegler–Natta-type polymerization of isoprene catalyzed by trialkylaluminum and titanium tetrachloride in hydrocarbon solvent yields polyisoprene whose microstructure is 95% cis-1,4. This reaction is highly regio- and stereoselective.[7,8]

We were interested in achieving stereo- and regioselective 1,4-polymerization of 2-[(trimethylsilyl)methyl]-1,3-butadiene. Such a polymer would have reactive allylic silane functional groups regularly arranged along the polymer backbone. While there has been considerable work done on regiospecific electrophilic substitution reactions of monomeric allylic silanes,[9] similar reactions in polymeric systems have not been explored.

Experimental Section

^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad-band proton decoupling. ^1H and ^{29}Si NMR spectra were obtained on a Brucker WP-270-SY spectrometer operating in the FT mode. Ten to fifteen percent solutions in chloroform-d_1 were used to obtain ^{29}Si spectra, whereas five percent solutions were used for ^1H and ^{13}C spectra. Chloroform was utilized as an internal standard for ^1H, ^{13}C, and ^{29}Si NMR spectra. All chemical shifts reported were externally referenced to TMS. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least one methyl group bonded to them.[10]

IR spectra were recorded on a Perkin-Elmer PE 281 spectrometer. These were taken on films on NaCl plates.

GPC analysis of the molecular weight distribution of the polymers was performed on a Perkin-Elmer series 10 liquid chromatograph equipped with an LC-25 refractive index detector (maintained at 25 °C), a 3600 data station, and a 660 printer. A 32 cm × 77 mm Perkin-Elmer PL 10-μm particle size, mixed pore size, cross-linked polystyrene gel column was used for the separation. The eluting solvent was reagent THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: $\bar{M}_p$ 3600000, 194000, 28000, and 2550 whose $\bar{M}_w/\bar{M}_n$ are less than 1.09.

TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm^3/min. The temperature program for the analysis was 100 °C for 10 min followed by an increase of 5 °C/min to 500 °C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. Satisfactory analyses (±0.6%) were obtained for polymers prepared both by Ziegler–Natta catalysis as well as that made by anionic polymerization.

2-[(Trimethylsilyl)methyl]-1,3-butadiene was prepared by the reaction of [(trimethylsilyl)methyl]magnesium chloride with 2-chloro-1,3-butadiene catalyzed by the nickel chloride complex of 1,3-bis(diphenylphosphino)propane. It had properties in complete agreement with literature values.[11]

Polymerization Reactions. Polymerizations were carried out in flame-dried apparatus under an atmosphere of prepurified nitrogen. In a 100-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar and a rubber septum was placed 50 mL of hexane (freshly distilled from sodium metal). The flask and its contents were cooled to 0 °C. To this were added via a syringe 0.11 mL (0.2 mmol) of titanium tetrachloride and triethylaluminum (Aldrich) (0.22 mmol, 0.6 mL of a 25% solution in CH_2Cl_2). The contents of the flask were stirred for 1 h while it warmed to room temperature. 2-[(Trimethylsilyl)methyl]-1,3-butadiene (3.5 g, 25 mmol) was added via syringe. The reaction mixture was stirred for 4 h at room temperature. The reaction was quenched by addition of a mixture of tetrahydrofuran and methanol. The polymer was precipitated from the tetrahydrofuran solution by addition of methanol. This process was repeated several times. In this way, 1.4 g (40% yield) of a white rubbery polymer was obtained. Removal of the solvents from the su-

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