Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

The Synthesis of Poly(Dimethylsiloxane-*b*-Isobutylene-*b*-Dimethylsiloxane) and Poly-(Dimethylsiloxane-*b*-Isobutylene-*b*-Dimethylsiloxane) from Alcohol-Telechelic Polyisobutylenes

Lech Wilczek[ab]; Munmaya K. Mishra[a]; Joseph P. Kennedy[a]
[a] Institute of Polymer Science The University of Akron, Akron, Ohio [b] Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland

To cite this Article Wilczek, Lech , Mishra, Munmaya K. and Kennedy, Joseph P.(1987) 'The Synthesis of Poly(Dimethylsiloxane-*b*-Isobutylene-*b*-Dimethylsiloxane) and Poly-(Dimethylsiloxane-*b*-Isobutylene-*b*-Dimethylsiloxane) from Alcohol-Telechelic Polyisobutylenes', Journal of Macromolecular Science, Part A, 24: 9, 1033 — 1049

To link to this Article: DOI: 10.1080/00222338708078141

URL: http://dx.doi.org/10.1080/00222338708078141

J. MACROMOL. SCI.–CHEM., A24(9), pp. 1033-1049 (1987)

THE SYNTHESIS OF POLY(DIMETHYLSILOXANE-*b*-ISOBUTYLENE-*b*-DIMETHYLSILOXANE) AND POLY-(DIMETHYLSILOXANE-*b*-ISOBUTYLENE-*b*-DIMETHYLSILOXANE)$_n$ FROM ALCOHOL-TELECHELIC POLYISOBUTYLENES*

LECH WILCZEK,[†] MUNMAYA K. MISHRA, and JOSEPH P. KENNEDY[‡]

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

ABSTRACT

The purpose of these studies was to combine polydimethylsiloxane (PDMS) and polyisobutylene (PIB) sequences into novel triblock, PDMS-*b*-PIB-*b*-PDMS, and multiblock, $\leftarrow$PDMS-*b*-PIB-*b*-PDMS$\rightarrow_n$, copolymers. The key toward syntheses was the definition of conditions for the initiation of living anionic polymerization of hexamethylcyclotrisiloxane (D_3) at the $-CH_2OLi$ termini of well-defined telechelic PIB sequences. Subsequent deactivation of living D_3 polymerization charges with Me_3SiCl yielded the target triblock whereas stoichiometric amounts of Me_2SiCl_2 gave the multiblock copolymer.

---

*Also Part LIV of New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers).

[†] Visiting scientist. Permanent address: Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Boczna 5, 90-362 Lodz, Poland.

[‡] To whom correspondence should be addressed.

Conditions for the fast quantitative initiation of D_3 from the $-CH_2OLi$ end groups of PIB were worked out by model studies with the Li salt of 2,4,4-trimethyl-1-pentanol (TMP-OH), a molecule that exactly mimics the alcoholate termini of PIB. Initiation (i.e., "blocking") of D_3 polymerization from Li phenolate-ended PIB has also been studied by the use of the Li salt of the 2,4,4-trimethyl-2-(*p*-hydroxyphenyl)pentane (TMP-PhOH) model compound. However, the phenolate exhibited a much lower initiating efficeincy for D_3 polymerization than the alcoholate under the same conditions (THF, 0-60°C). The triblock copolymer exhibits satisfactory hydrolytic resistance under certain conditions.

INTRODUCTION

Both PIB and PDMS exhibit a combination of desirable physical properties and are valuable commercially available materials for a great variety of applications [1-3]. One aim of this research was to link these polymers into PIB-PDMS block copolymers and thus to create new materials that exhibit a combination of the properties of the two components. The recent semicommercial availability of alcohol- and phenol-capped telechelic PIBs [4] opens up the possibility toward the synthesis of these unique block copolymers.

An examination of synthetic options yielded two approaches toward the preparation of PIB-PDMS block copolymers: 1) polycondensation of difunctional silanes leading to telechelic polysiloxanes followed by chain extension with hydroxyl-telechelic PIB, and 2) living polymerization of cyclotrisiloxanes initiated by alcoholate- or phenolate-ended PIB [5, 6]. Since the former method was expected to yield a broad distribution of polysiloxanes and block copolymers contaminated by homopolymers [6-9], we chose to concentrate on the more promising second method. Specifically, we were interested in finding conditions conducive for the living anionic polymerization of D_3 with Li alcoholate-ended PIB [10-14]. We theorized that well-defined PDMS-*b*-PIB-*b*-PDMS triblocks and $\left(\text{PDMS-}b\text{-PIB-}b\text{-PDMS}\right)_n$ multiblocks could be obtained by quenching the living D_3 polymerization by Me_3SiCl or by stoichiometric quantities of Me_2SiCl_2, respectively. Figure 1 shows the schemes envisioned. This paper demonstrates that, under suitable conditions, Li alcoholates can induce the rapid and quantitative initiation of living D_3 polymerization and that this technique can be used for the clean synthesis of diverse PIB-PDMS block copolymers.

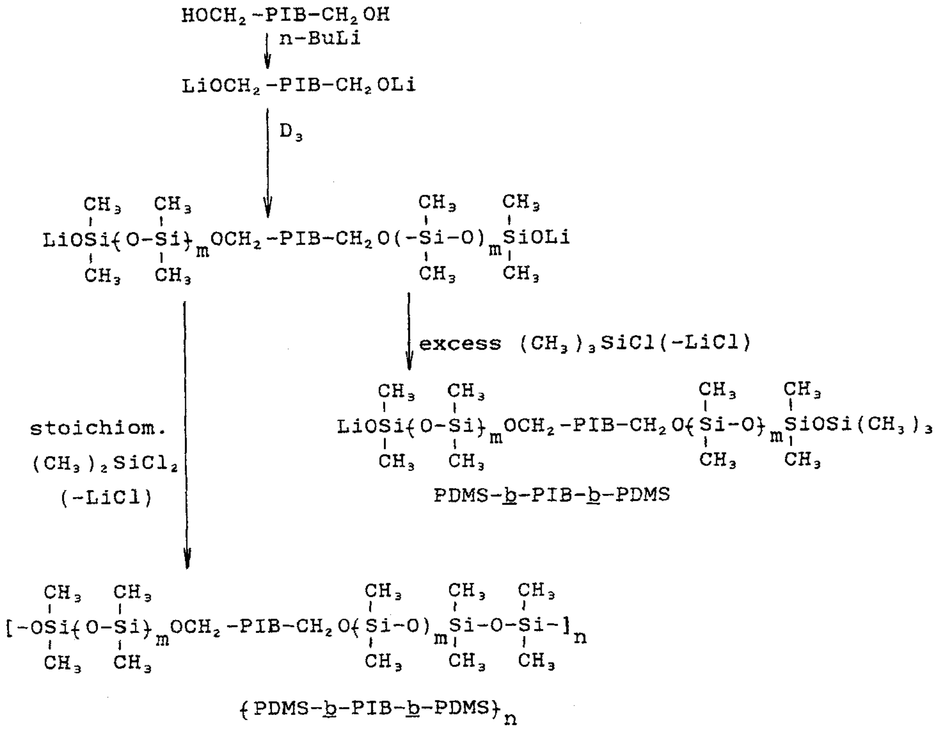


FIG. 1. Scheme for the synthesis of PDMS-*b*-PIB-*b*-PDMS and $\left(\text{PDMS-}b\text{-PIB-}b\text{-PDMS} \right)_n$.

EXPERIMENTAL

Materials

The source and purity or purification of isobutylene (IB), BCl_3, methylene chloride, and hexanes have been described [15, 16]. THF was purified by high-vacuum techniques and stored over Na-K alloy in a flask equipped with a Rotaflo stopcock. *n*-Undecane (Chemical Samples Co.) was refluxed over CaH_2 and condensed into an ampule with a Rotoflo stopcock under high vacuum. *n*-BuLi (~1.5 mol/L in hexanes, Aldrich Co.) was titrated with benzyl chloride [17]. 1,10-Phenanthroline (Aldrich Co., Gold Label) and CaH_2 (Aldrich Co.) were used as received.

1,4-Di(-2-chloro-2-propyl)benzene (dicumyl chloride) was prepared from 1,4-di(-2-hydroxy-2-propyl)benzene (dicumyl alcohol) with hydrogen chloride [18]. 2,4,4-Trimethyl-1-pentanol (TMP-OH) (Aldrich Co.) was refluxed over CaH_2 under N_2 and condensed into an ampule with a Rotaflo stopcock under high vacuum. 2,4,4-Trimethyl-2-(*p*-hydroxyphenyl)pentane (TMP-PhOH) was prepared by alkylating phenol (Fisher Scientific Co.) with 2,4,4-trimethyl-1-pentene (Aldrich Co.) [19]. The TMP-PhOH solution in hexanes was refluxed over CaH_2 under N_2 and filtered, then the solvent was evaporated. Finally the TMP-OH was dried in high vacuum for 6-8 h. Hexamethylcyclotrisiloxane (D_3) (Petrarch Inc.) was dried over CaH_2 at ~80°C in a vial with a Rotaflo stopcock and then sublimed under high vacuum. Trimethylchlorosilane and dimethyldichlorosilane (Petrarch Inc.) were distilled under N_2, quinoline (Aldrich Co.) was added (10 vol%) and the chlorosilanes were condensed into vials with a Rotaflo stopcock under high vacuum.

Procedures

^1H-NMR spectra were recorded on a Varian T-60 NMR spectrometer. GC analyses were done on a Hewlett-Packard HP-5750 instrument using a 12-ft column packed with SE-30; He carrier gas, temperature programming from 25 to 250°C, *n*-undecane internal standard. The GPC technique has been described [15]. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer [20]. Osmometric measurements were performed with a Knauer vapor-pressure osmometer (No. 1100, Utopia Instrument Co.) and a high-speed membrane osmometer (Model 503, Hewlett-Packard) with toluene solvent at 40°C. Isobutylene polymerization and general experimental procedures have been described [15].

The Syntheses of Alcohol-Telechelic PIB (HO-PIB-OH)

The *t*-chloro-telechelic PIB prepared by the semicontinuous "inifer" method [16] was converted to α,ω-di(isopropenyl)polyisobutylene by dehydrochlorination with *t*-BuOK [21] and the latter to the alcohol-telechelic PIB by hydroboration with $BH_3 \cdot THF$ [20]. The HO-PIB-OH starting material had $\bar{M}_n = 4200$, $\bar{M}_w/\bar{M}_n = 2.25$, as determined by GPC, vapor pressure osmometry, and ^1H NMR. The number-average functionality was $\bar{F}_n = 1.96 \pm 0.08$ by infrared spectrometry. After purification the HO-PIB-OH was refluxed in hexanes solution over CaH_2 (granules) overnight, the required amount of the solution was transferred with a syringe to a polymerization reactor equipped with a Rotaflo stopcock under N_2, and the hexanes were evaporated under high vacuum.

Kinetic Studies of D_3 Polymerization Initiated with TMP-PhOLi, TMP-OLi, and *n*-BuLi

About 20 mL of a D_3 solution in THF (2.0 mol/L) was prepared in a vial equipped with a Rotaflo stopcock by subliming into it the required amount of D_3 and condensing THF under high vacuum. *n*-Undecane (~2 mL) was added with a syringe under N_2. TMP-OLi or TMP-PhOLi solutions in THF (~0.4 mol/L) were prepared as follows: About 0.5 mL TMP-OH or TMP-PhOH solution in hexanes was placed in a vial equipped with a Rotaflo stopcock (evaporating the hexanes under high vacuum in case of TMP-PhOLi), and ~10 mL THF was added with a syringe under N_2. Then, these hydroxyl compounds were converted to the corresponding lithium salts by adding, dropwise with a syringe, *n*-BuLi solutions in the presence of a small amount of 1,10-phenanthroline until the reddish end point was reached [22]. The quantity of *n*-BuLi used was always within experimental error of the calculated equimolar amount of hydroxyl groups (*n*-BuLi/OH < 1.05), confirming the high purity of the system.

D_3 polymerizations were carried out in ~10 mL reactors equipped with Rotaflo stopcocks. Usually 0.1-2 mL D_3 solution in THF and 2-4 mL THF were transferred with syringes to the reactor under N_2. The reactions were initiated by the addition of ~0.2 mL TMP-OLi or TMP-PhOLi (~0.4 mol/L solutions in THF) or ~0.05 mL *n*-BuLi (~1.5 mol/L in hexanes) with a syringe under N_2. At suitable time intervals, samples (~0.3 mL) were withdrawn by a syringe under N_2, the charges deactivated with Me_3SiCl (50% molar excess relative to ~OLi) and after ~15 min subjected to GC analysis to determine the unreacted D_3, TMP-$OSiMe_3$, and TMP-Ph$OSiMe_3$ quantitatively.

Synthesis of Me_3Si-PDMS-*b*-PIB-*b*-PDMS-$SiMe_3$ and $\lfloor$PDMS-*b*-PIB-*b*-PDMS-$SiMe_2\rfloor_n$

Into a 50-mL reactor equipped with a Teflon stopcock was placed a HO-PIB-OH solution (~5 mL in hexanes, ~20 vol%, dried by refluxing over CaH_2) with a syringe under N_2. The hexanes were evaporated under high vacuum, and ~ 10 mL THF was added with a syringe under N_2. After the polymer was dissolved, an equimolar amount of *n*-BuLi (~0.3 mL 1.5 mol/L solution in hexanes) relative to the hydroxyl groups was added with a syringe under N_2. The D_3 polymerization was initiated by adding 1-10 mL D_3 solution in THF (~2.0 mol/L) at 26°C. The conversion of D_3 was followed by GC as described above. Samples were withdrawn by syringes and deactivated with either Me_3SiCl (50% molar excess relative to ~OLi) or Me_2SiCl_2 (equimolar amounts of Cl—Si— relative to the ~OLi groups). The volatiles were evaporated *in vacuo*. The polymers were dissolved in small amounts of hexanes, precipitated with methanol, separated, washed with methanol, and the volatiles were removed by evaporation under high vacuum for 2-3 days. (Previous experience has shown that precipitation of PDMS from THF into MeOH may result in some loss of polymer; however, precipitation from *n*-hexane is almost quantitative [14].) The polymer samples were subjected to GPC and osmometry.

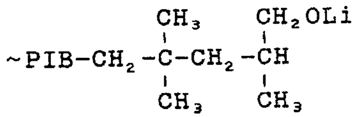
Studies of Hydrolytic Stability of PDMS-*b*-PIB-*b*-PDMS

About 0.2 g of PDMS-*b*-PIB-*b*-PDMS ($\bar{M}_n$ = 18 500, Experiment 3 in Table 1) in bulk or in solutions was treated with an equal volume of aqueous HCl solutions under the conditions shown in Table 2. After 16-72 h the systems were washed several times with water, dried over $CaCl_2$, and the volatiles were evaporated. The polymer samples were subjected to GPC analysis to determine degradation.

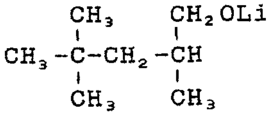
RESULTS AND DISCUSSION

Model Studies

Our first task was to develop conditions for the rapid and quantitative initiation of living D_3 polymerization at the termini of telechelic PIBs. While the polymerization of D_3 initiated by various alcoholates [23, 24] and phenolates [13, 23] has been reported, quantitative aspects of these reactions have not yet been investigated. We decided to start with model experimentation by the use of TMP-OLi and TMP-PhOLi, i.e., compounds that exactly mimic the termini of PIBs capped by $-CH_2OLi$ and $-C_6H_4OLi$ groups:

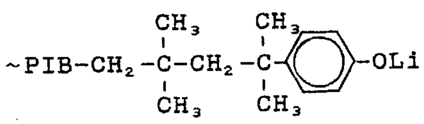


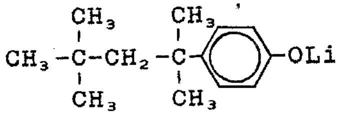
$$\sim\mathrm{PIB{-}CH_2{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}\overset{\displaystyle \mathrm{CH_2OLi}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{CH}}}$$



$$\mathrm{CH_3{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}\overset{\displaystyle \mathrm{CH_2OLi}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{CH}}}$$

TMP-OLi





TMP-PhOLi

TABLE 1. Syntheses of Me$_3$Si-PDMS-*b*-PIB-*b*-PDMS-SiMe$_3$ and -(PDMS-*b*-PIB-*b*-PDMS-SiMe$_2$)-$_n$[a]

Expt	LiO-PIB-OLi,[b] mmol/L	D$_3$ mol/L	D$_3$ Conversion, %	$\bar{M}_n$, Me$_3$Si-PDMS-*b*-PIB-*b*-PDMS-SiMe$_3$ theor[c]	$\bar{M}_n$, Me$_3$Si-PDMS-*b*-PIB-*b*-PDMS-SiMe$_3$ exp[d]	$\bar{M}_n$, -(PDMS-*b*-PIB-*b*-PDMS-SiMe$_2$)-$_n$[a]
1	10	0.99	30	10 900	9 800	30 800
2	10	"	43	13 700	13 900	–
3	10	"	71	19 700	18 500	–
4	5	0.52	20	8 900	8 100	25 400
5	5	"	47	15 400	13 800	47 200
6	5	"	80	22 800	19 600	–
7	5	0.22	33	7 500	6 800	20 100
8	5	"	65	10 600	9 600	44 800
9	4.8	0.08	90	7 600	6 800	27 100

[a] In THF, 26°C; further details in Experimental section.

[b] $\bar{M}_n = 4200$.

[c] Calculated by $\bar{M}_n = 4200 + 222([D_3]_0 - [D_3]_t)/[\text{HO-PIB-OH}] + 146$, where $[D_3]_0$ and $[D_3]_t$ are D$_3$ concentrations at the start and the end of polymerization, respectively. The molecular weight of D$_3$ is 222, and that of $2x$ $-\text{Si(CH}_3)_3$ is 146.

[d] By VPO for $\bar{M}_n < 10\,000$; otherwise by membrane osmometry.

TABLE 2. Hydrolytic Stability of Me_3Si-PDMS-*b*-PIB-*b*-PDMS-$SiMe_3$

	Me_3Si-PDMS-*b*-PIB-*b*-PDMS-$SiMe_3$						
Expt	Conc, vol%	Solvent	Volume ratio	Hydrolysis agent	Temperature, °C	Time, h	Results
1	10	THF:PDMS	80:20	H_2O	Reflux	18	Stable
2	100	–	–	0.5% aq HCl	25	72	Stable
3	30	$(Me_2SiO)_4$	–	12% aq HCl	24	17	Stable
4	25	THF:$(Me_2SiO)_4$	35:65	12% aq HCl[a]	24	22	Degraded
5	35	THF	–	12% aq HCl[a]	24	22	Degraded
6	20	C_6H_{14}:PDMS	50:50	Conc HCl	25	18	Stable
7	20	PDMS	–	Conc HCl[a]	25	22	Degraded
8	20	THF:PDMS	50:50	Conc HCl[a]	25	22	Degraded
9	10	THF:PDMS	50:50	Conc HCl[a]	25	16	Degraded

[a] Control experiment with PDMS shows degradation.

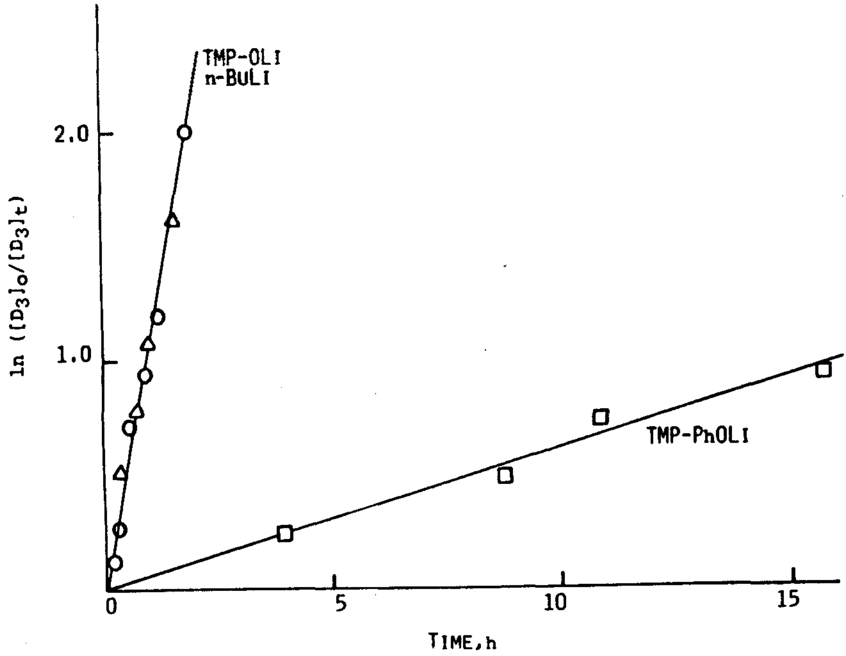


FIG. 2. First-order plots of D_3 conversion in the presence of (△) *n*-BuLi, (○) TMP-OLi, and (□) TMP-PhOLi, $[D_3] = 1.0$ mol/L; [initiator] = 20 mmol/L; THF; 26°C.

The use of the Li counterion was dictated by the results of previous workers who found that lithium-based initiators exhibit high selectivity toward the anionic polymerization of cyclotrisiloxanes and are slow to react with linear siloxanes [12-14]. The danger of parasitic initiation of D_3 polymerization by moisture [12, 25, 26] was substantially removed by employing rigorously dry systems (working under high vacuum and a dry nitrogen atmosphere). To obtain high "blocking" i.e., initiation efficiency and preferably narrow molecular weight distribution (MWD) of the PDMS segments, conditions for high I_{eff} (initiation efficiency) and high R_i/R_p (rate of initiation/propagation) had to be worked out.

Quantitative information in regard to rates of initiation/propagation of D_3 was obtained by kinetic studies. Figure 2 shows conversion/time plots of D_3 polymerizations obtained with TMP-OLi and TMP-PhOLi (and for comparison with *n*-BuLi) initiators. According to these data, the conversion of D_3 is a first-order process, and initiation is fast with respect to propagation with both initiators used. Since initiation of D_3 polymerization is quantitative with *n*-BuLi [27, 28], and the rate of propagation with TMP-OLi is the same as that with *n*-BuLi, initiation must be close to quantitative with the Li alcoholate system as well. The kinetics and mechanism of the polymerization are discussed in detail in a separate paper [29].

In contrast, the rate of D_3 polymerization by the TMP-PhOLi system was found to be almost 20 times slower than by TMP-OLi under the same conditions. Indeed, the initiation efficiency of TMP-PhOLi may be even lower than that, as suggested by the differences in the rates in Fig. 2, due to the presence of moisture in the systems (i.e., the effect of 0.1-1 mmol/L moisture in the charges may be much larger on the slower polymerization induced by the phenolate than on the faster process due to the alcoholate) [12, 25, 26]. Evidently the I_{eff} of TMP-OLi is much higher than that of TMP-PhOLi.

To get further insight into the details of initiation of D_3 by TMP-OLi and TMP-PhOLi, the rates of disappearance of these compounds under simulated polymerization conditions were simultaneously followed by GC. Figure 3 shows the conversion/time plots for the D_3/TMP-OLi system; the samples were quenched by the addition of Me_3SiCl, which instantaneously converts the $-CH_2OLi$ and $-SiMe_2OLi$ termini into $-CH_2OSiMe_3$ and $-SiMe_2OSiMe_3$ end groups. According to the data, $-CH_2OLi$ induces quantitative and rapid initiation of D_3 polymerization in THF at 26°C. Initiation and subsequent propagation occur at comparable rates (cf. Curves 2). The somewhat faster conversion observed at $[D_3]_0 = 1$ mmol/L is due to a significant contribution of initiation to conversion. These facts also indicate that initiation is somewhat faster than propagation. Initiation is complete at ~5% D_3 conversion (cf. Curves 1) under simulated polymerization conditions ($[D_3]_0/[\text{TMP-OLi}]_0 \approx 50$). Since initiation is fast, the molecular weight distribution is expected to be narrow in this system.

In contrast, TMP-PhOLi is a low-efficiency initiator for D_3 polymerization. As shown by the date in Fig. 4, less than 20% TMP-PhOLi was converted to  $-\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}\text{OLi}$ in the 0-60°C range. The low conversions are evidently due to the inherently higher stability of TMP-PhOLi relative to $-SiMe_2OLi$. A complete analysis of the reasons why TMP-PhOLi is a low-efficiency initiator of D_3 polymerization is beyond the scope of these investigations.

According to these model experiments, Li-phenolate-capped PIBs are un-

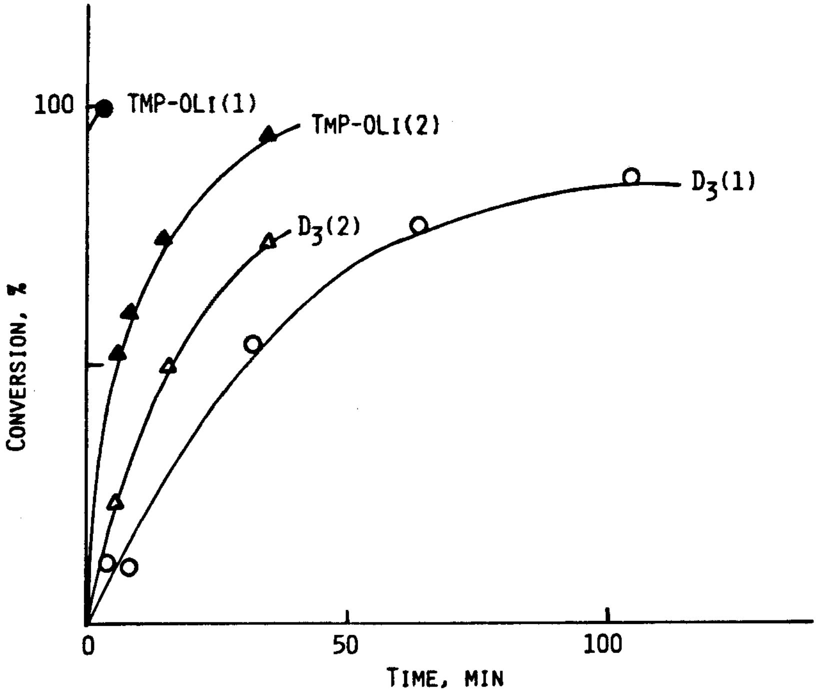


FIG. 3. D_3 and TMP-OLi conversion/time plots, (1) $[D_3] = 1.0$ mol/L, [TMP-OLi] = 20 mmol/L; (2) $[D_3] = 50$ mmol/L, [TMP-OLi] = 20 mmol/L; THF; 26°C.

suitable for efficient initiation of D_3 polymerization, but PIB-PDMS blocks still may be prepared by coupling PDMS capped by highly electrophilic end groups, e.g., $-\overset{|}{\underset{|}{Si}}-Cl$, and PIB-phenolates.

Polymerization Studies

Guided by the results of the model experiments, we studied the block copolymerization of D_3 initiated by $-CH_2OLi$-capped PIB. Conditions and results are summarized in Table 1. Strong direct evidence for triblock copolymer formation is the satisfactory agreement between theoretical and experimental molecular weights (Columns 5 and 6 in Table 1). Separation of the products

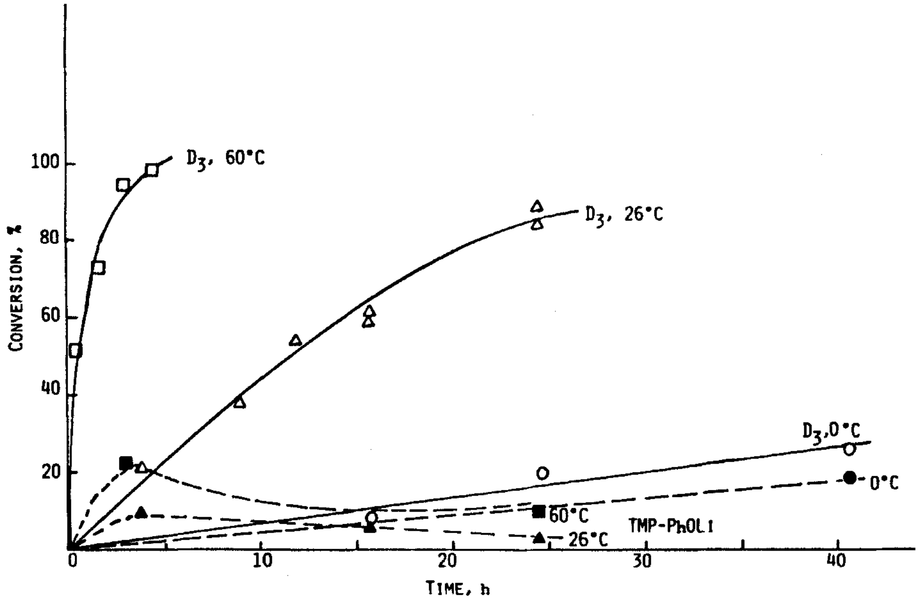


FIG. 4. D_3 and TMP-PhOLi conversions/time plots at various temperatures. $[D_3]$ = 1.0 mol/L; [TMP-PhOLi] = 20 mmol/L; THF

by selective solvent extraction could not be carried out due to the similar solubility characteristics of PIB and PDMS.

Extensive GPC studies substantiated the conclusion reached from $\bar{M}_n$ determinations. Figure 5 shows GPC traces by the UV detector of the series of triblocks defined in Experiments 1-3 in Table 1 together with the starting HO-PIB-OH. The traces are due to the inifer residue in the PIB segment, which becomes incorporated into the HO-PIB-OH during synthesis [15, 20, 21] (the PDMS moiety is transparent at 254 nm, the operational wavelength of the UV detector). The fact that the UV traces become markedly narrower (i.e., the molecular weight distributions of the triblocks grow narrower) with conversion indicate quantitative "blocking" of (i.e., initiation by) D_3 and the absence of MWD

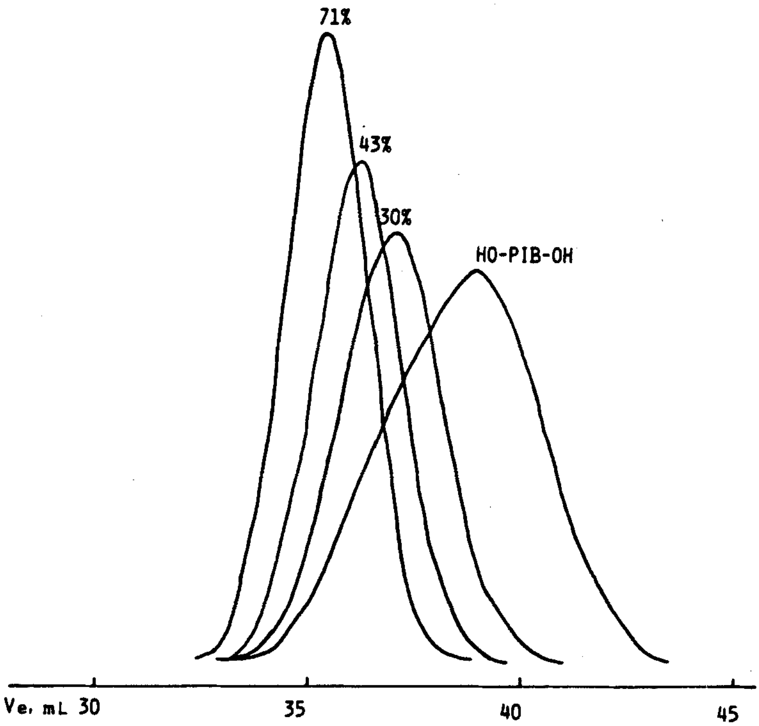


FIG. 5. Normalized GPC traces (UV detector) of HO-PIB-OH and Me_3Si-PDMS-*b*-PIB-*b*-PDMS-$SiMe_3$ at different D_3 conversions, as shown in Experiments 1-3 in Table 1.

broadening processes (e.g., redistribution). Indeed, GC analysis of charges even up to ~90% conversion failed to indicate the presence of octamethylcyclotetrasiloxane, D_4 ($<5\%$), proving the essential absence of redistribution processes.

When the block copolymer contains a comparable amount of PIB and PDMS sequences, the RI trace of the GPC instrument may also give a good approximation of the PIB segments present because the response factor of PIB is more than 10 times higher than that of PDMS in THF. Figure 6 shows representative RI traces of a tri- and a multiblock copolymer containing ~50% PIB, together with the starting HO-PIB-OH.

In all the GPC scans (Figs. 5 and 6), the elution volumes of the block copolymers are much lower than that of the HO-PIB-OH prepolymer, which indi-

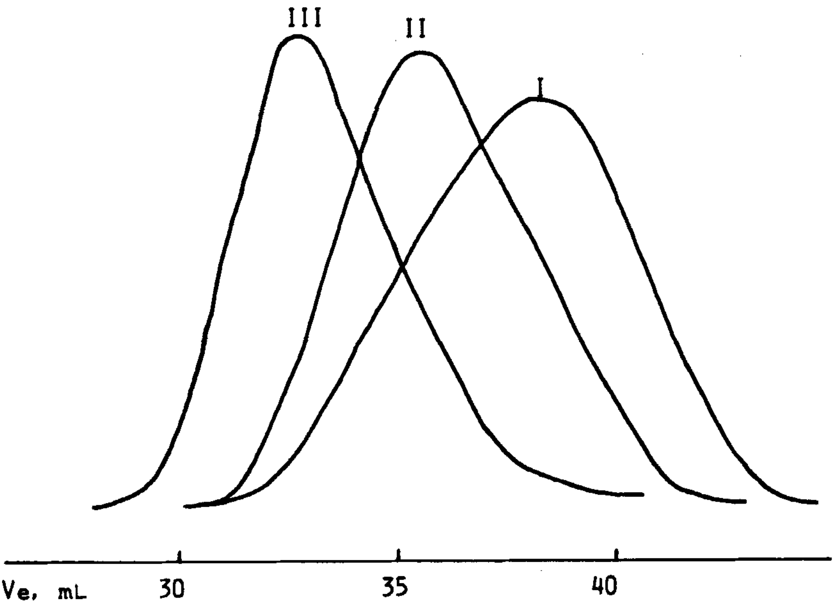


FIG. 6. Normalized refractive-index GPC traces of (I) starting HO-PIB-OH; (II) Me_3Si-PDMS-*b*-PIB-*b*-PDMS-$SiMe_3$; (III) $\leftarrow$PDMS-*b*-PIB-*b*-PDMS-$SiMe_2\rightarrow_n$ (Experiment 9 in Table 1).

cates an increase of the hydrodynamic volume on account of "blocking" and subsequent extension.

The molecular weights of the multiblock copolymers (Column 7 of Table 1) give at least an approximate value of *n* (block number). Thus, dividing the $\bar{M}_n$ in Column 7 by that in Column 6 of Table 1 gives an *n* value of about 3 to 5.

The living systems encountered in this research exhibited very high viscosities even with ~ 10% triblock and ~10 mmol/L living $-SiMe_2OLi$ end in THF at 26°C. Stirring was impossible due to gelation of a ~20 vol% solution (e.g., Experiment 3, Table 1). These gels, however, can be readily broken to much less viscous solutions, e.g., η_{sp} = 9.5, by quenching the living charge with Me_3SiCl. Evidently the living ends are strongly associated and may even lead to gels. This very large drop in viscosity upon quenching with both Me_3SiCl and Me_2SiCl_2 suggests that the degree of aggregation of the $-SiMe_2OLi$ groups is higher than two. Similar gelation phenomena have been observed with difunctional polyalkoxides from ethylene oxide [30]. The living anionic polymerization of D_3 with Li compounds is a useful system to study aggregation phenomena in siloxane polymerizations because complicated redistribution processes would be absent [31, 32]. Investigations along these lines are in progress.

In sum, according to our model and subsequent polymerization experiments, the rapid and quantitative living polymerization of D_3 at α,ω-CH_2OLi end groups of telechelic PIBs is feasible and leads to various PIB-PDMS block copolymers. Figure 1 illustrates the processes involved. The principles of these methods could be used for the synthesis of blocks over the entire PIB/PDMS composition (molecular weight) range.

Hydrolytic Stability of PDMS-*b*-PIB-*b*-PDMS

The hydrolytic stability of a representative triblock copolymer ($\bar{M}_n$ = 18 500; cf. Experiment 3, Table 1) was estimated by comparing the GPC UV traces of the triblock sample before and after hydrolysis. The area under the UV trace is linearly proportional to the aromatic inifer residue in PIB and thus is a measure of the $-PIBCH_2-O-SiMe_2PDMS$ linkages. Hydrolysis of the C—O—Si linkages yields the HO-PIB-OH prepolymer. No change in the area under and the position of the UV trace is evidence for stability, whereas a decrease in the area under the UV trace and a corresponding appearance of a UV trace of the HO-PIB-OH starting material indicates degradation. We judged, arbitrarily, that degradation has occurred when the area under the original UV trace has diminished by >80% with a corresponding appearance of the HO-PIB-OH starting material (see Results column, Table 2).

Conditions and results are summarized in Table 2. The triblock was stable in refluxing wet THF for 18 h (Experiment 1, Table 2). Heterogeneous systems (i.e., in bulk or in blend with PDMS) or hydrophobic (hexanes) solutions of the triblock were resistant to aqueous HCl (Experiments 2, 3, 6, Table 2). In contrast, the triblock in THF solution degraded in the presence of HCl (Experiments 4, 5, 7-9, Table 2). According to control experiments, Me_3Si-PDMS-$SiMe_3$ degrades in THF solution under the influence of concentrated HCl. Thus, the triblock copolymer exhibited enhanced resistance toward hydrolysis compared with low molecular weight alkoxysilanes [33, 34], which is most likely due to the presence of hydrophobic PIB and PDMS segments protecting the vulnerable C—O—Si bond and/or steric hindrance due to the macrosubstituents.

ACKNOWLEDGMENT

A grant by the Dow Corning Corporation is gratefully acknowledged.

REFERENCES

[1] J. P. Kennedy and E. Maréchal, *Carbocationic Polymerization*, Wiley, New York, 1982, p. 478.

[2] W. Noll, *Chemistry and Technology of Silicones*, Academic, New York, 1968, p. 437.

[3] H. K. Lichtenwalner and H. S. Sprung, "Silicons," in *Encyclopedia of Polymer Science and Technology*, Vol. 12, Wiley, New York, 1970.

[4] Akron Cationic Polymer Development Co., Akron, Ohio.

[5] D. C. Allport and W. H. Janes, *Block Copolymers*, Wiley, New York, 1973, p. 79.

[6] Ref. 5, p. 316.

[7] E. Bostick, "Synthesis and Properties of Siloxane Block Polymers," in *Block Polymers* (S. L. Aggarwal, ed.), Plenum, New York, 1970, p. 237.

[8] K. Kato, *Jpn. Plast.*, *6* (1968); *J. Polym. Sci., Part B*, *4*, 35 (1966).

[9] H. Hendus, K. H. Illers, and E. Ropte, *Kolloid-Z. Z. Polym.*, *216/217*, 110 (1967).

[10] P. V. Wright, "Cyclic Siloxanes," in *Ring-Opening Polymerization*, Vol. 2 (K. J. Ivin and T. Saegusa, eds.), Elsevier, London, 1984, p. 1116.

[11] E. E. Bostick, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, *10*(2), 277 (1969).

[12] C. L. Lee, C. L. Frye, and O. K. Johannson, *Ibid.*, *10*(2), 1361 (1969).

[13] H. J. Hölle and B. R. Lehnen, *Eur. Polym. J.*, *11*, 663 (1975).

[14] L. Wilczek, R. Tymczynski, and P. Szewczyk, *Pol. J. Chem.*, *55*, 2415 (1981).

[15] J. P. Kennedy and R. A. Smith, *J. Polym. Sci., Polym. Chem. Ed.*, *18*, 1523 (1980).

[16] R. Faust, A. Fehervari, and J. P. Kennedy, *Am. Chem. Soc. Symp. Ser.*, *282*, 125 (1985).

[17] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, *66*, 1515 (1944).

[18] M. K. Mishra, B. Sar- Mishra, and J. P. Kennedy, *Polym. Bull.*, In Press.

[19] J. P. Kennedy, S. C. Guhaniyogi, and V. Percec, *Polym. Bull.*, *8*, 563 (1982).

[20] B. Sar-Mishra, M. K. Mishra, and J. P. Kennedy, *Macromol. Synth.*, In Press.

[21] J. P. Kennedy, V. S. C. Chang, R. A. Smith, and B. Ivan, *Polym. Bull.*, *1*, 575 (1979).

[22] L. M. Jackman and C. W. DeBrosse, *J. Am. Chem. Soc.*, *195*, 4177 (1983).

[23] E. L. Warrick, U.S. Patent 2,634,252 (1949); *Chem. Abstr.*, *47*, 8415a (1953).

[24] T. Rhein and R. C. Schulz, *Makromol. Chem.*, *186*, 2301 (1985).

[25] C. L. Lee and O. K. Johannson, *J. Polym. Sci., Polym. Chem. Ed.*, *14*, 729 (1976).

[26] C. L. Lee, O. W. Marko, and O. K. Johannson, *Ibid.*, *14*, 743 (1976).

[27] C. L. Frye, R. M. Salinger, F. W. G. Fearon, J. M. Klosowski, and T. de Young, *J. Org. Chem.*, *35*, 1308 (1970).

[28] W. A. Fessler and D. C. Juliano, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, *12*(2), 150 (1971); *Ind. Eng. Chem., Prod. Res. Dev.*, *11*, 407 (1972).

[29] L. Wilczek and J. P. Kennedy, *Polym. J.*, In Press.

[30] H. Brody, D. H. Richards, and M. Szwarc, *Chem. Ind.*, p. 1473 (1958).

[31] Z. Laita and M. Jelinek, *Vysokomol. Soedin.*, *5*, 1268 (1963).

[32] J. Chojnowski and M. Mazurek, *Makromol. Chem.*, *176*, 2999 (1975).

[33] C. Eaborn, *Organosilicon Compounds*, Academic, London, 1960, p. 301.

[34] V. Bazant, V. Chvalovsky, and J. Rathousky, *Organosilicon Compounds*, Vol. 1, Academic, New York, 1965, p. 57

Received October 9, 1986
Revision received December 16, 1986