Living Carbocationic Polymerization. 48. Poly(isobutylene-*b*-methyl vinyl ether)[†]

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ABSTRACT: The synthesis of poly(isobutylene-*b*-methyl vinyl ether) (PIB-*b*-PMeVE) by living carbocationic polymerization (LC^+Pzn) employing the sequential monomer addition (SMA) technique is described. The process starts by producing the living PIB^+ block employing the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system in the presence of the common ion salt tetra-*n*-butylammonium chloride ($n Bu_4NCl$) in $CH_3Cl/n\text{-}C_6H_{14}$ or $CH_2Cl_2/n\text{-}C_6H_{14}$ mixed solvents at −80 °C and continues by the addition of methyl vinyl ether (MeVE). The second living block forms only in the presence of excess $TiCl_4$, suggesting that the species that starts the second block and subsequently sustains its growth is a MeVE·$TiCl_4$ complex. The stoichiometry of this complex (1:1 or 1:2) is uncertain. The $TiCl_4$ remains attached to the MeVE units after their incorporation into the diblock; however, it can be readily removed by water. PMeVE obtained in the presence of excess $TiCl_4$ degrades by dealcoholation; however, degradation is prevented by the use of $n Bu_4NCl$. Various length (composition) diblocks have been prepared and characterized. The novel PIB-*b*-PMVEs exhibit strongly amphiphilic character.

I. Introduction

Although the living carbocationic polymerization (LC^+Pzn) of olefins (e.g., isobutylene, styrene, various styrene derivatives) has only recently been discovered,[1] this mechanism and the use of the sequential monomer addition (SMA) technique has already led to a variety of new potentially useful materials including narrow dispersity homopolymers,[2] macromonomers,[3] blocks,[4] and networks.[5]

Until now one of our key objectives was the synthesis of polyisobutylene (PIB)-based thermoplastic elastomers (TPEs), that is, triblocks (or three-arm stars) comprising a soft (rubbery) PIB center block flanked by hard (or glassy) outer blocks. This objective was attained, and various glassy–rubbery–glassy triblocks with polystyrene,[6] polyindene,[7] etc., outer blocks have been prepared. In these TPEs the glassy segments were polymers of styrene or its derivatives. In regard to these TPEs, the critical synthesis step was the quantitative and rapid crossover from the first PIB^+ block to styrene (or a styrene derivative):

$$PIB^+ + St \rightarrow PIB\text{-}St^+$$

Because of the similar stability/reactivity of the olefinic monomers involved, these crossovers proceeded without too much difficulty.[6]

Another objective which seemed attainable by LC^+Pzn is the one-pot synthesis of amphiphilic diblocks, i.e., A–B blocks in which a hydrophobic block (e.g., PIB) is bonded to a hydrophilic [e.g., poly(methyl vinyl ether) (PMeVE)] block. Such amphiphilic blocks are potentially useful emulsifying or blending agents, detergents, and viscosifiers. The synthetic challenge was to develop conditions under which the $PIB^+ + MeVE \rightarrow PIB\text{-}MeVE^+$ crossover occurs quantitatively and rapidly, and desirable molecular weight PMeVE blocks can be attained. This goal has now been achieved, and a general technique for the synthesis of PIB–PMeVE blocks was developed. This paper describes the first LC^+Pzn synthesis of a novel amphiphilic diblock comprising an olefin (IB) and an alkyl vinyl ether (MeVE) by a one-pot SMA technqiue.

II. Experimental Section

The source and purification of solvents (methyl chloride, methylene chloride, and *n*-hexane), $TiCl_4$, and isobutylene (IB) have been described.[2,6] 2-Chloro-2,4,4-trimethylpentane (TMPCl) was obtained by hydrochlorination of 2,4,4-trimethyl-1-pentene and vacuum-distilled before use.[1] Methyl vinyl ether (Aldrich Chemical Co.) was condensed prior to use. Tetra-*n*-butylammonium chloride ($n Bu_4NCl$; American Tokyo Kasei) was used as received.

Polymerizations were carried out in a drybox under a dry-nitrogen atmosphere by the use of large (75-mL) culture tubes or round-bottomed flasks (200 mL). The equipment including the cooling assembly has been described.[1] The reactors were usually filled in order: solvent mixture, initiator, monomer, and if used $n Bu_4NCl$. The polymerization was started by the addition of $TiCl_4$. The $n Bu_4NCl$ was dissolved in CH_2Cl_2, usually 4.3 g in 50 mL of CH_2Cl_2.

In the experiments where the first step was the synthesis of the living PIB^+ block, the procedure was essentially identical to that described in earlier reports.[1,2,6,7] The second step was the addition of MeVE: The condensed prechilled monomer was added to the charge under constant agitation. The charges immediately turned straw yellow, indicating the formation of MeVE·$TiCl_4$ complexes. The yellow is viewed to be characteristic of $TiCl_4$ complexes of MeVE[8] and PMeVE. The color persists throughout the living polymerization, but it is immediately discharged upon MeOH addition.

The purification and analysis of the PIB segment has been described and is now a routine procedure.[1,2,6,7] The isolation of PIB-*b*-PMeVE, however, is cumbersome due to its amphiphilic nature. After quenching the blocking reaction with MeOH, emulsions are obtained which remain even after dilution with excess MeOH and/or H_2O. The emulsions persist on heating (to reflux) or diluting with aqueous saline solutions. Our procedure for the isolation of these amphiphilics was evaporating the solvents and traces of residual monomer, dissolving the products in CCl_4, washing repeatedly with water/methanol (80/20, v/v) mixtures, separating the organic layers, and removing the solvents by evaporation (or rotavap). The products were dried at room temperature in vacuo. The captions of the figures and tables give detailed concentrations and conditions.

Molecular weights and molecular weight distributions were obtained by a Waters high-pressure GPC assembly.[1,2,6] The equipment and analysis procedure for PIB have been described.[1,2,6] The $\bar{M}_n$s were obtained with a PIB calibration curve

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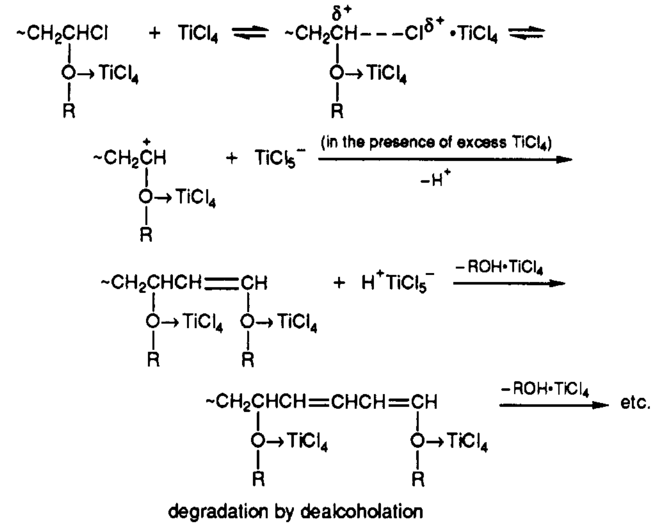
Scheme I



constructed with a set of narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.05–1.1) PIBs. This calibration curve was also used for $\bar{M}_n$ determination of PIB-*b*-PMeVE; thus, $\bar{M}_n$ values for the diblocks are approximations.

The ^1H and ^{13}C NMR spectra were taken on a Varian 200-MHz spectrometer using $CDCl_3$ as solvent. The equipment and procedures were described.[9] The composition of the diblocks was calculated by comparing the proton resonance intensities obtained for $-OCH_3$ and $>CH-$ in the PMeVE segment[10] and $-CH_3$ protons in the PIB segment.

III. Results and Discussion

1. Preliminary Experiments. Since the crossover $PIB^+ + MeVE \rightarrow PIB\text{–}MeVE^+$ appeared energetically favorable, a series of experiments have been carried out in which MeVE was added to the living PIB^+ blocks under a great variety of conditions and the products were analyzed for block formation. While the first step, i.e., the synthesis of the living PIB^+, was a routine operation (as ascertained by conversion, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ data)[2], the second step, i.e., the addition of MeVE, invariably led to ill-defined products (i.e., bimodal distributions, molecular weights lower than those of the starting PIB block, and severe discoloration). Control experiments in which MeVE was polymerized by $TMPCl/TiCl_4$ or BCl_3 in the absence or presence of electron donors (e.g., dimethylacetamide (DMA)) and/or proton traps (i.e., di-*tert*-butylpyridine (D*t*BuP)) also gave discolored UV-active products of bi- or multimodal dispersities with molecular weights far lower than expected in a living process. Under the same conditions IB yields well-defined narrow-distribution ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2) products by living polymerization. For example, the systems $TMPCl/TiCl_4$ or BCl_3/DMA/MeVE/D*t*BuP/CH_3Cl-nC_6H_{14} (60/40) in the −40 to −80 °C range gave brown, violet, or black liquids with at least bimodal distributions. These ill-defined PMeVEs have not been further characterized.

Sustained efforts were made to understand the cause(s) of these observations. In line with suggestions in the literature,[11,12] it is assumed that discoloration and the appearance of UV activity in Friedel–Crafts acid-induced alkyl vinyl ether polymerizations are due to dealcoholation as shown in Scheme I.

Similar to the proposition developed for living IB polymerization,[13] excess $TiCl_4$-induced alkyl vinyl ether polymerizations may also rapidly produce a chlorine-terminated polymer in equilibrium with a hypothetical living species (stretched polarized covalent bond) which in turn is in equilibrium with the ionic entity leading to conventional polymerization. In the presence of excess $TiCl_4$ the equilibria are pushed by mass law action toward the ionic species which inevitably deprotonate and hence lead to dealcoholation. This view is essentially identical to that used to explain some aspects of living polymerization of IB[13] and other olefins.[14] Proton loss in the poly(alkyl vinyl ether) system gives rise to an allylic alcohol substituent, which, due to complexation with $TiCl_4$, undergoes rapid repetitive dealcoholation and thus leads to a sequence of conjugated double bonds.

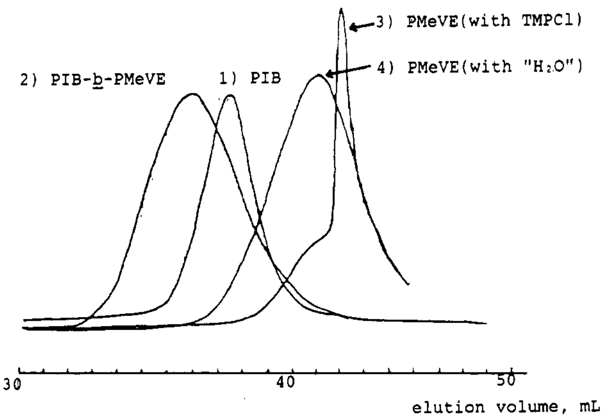


Figure 1. GPC traces of starting (1) PIB, (2) PIB-*b*-PMVE, and polymers obtained in control experiments: (3) $TMPCl/TiCl_4/nBu_4NCl/MeVE/CH_3Cl/nC_6H_{14}$ (−80 °C); (4) "H_2O"/$TiCl_4/nBu_4NCl/MeVE/CH_3Cl/nC_6H_{14}$ (−80 °C/90 min). (1) [TMPCl] = 3×10^{-4} mol, [$TiCl_4$] = 3.6×10^{-3} mol, [nBu_4NCl] = 1.6×10^{-3} mol, [IB] = 2.5×10^{-2} mol at −80 °C, 8 min, $\bar{M}_n$ = 4800, $\bar{M}_w/\bar{M}_n$ = 1.16. (2) Trace 1 after blocking with [MeVE] = 3.1×10^{-2} mol, 90 min, $\bar{M}_n$ = 5600, $\bar{M}_w/\bar{M}_n$ = 1.27. (3) $\bar{M}_n$ = 750. (4) $\bar{M}_n$ = 960.

According to this hypothesis, the main difficulty in synthesizing olefin–alkyl vinyl ether blocks by SMA is the inherent instability of the –Cl terminus of the poly(alkyl vinyl ether) block in the presence of strong Friedel–Crafts acids. In other words, the desirable and rapid $PIB^+ + RVE \rightarrow PIB\text{–}RVE^+$ crossover and subsequent alkyl vinyl ether (RVE) polymerization do occur; however, as soon as the PRVE block arises, rapid degradation by dealcoholation commences.

At this point we postulated that dealcoholation could be avoided by reducing the ionicity of the system. Indeed, we found that PMeVE degradation can be prevented by the addition of nBu_4NCl, a common anion salt, to the living charge. Recently we have shown that nBu_4NCl rapidly and quantitatively interacts with $TiCl_4$ (i.e., $nBu_4NCl + TiCl_4 \rightarrow nBu_4N^+ + TiCl_5^-$) and that the common anion $TiCl_5^-$ reduces the ionicity of the system.[13]

Figure 1 shows a set of representative GPC traces of products obtained in the presence of nBu_4NCl (the caption gives detailed conditions and data). Specifically, trace 1 shows the initial PIB block and trace 2 that of the PIB-*b*-PMeVE; traces 3 and 4 are PMeVE controls obtained by initiation with $TMPCl/TiCl_4$ and adventitious "H_2O"/$TiCl_4$, respectively, but otherwise under the same conditions as the blocks. Significantly, the GPC trace of the PIB block is symmetrical and narrow and is centered at a higher retention time (lower molecular weight) than that of the PIB-*b*-PMeVE. The traces of the PMeVE controls are at much lower molecular weights. The position of the shoulder in trace 3 indicates that the PMeVE control produced by TMPCl was contaminated by PMeVE produced by adventitious moisture (H_2O). Importantly, all the products were colorless and UV inactive, indicating the absence of degradation (dealcoholation).

A closer comparison of the GPC traces 1 and 2 of Figure 1 reveals that trace 1 (initial PIB block) is somewhat

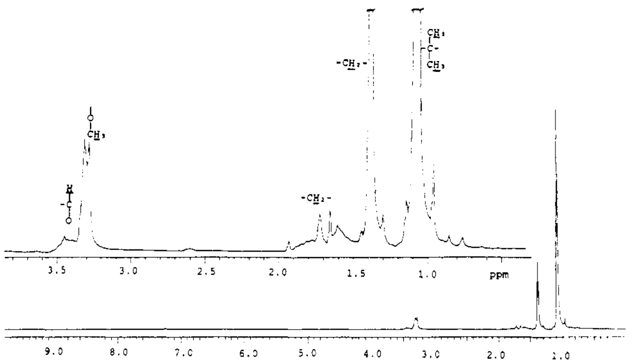


Figure 2. Representative ^{1}H NMR spectrum of a PIB-*b*-PMVE diblock copolymer.

narrower than trace 2 (PIB-*b*-PMeVE diblock). The broadening of the molecular weight distribution of the diblock may be due to several causes or to a combination of these, for example: (1) relatively slow crossover $PIB^+ + MeVE \rightarrow PIB\text{-}MeVE^+$, followed by relatively fast propagation of MeVE; (2) increased concentration of the dormant species after MeVE addition (after blocking has started) relative to that which prevailed before blocking; (3) incomplete blocking. The blocking efficiency must be quite high because the GPC trace of the block copolymer is monomodal. In view of the solubility characteristics of the diblock, it would be difficult to determine quantitatively the possible presence of a small amount of homopolymer contaminant in the diblock by selective precipitation or dissolution.

A set of orienting experiments was designed to probe the effect of polymerization time and MeVE concentration on diblock molecular weight. Thus in a series of six reactors living PIB^+ blocks were prepared, a quantity of MeVE was added, and the polymerizations were quenched after various times (from 0.17 to 18 h). In a companion set of four experiments we added various quantities of MeVE (from 0 to 0.06 mol) to living PIB^+ blocks and quenched the charges after various times. According to the results (see detailed data in Table I), neither MeVE concentration nor time affects the amount of diblock formed or its molecular weight. Importantly, a comparison of the results with the PIB controls (i.e., charges in which MeVE was absent) shows that a small measure of MeVE blocking did occur and that the PMeVE blocks grew only a few monomer units (i.e., from ~4800 to ~5300 or about nine units). Significantly, the number of moles of product N remained constant and blocking efficiencies (i.e., N/[TMPCl]) were close to quantitative in these experiments.

Quenching the charges with methanol gave stable white emulsions (see the Experimental Section), which suggested the presence of amphiphilic products. Figure 2 shows the ^{1}H NMR spectrum of a representative product (i.e., after dissolving in CCl_4 and extracting with water/methanol; see the Experimental Section) and indicates the presence of both PIB and PMeVE sequences.

Proof positive for the anticipated blocking was obtained by solubility studies and by ^{13}C NMR analysis of the water-soluble fraction of the product. Thus the product formed hazy solutions in methanol and water (good solvents for PMeVE) *and* pentane and hexane (good solvents for PIB) but dissolved in THF (good solvent for both PIB and PMeVE). The ^{13}C NMR spectrum of the water-soluble fraction showed evidence for PIB sequences (see Figure 3 for assignments); since PIB is insoluble in water, this PIB must be due to PIB-*b*-PMeVE diblocks.

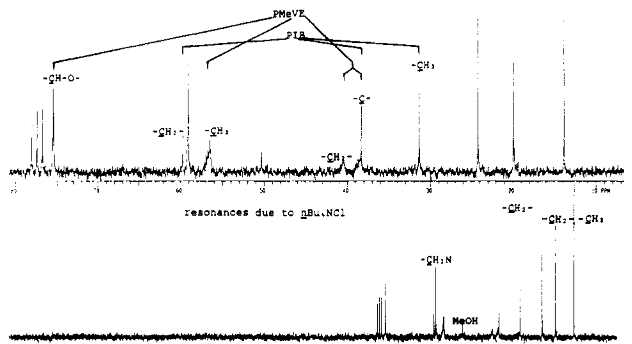


Figure 3. ^{13}C NMR spectra of the water-soluble fraction after purification of PIB-*b*-PMeVE.

Table I
Molecular Weight of the Diblock

	MeVE × 10^{-2}, mol	polmn time, h	W_p, g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$N \times 10^4$ [a]
		Versus Time[b]				
control		0.17	1.193	4800	1.16	2.47
1	6.1	0.17	1.274	5200	1.16	2.45
2	6.1	1.5	1.329	5200	1.27	2.55
3	6.1	3.0	1.401	5400	1.40	2.59
4	6.1	6.0	1.473	5300	1.37	2.78
5	6.1	9.0	1.521	5400	1.42	2.81
6	6.1	18.0	1.371	5500	1.38	2.49
		Versus [MVE][c]				
control		0.17	1.254	4900	1.32	2.56
7	1.5	1.5	1.312	5400	1.36	2.43
8	3.0	1.5	1.361	5300	1.42	2.57
9	6.1	18.0	1.371	5500	1.38	2.49

[a] $N = W_p/\bar{M}_n$. [b] [TMPCl] = 2.7×10^{-4} mol, [nBu_4NCl] = 1.7×10^{-3} mol, [IB] = 2.5×10^{-2} mol, [$TiCl_4$] = 3.4×10^{-3} mol in CH_3Cl/nC_6H_{14} (60/40) at −80 °C, 8 min. Total volume = 20 mL. [c] [TMPCl] = 2.7×10^{-4} mol, [nBu_4NCl] = 1.8×10^{-3} mol, [IB] = 2.5×10^{-2} mol, [$TiCl_4$] = 3.5×10^{-3} mol in CH_2Cl_2/nC_6H_{14} (60/40) at −80 °C, 8 min. Total volume = 20 mL.

2. Blocking of MeVE from Living PIB^+ by Sequential Monomer Addition. According to the data in Table I, irrespective of the polymerization time and MeVE concentration, the amount and molecular weight of the PMeVE blocks remain the same, within experimental error. To explain these findings we postulate that crossover and subsequent blocking of MeVE from PIB^+ are controlled by the presence of available $TiCl_4$ in the charge and, specifically, that MeVE incorporation occurs by MeVE·$TiCl_4$ complexes.

The existence of complexes between $TiCl_4$ and O-containing compounds, particularly etherates, is well-known.[10,15,16] In line with the literature, we have expected the rapid formation of 1:1 or 1:2 MeVE·$TiCl_4$ complexes; however, the data in Table I are insufficient to distinguish between these two stoichiometries.

Two series of key experiments were carried out to test our hypothesis that MeVE incorporation is controlled by MeVE·$TiCl_4$ complexes and to examine the stoichiometry of these complexes. In the first series of experiments we have prepared charges containing the living PIB^+ block, added a relatively large amount of MeVE, and studied the effect of the addition of increasing amounts of $TiCl_4$ upon diblock yield and molecular weight. Table II details reaction conditions and reagent concentrations used. Sample 0 (control) was obtained with the TMPCl/$TiCl_4$/nBu_4NCl/IB system in the absence of MeVE and gives the weight and $\bar{M}_n$ of the first PIB block formed (columns 3 and 4). Sample 1 shows the amount and molecular weight of the initial living PIB-*b*-PMeVE diblock that formed upon the addition of a large excess of MeVE to the living PIB^+ block. Note that only a small fraction of the added

Table II
Blocking MeVE from Living PIB Block: Orienting Experiments with $TiCl_4$ Addition[a]

	$TiCl_4$ added, $10^3 \times$ mol	W_p, g	$\bar{M}_n$	PMeVE contents (wt %) calcd with 1:1 or 2:1 complexes		PMeVE content	
				MeVE·$TiCl_4$	2MeVE·$TiCl_4$	by NMR, mol %	by GPC, wt %
0[b]		0.352	1250				
1		0.576	1900	19.2	34.6	39.0	34.2
2	1.48	0.729	2100	32.3	50.0	43.3	40.5
3	2.59	0.781	2800	47.1	64.7	44.0	55.3
4	4.00	0.795	2500	60.5	75.7	41.0	50.0
5	5.50	1.246	4200	70.7	84.7	56.0	70.3

[a] Addition sequence of reagents in a series of six reactors: CH_2Cl_2/nC_6H_{14} (60/40), [TMPCl] = 2.7×10^{-4} mol, [nBu_4NCl] = 1.85×10^{-3} mol, [IB] = 6.43×10^{-3} mol, [$TiCl_4$] = 3.7×10^{-3} mol, at −80 °C, 8 min; [MeVE] = 1.4×10^{-2} mol added to reactors 1–5. [b] Starting PIB block prior to MeVE addition (see footnote *a*).

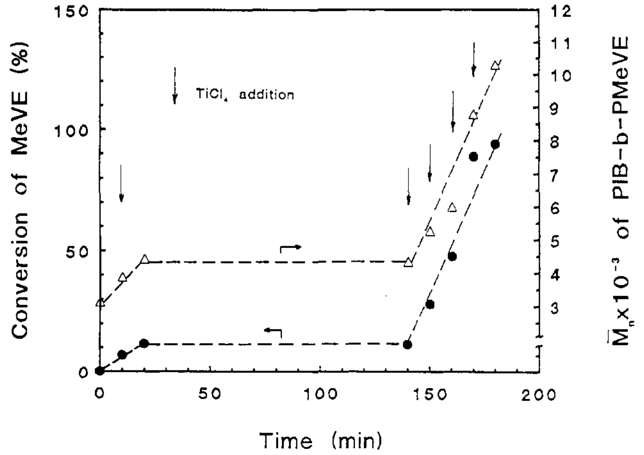


Figure 4. MeVE conversion (of MVE) and molecular weight vs time. Step 1: CH_2Cl_2/nC_6H_{14} (60/40), [nBu_4NCl] = 3.9×10^{-3} mol, [TMPCl] = 9.3×10^{-4} mol, [IB] = 4.88×10^{-2} mol, [$TiCl_4$] = 1.17×10^{-2} mol at −80 °C, 8 min. Step 2: [MeVE] = 1.19×10^{-1} mol. Step 3: [$TiCl_4$] = 1.6×10^{-2} mol added 10, 140, 150, 160, 170, and 180 min after MeVE addition.

MeVE was consumed by blocking. Samples 2–5 show the amounts and molecular weights of the diblocks formed upon the addition of successive aliquots of $TiCl_4$. Evidently, the amount and molecular weight of the PIB-*b*-PMeVE increase upon $TiCl_4$ additions.

Table II also shows the composition (PMeVE content) of the PIB-*b*-PMeVEs determined by ^1H NMR spectroscopy and GPC and the expected compositions of the diblocks assuming monomer incorporation via MeVE·$TiCl_4$ or 2MeVE·$TiCl_4$ complexes. Unfortunately the data are insufficient to distinguish between these two alternatives.

To firm up our conclusion that MeVE incorporation occurs exclusively by MeVE·$TiCl_4$ (stoichiometry unspecified) complexes, a second series of experiments were carried out. In these experiments a series of aliquots of $TiCl_4$ were added to a stirred reactor containing a charge of living PIB^+ block plus a large quantity of excess MeVE, and the amount (W_p) and molecular weight ($\bar{M}_n$) of the growing diblock were determined as a function of the aliquots of $TiCl_4$ added. Figure 4 shows the MeVE conversion and PIB-*b*-PMeVE molecular weight versus time profiles obtained. Specifically, the experiment started by producing a living PIB^+ block targeted for $\bar{M}_n$ ~3000 (TMPCl/$TiCl_4$/nBu_4NCl/IB/CH_2Cl_2/nC_6H_{14}/−80 °C/8 min). After a sample was withdrawn to ascertain the formation of the targeted PIB molecular weight ($\bar{M}_n$ = 3100, see the data point at 0 time), a relatively large quantity of MeVE was added to the living charge. After 10 min of stirring a sample was withdrawn to probe for the amount of MeVE converted and the molecular weight of the diblock. As shown by the data points at 10 min, 7% of the added MeVE was converted and the molecular weight rose to 3900. This conversion and molecular weight increase is due to the incorporation of MeVE·$TiCl_4$ into the living diblock chain; the MeVE·$TiCl_4$ arose from the residual $TiCl_4$ that remained after the first living PIB^+ block was formed plus a fraction of the MeVE added (note that [$TiCl_4$] > [nBu_4NCl]). Immediately after the withdrawal of the 10-min sample, the first aliquot of $TiCl_4$ was added and the charge stirred for 10 min. At this point the third sample was withdrawn (see conversion and molecular weight at 20 min) which showed ~12% MeVE conversion and diblock molecular weight ~4400. Subsequently the charge was stirred for 120 min, at which point another sample was taken. According to this sample (140 min), the conversion and the molecular weight remained unchanged during this quiescent stirring period, although a large amount of unreacted MeVE was still available in the charge.

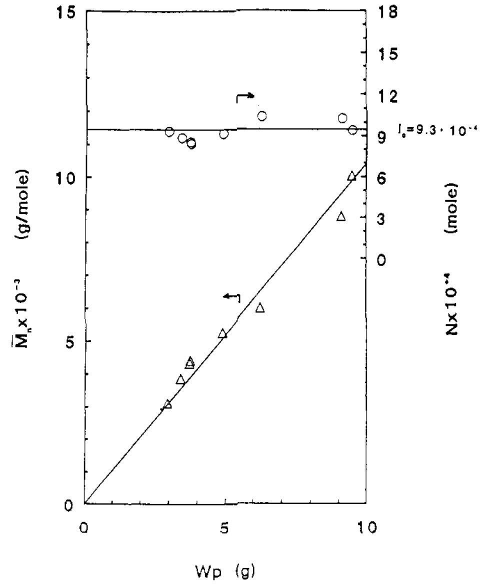


Figure 5. Living block copolymerization of IB and MeVE.

At this point a fresh aliquot of $TiCl_4$ was added and the system was stirred for 10 min and sampled. According to this, the 150-min sample MeVE conversion increased to ~28% and the diblock molecular weight to ~5300. From this point on successive aliquots of $TiCl_4$ were added to the living charge, the solution was stirred for 10 min, and a sample was taken. As indicated by the plots in Figure 4 both the MeVE conversion and diblock molecular weight increased in proportion with the $TiCl_4$ added. The dispersities of the samples were in the range $\bar{M}_w/\bar{M}_n$ = 1.4–1.7. These data suggest that MeVE incorporation is controlled by $TiCl_4$, that is, most likely by MeVE·$TiCl_4$ complexes, and that "free" MeVE does not add to the living block.

Figure 5 shows the diblock molecular weight ($\bar{M}_n$) versus grams of diblock formed (W_p) and the number of moles of living species (*N*) versus gram of diblock formed plots, respectively. The experimental points are certainly within experimental error of the theoretical values (solid lines), indicating that the number of living chains remains constant and equal to the initial initiator concentration, $[I]_0$ = $[TMPCl]_0$ = 9.3×10^{-4} mol, throughout the experiment. These data prove that both phases of the blocking experiment involved living species. The de facto

Table III
Synthesis of PIB-*b*-PMeVE by Sequential Addition of $TiCl_4$

conditions[a]	$\bar{M}_n$ of the PIB segment	$\bar{M}_n$[b] of PMeVE expected	$\bar{M}_n$ of the PIB-*b*-PMeVE diblock	$\bar{M}_w/\bar{M}_n$
$[nBu_4NCl] = 1.8 \times 10^{-3}$ mol, $[TMPCl] = 5.3 \times 10^{-4}$ mol, $[IB] = 1.28 \times 10^{-2}$ mol, $[TiCl_4] = 3.7 \times 10^{-3}$ mol; after 8 min of polymn, $[MeVE] = 1.4 \times 10^{-2}$ mol and $[TiCl_4] = 3.7 \times 10^{-3}$ mol	1300	1200	2600	1.37
$[nBu_4NCl] = 1.8 \times 10^{-3}$ mol, $[TMPCl] = 2.7 \times 10^{-4}$ mol, $[IB] = 1.28 \times 10^{-2}$ mol, $[TiCl_4] = 3.6 \times 10^{-3}$ mol; after 8 min of polymn, $[MeVE] = 2.6 \times 10^{-2}$ mol and $[TiCl_4] = 8.8 \times 10^{-3}$ mol	2600	4500	5000	1.39
$[nBu_4NCl] = 1.8 \times 10^{-3}$ mol, $[TMPCl] = 2.7 \times 10^{-4}$ mol, $[IB] = 2.5 \times 10^{-2}$ mol, $[TiCl_4] = 3.7 \times 10^{-3}$ mol; after 8 min of polymn, $[MeVE] = 7.6 \times 10^{-3}$ mol and $[TiCl_4] = 1.7 \times 10^{-3}$ mol	5000	1500	6500	1.65

[a] Block copolymerizations in CH_2Cl_2/*n*-hexane (60/40, v/v). [b] Calculated $\bar{M}_n$ of the PMeVE block assuming $2MeVE{\cdot}TiCl_4$ stoichiometry.

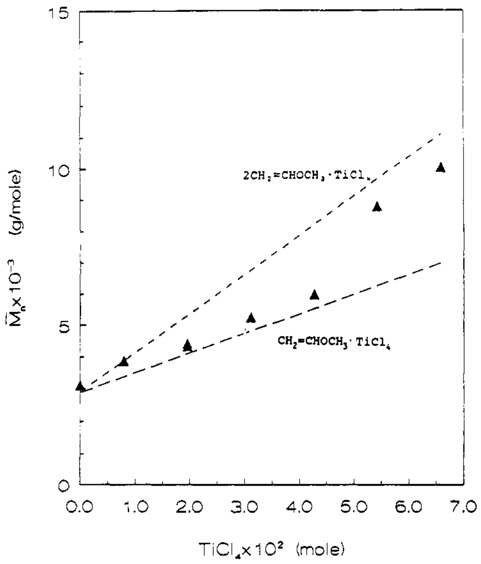


Figure 6. $\bar{M}_n$ vs $[TiCl_4]$ added for the block copolymerization of IB and MVE.

"monomer", i.e., the $MeVE{\cdot}TiCl_4$ complex, is formed in situ in the charge and is essentially quantitatively incorporated into the living PMeVE block upon $TiCl_4$ addition. After the last $TiCl_4$ addition the conversion of MeVE was virtually complete. According to this evidence the block copolymerization of IB and MeVE is living under the conditions employed.

Figure 6 shows the relationship between the molecular weight of the diblocks formed and the amount of $TiCl_4$ introduced. The upper broken line indicates this relationship assuming the presence of a $2MeVE{\cdot}TiCl_4$ complex, and the lower one shows the same relationship assuming the presence of $MeVE{\cdot}TiCl_4$. The experimental data fall between these limits, so the stoichiometry of the active complex remains obscure. It is conceivable that both stoichiometries may coexist and that the complexes are connected by a rapid equilibrium.

On hand of this diagnostic information we have carried out a large number of diblocking experiments and have prepared a series of PIB-*b*-PMeVEs of potential interest as emulsifying agents. Table III shows the results of three representative diblock syntheses. In these experiments we first prepared the PIB block of desirable sequence length ($\bar{M}_n$ = 1000–5000) and subsequently blocked MeVE from the living PIB^+ by adding predetermined amounts of $TiCl_4$. The PMeVE blocks were targeted to be in the $\bar{M}_n$ = 1300–3500 range. Evidently, the molecular weights of the PMeVE blocks (i.e., the PIB-*b*-PMeVE diblocks) are within experimental error of the theoretical values.

As anticipated the diblocks were strong, nonionic, emulsifying agents. For example, an emulsion that formed upon dissolving 0.1 g of a PIB-*b*-PMeVE ($\bar{M}_n$ = 2600, 50 wt % PMeVE) in 5 mL of methanol/hexane (50/50, v/v) and adding 3 mL of water was stable for several months of storage at room temperature. Another emulsion prepared by using 0.1 g of PIB-*b*-PMeVE ($\bar{M}_n$ = 5000, 50 wt % PMeVE) in 3 mL of hexane plus 2 mL of methanol plus 2 mL of water was stable for close to a year.

IV. Conclusions and Speculations

The fact that $TiCl_4$ is inactive after the incorporation of the $MeVE{\cdot}TiCl_4$ complex into the polymer chain suggests that the Friedel–Crafts acid remains attached to the ether unit in the polymer. This would explain the need for the use of stoichiometric (not catalytic) amounts of $TiCl_4$. The Friedel–Crafts acid, however, can be readily removed by washing the diblock with nucleophiles (water and methanol).

The above data also indicate that $TiCl_4$ is certainly not a coinitiator (for the definition of coinitiator see ref 17) in these polymerizations but an "activator". The mechanism of activation by $TiCl_4$ is obscure; the $TiCl_4$ may complex with the MeVE and enhance its dipole character, i.e., reactivity, toward the living site (most likely a stretched polarized covalent $\sim CH_2C^{\delta+}H(OCH_3)\text{- - -}Cl^{\delta-}$ bond). This proposition is similar to that developed to account for the free-radical-initiated alternating copolymerization of Friedel–Crafts acid activated electron donor monomers (e.g., acrylonitrile and methyl methacrylate).[18]

In this context the question arises whether the picture developed here may not be also valid for the mechanism of living alkyl vinyl ether polymerization induced by HI/ZnX_2 (X = Cl, Br, I) systems proposed by the pioneering Japanese investigators.[19] Thus, in contrast to the original authors, who regard these polymerizations to proceed by insertion of vinyl ethers into $\sim CH_2CH(OR){-}I$ bonds activated by zink halides,[19] we posit that the process involves the insertion of "activated" vinyl ether Friedel–Crafts acid complexes (e.g., $MeVE{\cdot}ZnCl_2$) into relatively weak $\sim CH_2CH(OR){-}I$ bonds. Investigations to gain insight into this possibility are in progress and will be reported elsewhere.

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Registry No. IB, 115-11-7; MeVE, 107-25-5; TMPCl, 6111-88-2; PIB-*b*-PMVE (block copolymer), 138983-66-1; $TiCl_4$, 7550-45-0; *n*-Bu_4NCl, 1112-67-0.