Amphiphilic Block Copolymers by Sequential Living Cationic Polymerization: Synthesis and Characterization of Poly(isobutylene-*b*-methyl vinyl ether)

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ABSTRACT: The living polymerization of methyl vinyl ether (MeVE) was achieved using initiators obtained by capping 2,4,4-trimethyl-2-chloropentane (TMPCl) with 1,1-diphenylethylene (DPE), or 1,1-ditolylethylene (DTE) in conjunction with $TiCl_n(OEt)_{4-n}$ ($n = 2-2.4$) coinitiator in CH_2Cl_2/hexanes (60/40 v/v) solvent mixture at 0 °C. Sequential block copolymerization of isobutylene (IB) with MeVE has also been accomplished. Well-defined living poly(isobutylene) (PIB) was first prepared at −80 °C in the presence of $TiCl_4$, followed by capping with DPE or DTE. Then, $Ti(OEt)_4$ was added to reduce the Lewis acidity followed by the addition of MeVE, and the temperature was raised to 0 °C. Well-defined PIB-PMeVE diblock copolymers with controlled molecular weight and narrow molecular weight distribution ($M_w/M_n < 1.1$) have been obtained, with the virtual absence of homopolymer contaminants. According to differential scanning calorimetry, the diblock copolymers exhibit two T_gs, suggesting microphase separation. PIB-PMeVE diblock copolymers with ∼50/50 w/w composition were insoluble in water but soluble in methanol. The diblock copolymer with 80 wt % PMeVE content was soluble in water, exhibited excellent surfactant properties (critical micelle concentration = 2.3×10^{-5} M), and produced stable emulsions of oil in water (average particle size ∼200 nm).

Introduction

The discovery of living cationic polymerization of vinyl ethers[1] and olefins[2] provided the simplest and most convenient method for the preparation of block copolymers with well-defined architectures. The key to these living polymerizations is the strong interaction between the nucleophilic counteranion and the cationic active site. To effect living polymerization of the highly reactive vinyl ethers, weak Lewis acids, such as I_2, and Zn halides are required as coinitiators. However, they are ineffective to induce polymerization of the less reactive hydrocarbon monomers such as isobutylene (IB) and styrene (St). Therefore, the preparation of vinyl ether−IB or vinyl ether−St block copolymers (or the reverse sequences) by sequential monomer addition is difficult. Efficient crossover may be obtained when the reactivities of the two monomers are similar or when crossing from the slightly more reactive monomer to the less reactive one. It is difficult to attain, however, when the crossover is from the less reactive to the more reactive monomer, or from a much more reactive monomer to a much less reactive one.

In a series of publications, we reported on a novel method for the synthesis of block copolymers by living carbocationic sequential block copolymerization when the second monomer is more reactive than the first one. It involves capping with a highly reactive but non(homo)polymerizable monomer such as 1,1-diphenylethylene (DPE). This is followed by tailoring the Lewis acidity to the reactivity of the second monomer. The Lewis acidity moderation was accomplished by the addition of titanium alkoxides forming the weaker $TiCl_{4-n}(OR)_n$ (R = Et, nBu, iPr) Lewis acids in situ,[3−5] or by replacing the Lewis acid with a weaker one.[6] The success of the methods was demonstrated in the synthesis of PIB-*b*-PpMeSt[3] and PIB-*b*-PαMeSt[4] diblock or PpMeSt-*b*-PIB-*b*-PpMeSt[5] and PαMeSt-*b*-PIB-*b*-PαMeSt triblock[6] copolymers. Following our original reports, the living polymerization of isobutyl vinyl ether (IBVE) was also accomplished using separately prepared $TiCl_{4-n}(OiPr)_n$ or $TiCl_2(OPh)_2$.[7]

Quite recently, we have found that the same Friedel−Crafts acid may be a weak Lewis acid when the monomeric counteranions arise, but a strong acid when it forms dimers and/or dimeric gegenions. Thus the living polymerization of IBVE was accomplished when $[TiCl_4] <$ [chain end].[8] Under these conditions, the gegenion is $TiCl_5^-$, a much stronger nucleophile compared to the $Ti_2Cl_9^-$ dimeric gegenion which dominates at $[TiCl_4]$/[chain end] ≥ 2. Following this lead, the synthesis of PIB-PIBVE was accomplished by capping the living PIB end with DPE and decreasing the $[TiCl_4]$ to <[chain end] before the addition of IBVE.

Continuing our studies on the synthesis of block copolymers, we set out to broaden the scope of our technique and prepare amphiphilic PIB-PMeVE diblock copolymers, important not only from a scientific but also from a practical point of view.

According to Ledwith et. al.[9,10,11,12] methyl and 2-chloroethyl vinyl ethers exhibit much lower reactivities [k_p(obs) ∼2×10^2 $M^{-1}{\cdot}s^{-1}$ at 0 °C], compared to ethyl, cyclohexyl, *tert*-butyl, and isobutyl vinyl ethers, which have similar reactivities [k_p(obs) ∼3×10^3 $M^{-1}{\cdot}s^{-1}$ at 0 °C]. Based on the initiation rate constants against $Ph_3C^+SbCl_6^-$ in CH_2Cl_2 at −40 to 0 °C, in a more detailed analysis by Subira et al.,[13] the monomer reactivity order was found to be similar, i.e., MeVE < EVE ≤ IBVE. Differences in the apparent k_ps for MeVE and EVE, however, were much larger (MeVE ≪ EVE), which was explained by the different reactivity of the active centers due to differences in intramolecular solvation. In line with this, the lowest k_t value (most stable cation) was obtained with MeVE. In spite of this, it is rather difficult to achieve living cationic polymerization of MeVE. While the ether bond in IBVE and its polymer is sterically hindered, most Lewis acids easily form complexes with MeVE and its polymer.

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Furthermore, using a strong Lewis acid facile dealcoholation results in colored products. It is no doubt the consequence of these difficulties that while the literature on the cationic polymerization of IBVE is abundant, that of MeVE is rather scarce.

The living polymerization of MeVE by the (1-iodoethoxy)ethane/I_2 initiating system in toluene or toluene/CCl_4 (1/1 v/v) at −35 and −15 °C was first reported by Miyamoto et al.[14] Amphiphilic block copolymers of MeVE and RVE, where R is hexadecyl (CVE), octadecyl (ODVE),[15] and isobutyl (IBVE) or chloroethyl (CEVE),[16] prepared by sequential monomer addition have also been reported. Interestingly, methanol solutions of $(MeVE)_{120}$-$(CVE)_{20}$ diblock copolymers remained cloudy up to 75 °C.

The synthesis of well-defined block copolymers of MeVE and *p*-methoxystyrene (pMOSt) {$(MeVE)_{38}$-$(pMOSt)_{38}$ and $(MeVE)_{38}$-$(pMOSt)_{102}$} have been reported by the HI/ZnI_2 initiating system in toluene at −15 °C.[17] The order of monomer addition is important; the synthesis of PpMOSt-*b*-PMeVE block copolymer (i.e., reverse sequence) was unsuccessful, due to the large difference in reactivity between MeVE and pMOSt (MeVE $\gg$ pMOSt).

Quite recently, Ohmura et al.[18] published the homopolymerization of MeVE in CH_2Cl_2 using $SnCl_4$ in the presence of equimolar amounts of nBu_4NCl at −15 and −78 °C. At −15 °C, chain transfer to monomer was operational, resulting in broad molecular weight distributions and loss of molecular weight control. This was attributed to the lower stability of the growing PMeVE cation at −15 °C. However, at −78 °C well-defined polymers with controlled M_n (up to 3000) and narrow molecular weight distribution were obtained. The synthesis of PMeVE-PSt was also attempted. Polymerization of the less reactive St, however, only took place when an additional amount of $SnCl_4$ was added and the temperature was raised to −15 °C. Fractionation of the crude product resulted in pure diblock copolymers. The obtained diblocks {$(MeVE)_{20}$-$(St)_{18}$ and $(MeVE)_{20}$-$(St)_{33}$} were insoluble in water or ethanol.

Recently, Pernecker et al.[19] reported on the homopolymerization of MeVE and on the sequential block copolymerization of IB with MeVE using $TiCl_4$ as coinitiator. Complete polymerization of MeVE was only possible at $[TiCl_4] > [MeVE]$, which was explained by strong complexation between $TiCl_4$ and MeVE (and PMeVE) at the polymerization temperature, at −80 °C. It was postulated that the true monomer is the MeVE·$TiCl_4$ complex. The PIB-PMeVE diblocks prepared, although insoluble in water, were strong emulsifying agents for methanol/water mixtures in hexane. Complex formation between MeVE and $TiCl_4$ lowers the reactivity of the monomer close to that of IB. While this increases the crossover efficiency, $TiCl_4$ concentration higher than that of the monomer is impractical.

In this paper we describe the synthesis and characterization of PIB-PMeVE diblock copolymers using catalytic amounts of coinitiator.

Experimental Section

Materials. 1,1-Diphenylethylene (DPE) and 2,6-di-*tert*-butylpyridine (DTBP) were used as received from Aldrich. Methyl vinyl ether (MeVE) (99%, Matheson Gas Products Inc.) was purified by passing the gaseous monomer through a column of CaH_2 before condensing it at −80 °C. CH_3Cl (MeCl) was dried by passing the gas through in-line gas purifier columns packed with BaO/Drierite and condensed at −80 °C prior to polymerization. CH_2Cl_2 was purified by washing it with distilled water until neutral and drying over $MgSO_4$ overnight. It was refluxed for 24 h and distilled twice over P_2O_5, the second time just before use. Hexanes was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with deionized water and 10% NaOH aqueous solution until neutral, and was stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled.

Titanium(IV) chloride ($TiCl_4$, 99.9% Aldrich) was used as received. Titanium(IV) ethoxide ($Ti(OEt)_4$, tech. Aldrich) was rendered free from excess ethanol by leaving it under vacuum while stirring for 6 h and was stored under N_2 at −20 °C. It was evacuated again at least for an hour just before use.

1,1-Ditolylethylene (DTE) was synthesized according to the following procedure: **1,1-Ditolyl-1-ethanol:** In a 1 L three neck flask equipped with a dropping funnel, reflux condenser, and a stirrer were placed 200 mL of *p*-tolylmagnesium bromide (1 M in diethyl ether, Aldrich). To this a solution of 24 mL (0.18 mol) of 4-methylacetophenone (Aldrich) in 200 mL of diethyl ether was added dropwise, while the temperature was kept between 0 and 3 °C, under N_2 atmosphere. After the addition of the 4-methylacetophenone solution, the reaction mixture was refluxed for 2 h, cooled to room temperature, and hydrolyzed by pouring it into a mixture of 40 g of NH_4Cl and 400 g of ice. The organic layer was separated and the aqueous layer was further washed with additional amounts of diethyl ether. The organic layers were combined and washed with 20% $NaHCO_3$ solution and then with distilled water. The organic layer was left over $MgSO_4$ overnight to remove traces of water. After filtration, diethyl ether was evaporated on the rotavap to give the crude product 1,1-ditolyl-1-ethanol.

1,1-Ditolylethylene: The carbinol (1,1-ditolyl-1-ethanol) (31.48 g) was dehydrated by heating it to reflux in an oil bath at 210 °C for 15 min. It was cooled to room temperature, and then 20 mL of H_2SO_4 (20%) was added and then refluxed for an hour. After cooling to room temperature, the crude product crystallized out. After filtration to separate the crystals and three recrystallizations from petroleum ether, the pure product 1,1-ditolylethylene was obtained. ^1H NMR: 2.4 (s, 6H), 5.4 (s, 2H), 7.4−7.6 ppm (m, 8H).

The synthesis and purification of all other materials have been described.[8,20]

Procedures. Polymerizations were carried out in a stainless steel glovebox[20] using CH_2Cl_2/Hex (60/40 and 40/60 v/v) solvent mixtures. The homopolymerizations of MeVE were initiated by first capping 2,4,4-trimethyl-2-chloropentane (TMPCl) with DPE in the presence of proton trap and $TiCl_4$, followed by the addition of $Ti(OEt)_4$ dissolved in CH_2Cl_2/Hex (60/40 v/v). After 15 min, the monomer MeVE was added. In the diblock preparation, IB was first polymerized, followed by capping with DPE or DTE. The polymerization and capping reaction was carried out in a CH_2Cl_2/Hex (60/40 v/v) solvent mixture at −80 °C. In a representative procedure, IB (0.32 M) was polymerized for 15 min using TMPCl (4.0×10^{-3} M) in the presence of $TiCl_4$ (6.4×10^{-2} M) and DTBP (6.0×10^{-3} M). DPE (8.0×10^{-3} M) was added next and allowed to react for 90 min. Samples quenched with methanol, purified, and analyzed by ^1H NMR indicated that the capping was ~100% after 90 min reaction time (disappearance of the peaks at ~1.7 ppm {PIB-$CH_2C(CH_3)_2Cl$} and ~2.0 ppm {PIB-$CH_2C(CH_3)_2$-Cl} and appearance of new peaks at ~2.5 ppm {PIB-CH_2-$C(Ph)_2OCH_3$} and ~3.0 ppm {PIB-$CH_2C(Ph)_2OCH_3$}). The capping procedure with DTE was the same as with DPE. In addition to the peaks at 2.5 and 3.0 ppm, a new peak in the ^1H NMR at 2.3 ppm is due to the *p*-CH_3 of the phenyl rings. The capping was followed by the introduction of $Ti(OEt)_4$ solution in CH_2Cl_2/Hex (60/40 v/v) reacted for 15 min, which was followed by the addition of MeVE at −80 °C. After 10 min at −80 °C, the temperature was raised to 0 °C. After 15−20 h, the reactions were quenched with prechilled methanol and the reaction mixtures were poured into excess 10% ammoniacal methanol.

The water-insoluble diblock polymers were purified by dissolving them in $CHCl_3$ and washing with distilled water three times. They were left overnight over Na_2SO_4 drying agent and were filtered, and $CHCl_3$ was removed on the rotavap.

Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/vis detector, on-line multi-angle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), Model 712 sample processor, and five ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate of THF was 1.0 mL/min. The detector signals (RI, UV, and LS) were recorded on a MacIntosh computer for absolute molecular weight and molecular weight distribution determination by the laser light scattering detector using the ASTRette software. Refractive index increments (dn/dc) of 0.063 mL/g[21] for PMeVE $M_n = 25\,000$ in THF and 0.1026 mL/g[22] for PIB $M_n = 6000$ in THF were used. The dn/dc for the diblocks was calculated using the above values and the composition of diblock copolymer. Mole fractions were calculated from the conversion of each monomer.

The crossover efficiency was determined by column chromatography[23] on silica gel and by integration of the GPC RI peaks (ASTRette software). NMR spectroscopy was carried out on a Bruker 250 MHz instrument.

DSC measurements were carried out using Thermal Analyst 2000 (DuPont Instruments) coupled with DSC 2910 Modulated DSC (TA Instruments). Surface tension measurements were carried out on a SensaDyne 6000 surface tensiometer (Chem-Dyne Research Corp.), at a bubble rate of 1/s, using a data collection program version 3.2(c) (1989 Chem-Dyne Research Corp.). The particle size distribution of the oil in water emulsion was determined by an ultrafine particle analyzer (Microtrac, Leeds and Northrup).

Results and Discussion

a. Homopolymerization of MeVE and Block Copolymerization of IB with MeVE Using DPE as a Capping Agent. Experimentation started by using the conditions found successful in the synthesis of PIB-PIBVE block copolymers. Thus, the polymerization of MeVE was initiated with the 2,2,4,4-tetramethyl-6,6-diphenyl-6-chlorohexane[8] (TMDH-Cl)/$TiCl_4$ system using Hex/MeCl (60/40 v/v) solvent mixture at −40 °C. Three [initiator]/[$TiCl_4$] ratios of 1.0:0.3, 1.0:0.6, and1.0:0.9 were used. Under these conditions, however, only traces of polymers were obtained in 5 h, which we interpreted by a rapid and irreversible complexation of the coinitiator by the monomer (and polymer). The equilibrium constant of complexation is dependent on the temperature and on the nature (strength) of the Lewis acid. Therefore, increasing the temperature may free some coinitiator to induce polymerization. Increasing the temperature with a strong Lewis acid, however, may lead to proton elimination and dealcoholation, resulting in a colored product.

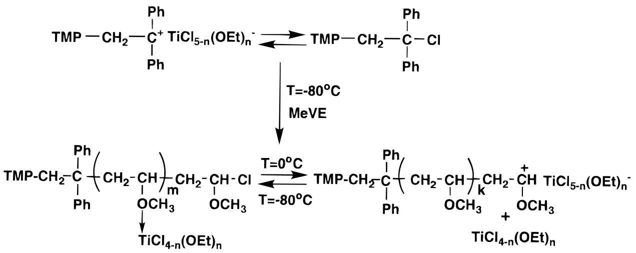
Thus, we decided to use a different approach, to reduce the Lewis acidity by introducing $Ti(OEt)_4$ before the addition of MeVE. In the reaction of $Ti(OEt)_4$ with $TiCl_4$, a weaker Lewis acid, $TiCl_{4-n}(OEt)_n$, is formed in situ, where n is determined by the stoichiometry. Thus, by changing the stoichiometry, the Lewis acidity can be moderated in a wide range. Due to the weaker nature of $TiCl_{4-n}(OEt)_n$ and the steric hindrance by the ethoxide groups, the equilibrium constant of complexation was expected to be lower. [$Ti(OEt)_4$]/[$TiCl_4$] ratios of 1.0:1.0 and 1.5:1.0, and two solvent mixtures, Hex/MeCl (60/40 and 40/60 v/v), were tested. At −80 °C the highest conversion obtained in 3 h was 19%. When the temperature was raised to −40 °C, conversions increased and reached 50% for the 1.0:1.0 ratio and 34% for the 1.5:1.0 ratio in the 40/60 solvent system. Polymerization conditions and results are shown in Table 1. All polymers exhibited narrow molecular weight distribution ($M_w/M_n < 1.1$). At −40 °C, 80% initiators efficiency (I_{eff}) was obtained using the [$Ti(OEt)_4$]/[$TiCl_4$] = 1.0:1.0 ratio and ~50% with the 1.5:1.0 ratio. Polymerization was practically absent in control experiments carried out in the absense of initiator (but in the presence of DTBP).

Table 1. Homopolymerization of MeVE Using DPE Capped TMPCl/($Ti(OEt)_4$/$TiCl_4$) Initiating System at −80 °C[a]

	[$Ti(OEt)_4$]/[$TiCl_4$]					
	1.5:1.0			1.0:1.0		
Hex/MeCl	conv (%)	M_n	M_w/M_n	conv (%)	M_n	M_w/M_n
			−80 °C			
60/40	8.0	−*	−*	15	−*	−*
40/60	15	−*	−*	19	−*	−*
			−40 °C			
40/60	34	2700	1.1	50	3200	1.06

[a] [TMPCl] = 1×10^{-2} M, [DTBP] = 6×10^{-3} M, [$TiCl_4$] = 4×10^{-2} M, [DPE] = 2×10^{-2} M, [MeVE] = 7.5×10^{-1} M. Reaction time: 180 min. *The polymers were not characterized by GPC.

Scheme 1



The low conversion of MeVE prompted us to find reaction conditions under which high conversions can be obtained. In order to achieve higher polymerization rate, MeCl was replaced with CH_2Cl_2, which allowed us to increase the temperature to 0 °C. In addition, the Lewis acidity was increased, and the 1.0:1.0, 0.8:1.0, and 0.6:1.0 [$Ti(OEt)_4$]/[$TiCl_4$] ratios were studied at three temperatures, at −80, −40, and 0 °C.

At −80 °C the conversion of MeVE after 4 h was only 15%, independently of the [$Ti(OEt)_4$]/[$TiCl_4$] ratios. However, at −40 °C the conversion in 4 h increased to ~50%, and at 0 °C the conversion was complete in 5 h. The conversion versus time plots for all three temperatures and all three [$Ti(OEt)_4$]/[$TiCl_4$] ratios are provided in Figure 1. According to Figure 1, the conversion at any temperature is independent of the [$Ti(OEt)_4$]/[$TiCl_4$] ratios. Two important conclusions can be reached based on the results of Figure 1. The decrease of polymerization rates at −80 and −40 °C (and the limiting conversions) suggests that the growing center concentration decreases during polymerization. Since the ether oxygen is more nucleophilic in PMeVE compared to MeVE, the equilibrium constant of the PMeVE·$TiCl_4$ complex formation is much higher than that of MeVE·$TiCl_4$. Thus, the free Lewis acid concentration and consequently the growing center concentration decrease during polymerization. At higher temperature, however, due to the lower equilibrium constant of complexation, the concentration of free Lewis acid and therefore the polymerization rate (and the limiting conversions) are higher (Scheme 1). Another important conclusion can be reached from the similar rates (and limiting conversions) at different Lewis acidity, indicating similar growing center concentration. This suggests that the equilibrium constant of complexation increases with the increase of Lewis acidity and therefore the decrease in the free Lewis acid concentration is compensated by the increased acidity.

The M_n versus conversion plot is shown in Figure 2 for all three ratios of [$Ti(OEt)_4$]/[$TiCl_4$] at −40 and 0 °C,

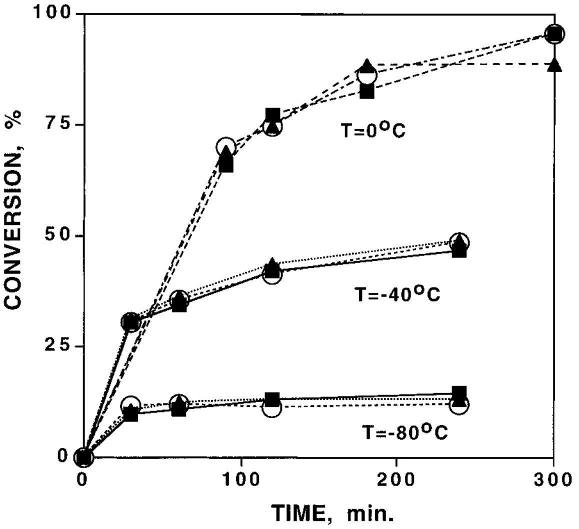


Figure 1. Homopolymerization of MeVE at different temperatures. Reaction conditions: [TMPCl] = 1 × 10^{-2} M, [DTBP] = 3 × 10^{-3} M, [DPE] = 2 × 10^{-2} M, [$TiCl_4$] = 4 × 10^{-2} M, [MeVE] = 1.35 M, [$Ti(OEt)_4$]/[$TiCl_4$] = (■) 1.0:1.0, (▲) 0.8:1.0, (○) 0.6:1.0, solvent CH_2Cl_2/Hex (60/40 v/v).

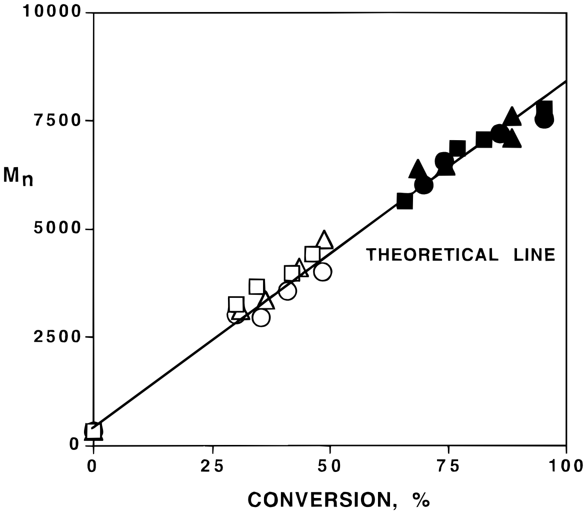


Figure 2. M_n versus conversion in the homopolymerization of MeVE. Reaction conditions: [TMPCl] = 1 × 10^{-2} M, [DTBP] = 3 × 10^{-3} M, [DPE] = 2 × 10^{-2} M, [$TiCl_4$] = 4 × 10^{-2} M, [MeVE] = 1.35 M, [$Ti(OEt)_4$]/[$TiCl_4$] = (□, ■) 1.0:1.0, (△, ▲) 0.8:1.0, (○, ●) l 0.6:1.0, solvent CH_2Cl_2/Hex (60/40 v/v). Open symbols, reaction at −40 °C; filled symbols, reaction at 0 °C.

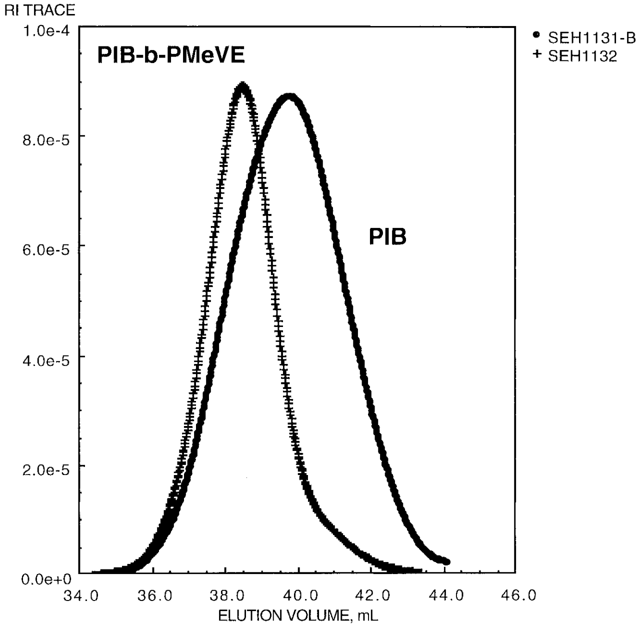


Figure 3. GPC RI traces of the original PIB and the PIB-PMeVE diblock copolymer. Reaction conditions: [TMPCl] = 1.0 × 10^{-2} M, [DPE] = 2.0 × 10^{-2} M, [$nBu_4N^+Ti_2Cl_9^-$] = 1.0 × 10^{-2} M, [$TiCl_4$] = 4.0 × 10^{-2} M, [$Ti(OEt)_4$] = 2.4 × 10^{-2} M, [IB] = 1.41 M, [MeVE] = 1.35 M, solvent system CH_2Cl_2/Hex (60/40v/v), M_{nPIB} = 8300, M_w/M_n = 1.36, $M_{nPIB\text{-}b\text{-}PMeVE}$ = 15 500, M_w/M_n = 1.14.

Table 2. Fractionation of the PIB-PMeVE on a Silica Gel Column[a]

no.	eluent	volume (mL)	Wp_i (g)	ΣWp_i (g)	Wp_i (%)	ΣWp_i (%)	M_n
1	hexanes	50	0.0898	0.0898	5.88	5.88	9000
2	hexanes	100	0.0120	0.1018	0.79	6.67	10000
3	hexanes	150	0.0000	0.1018	0.00	6.67	
4	THF	200	0.1458	0.2476	9.56	16.23	19 000
5	THF	250	0.9590	1.2066	62.86	79.09	15 000
6	THF	300	0.3118	1.5184	20.44	99.53	14 000
7	THF	350	0.0076	1.5260	0.50	100.03	
8	THF	400	0.0000	1.5260	0.00	100.03	
9	THF	450	0.0000	1.5260	0.00	100.03	

[a] Total amount of polymer loaded in the column 1.5257 g. [TMPCl] = 1.0 × 10^{-2} M, [DPE] = 2.0 × 10^{-2} M, [$nBu_4N^+Ti_2Cl_9^-$] = 1.0 × 10^{-2} M, [$TiCl_4$] = 4.0 × 10^{-2} M, [$Ti(OEt)_4$] = 2.4 × 10^{-2} M, [IB] = 1.41 M, [MeVE] = 1.35 M. Solvent system: CH_2Cl_2/Hex (60/40v/v).

Due to the low conversions, the polymers obtained at −80 °C were not characterized. A linear increase of the molecular weight with the conversion proves the absence of chain transfer to monomer. All polymers exhibited narrow molecular weight distribution (M_w/M_n < 1.05).

After the successful homopolymerization of MeVE, a block copolymerization was carried out by sequential addition. Since preliminary experiments indicated that the molecular weight distribution of PIB obtained in the CH_2Cl_2/hexane (60/40 v/v) solvent system is much broader compared to that observed with the CH_3Cl/hexane (60/40 v/v) solvent system, $nBu_4N^+Ti_2Cl_9^-$ was used (in equimolar amounts to the initiator) to obtain PIBs with $M_w/M_n \sim 1.4-1.6$. It is important to point out that block copolymers synthesized in the presence and in the absence of the common ion salt exhibited identical molecular weights, and similar molecular weight distributions and blocking efficiencies (see later). The only effect of the common ion salt was a molecular weight distribution narrowing of PIB, which may be due to the increased exchange rate in the active−dormant chain end equilibrium.

First, living PIB was prepared at −80 °C and capped with DPE. It was followed by the addition of $Ti(OEt)_4$ to reach the [$Ti(OEt)_4$]/[$TiCl_4$] = 0.6:1.0 ratio, and the monomer MeVE was added. After 15 min at −80 °C, the temperature was raised to 0 °C. Complete conversion of MeVE was reached in 5 h. The observed M_ns (M_{nPIB} = 8300, $M_{nPIB-PMeVE}$ = 15 500) were in good agreement with the theoretical M_ns (M_{nPIB} = 7500, $M_{nPIB-PMeVE}$ = 15 000). The GPC RI trace of the diblock and that of the starting PIB are shown in Figure 3. The results of fractionation are provided in Table 2 and Figure 4.

The fractions were characterized by ^1H NMR to determine their composition. Fractions 1 and 2 (Table 2) contained mostly PIB with little or no MeVE content, while fractions 4−7 were pure diblocks. From the weight of the fractions, ~90% blocking efficiency was calculated.

The obtained PIB-PMeVE diblock copolymer with a ~50/50 wt % composition was soluble in methanol, but

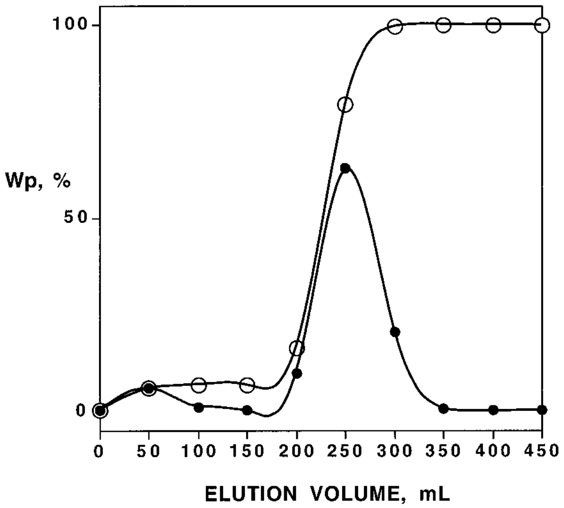


Figure 4. Chromatogram of the fractionation of the diblock on silica gel column. Reaction conditions provided in Table 2.

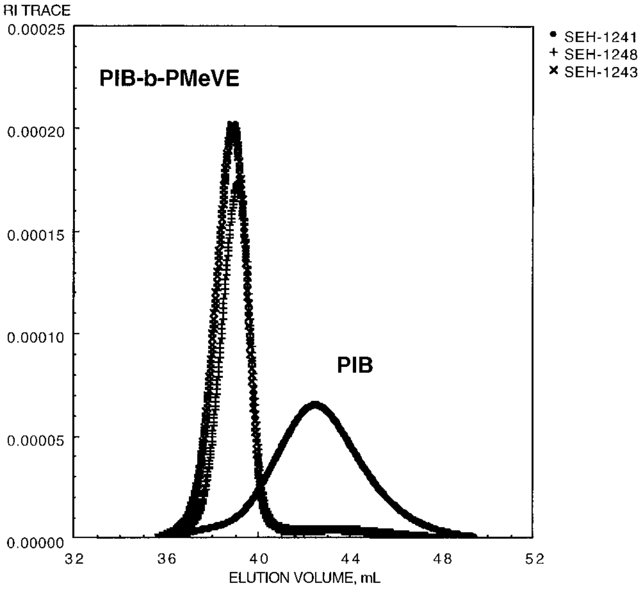


Figure 5. GPC RI traces of the original PIB and the PIB-PMeVE diblock copolymers prepared in the presence and the absence of $[nBu_4N^+Ti_2Cl_9^-] = 4 \times 10^{-3}$ M. Reaction conditions: $[TMPCl] = 4 \times 10^{-3}$ M, $[DTBP] = 6 \times 10^{-3}$ M, $[TiCl_4] = 6.4 \times 10^{-2}$ M, $[DPE] = 8 \times 10^{-3}$ M, $[IB] = 0.32$ M, $[MeVE] = 1.43$ M, $[Ti(OEt)_4] = 6.4 \times 10^{-2}$ M, solvent system CH_2Cl_2/Hex (60/40v/v), $M_{nPIB} = 5700$, $M_w/M_n = 1.6$.

it was insoluble in water. To obtain water-soluble diblock copolymers, we decided to synthesize diblocks with ~20 wt % PIB and ~80 wt % PMeVE. The theoretical segment M_ns were $M_{nPIB} = 5000$ and $M_{nPMeVE} = 20\,000$. The $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ and $0.6{:}1.0$ ratios were used; other polymerization parameters were unchanged.

In agreement with the former experiment, using the $[Ti(OEt)_4]/[TiCl_4] = 0.6{:}1.0$ ratio, ~92% blocking efficiency was obtained. However, with the $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ ratio, the blocking efficiency was unexpectedly low. The GPC chromatogram of the diblock shown in Figure 5 indicates that the crossover efficiency is much lower than 100%. Fractionation of the crude product by column chromatography on silica gel indicated that the blocking efficiency for PIB was only ~70%. ^{1}H NMR analysis of the homoPIB eluted by hexanes revealed the absence of DPE moiety and the presence of chloro end functions. Since routine sampling after DPE capping and before the addition of $Ti(OEt)_4$ verified complete capping, we concluded that the chain ends decapped after the addition of $Ti(OEt)_4$. Since the capping−decapping equilibrium constant is very sensitive to change in temperature,[24] if the crossover is not complete at −80 °C, decapping may also occur when the temperature is raised to 0 °C. Change in the reaction time between $TiCl_4$ and $Ti(OEt)_4$ (15 to 30 min) and longer time allowed for crossover at −80 °C (from 10 min to 4 h), however, did not change the blocking efficiency.

This prompted us to study the effect of the $[Ti(OEt)_4]/[TiCl_4]$ ratio on the capping−decapping equilibrium, and on the rate of crossover at −80 °C. In a series of experiments, after capping PIB with DPE a sample was taken and quenched with methanol to determine the extent of capping. To the rest of the solution $Ti(OEt)_4$ was added, and after 15 min the reaction mixture was quenched with methanol. Following purification of the polymers the end groups were analyzed by ^{1}H NMR. As expected, the PIB was completely capped with DPE before the addition of $Ti(OEt)_4$ (complete disappearance of the peaks at ~1.7 and ~2.0 ppm and appearance of new peaks at ~2.5 and ~3.0 ppm). Capping remained complete after the addition of $Ti(OEt)_4$ when the $[Ti(OEt)_4]/[TiCl_4] = 0.6{:}1.0$ ratio was used. However, using the $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ ratio, a substantial decapping occurred. ^{1}H NMR revealed that only 75% of the PIB remained capped with DPE, while 25% was PIB-Cl.

The crossover rate from the diphenylalkyl cation to MeVE was also studied by quenching the polymerization with methanol at −80 °C, 10 min after the addition of MeVE. Using the $[Ti(OEt)_4]/[TiCl_4] = 0.6{:}1.0$ ratio, complete disappearance of the peaks at ~2.5 and ~3.0 ppm and appearance of new peaks due to the presence of the PMeVE block, at 3.3−3.6 and 1.5−2.0 ppm, indicated that the crossover at −80 °C was fast and complete. Thus raising the temperature to 0 °C simply increases the rate of MeVE homopolymerization. Fast crossover from the DPE capped PIB was also obtained using the $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ ratio; however, as expected, the 25% PIB-Cl remained unreacted. These results clarified why it was not possible to achieve crossover efficiencies higher than 75% with the $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ ratio.

The following rationalization explains the results: The equilibrium constant of the capping reaction is described in:

$$K_1 = \frac{[\mathrm{PIBDPE^+Ti_2Cl_9^-}]}{[\mathrm{PLB^+Ti_2Cl_9^-}][\mathrm{DPE}]} \qquad (1)$$

The equilibrium constant of ionization of PIBCl is described in:

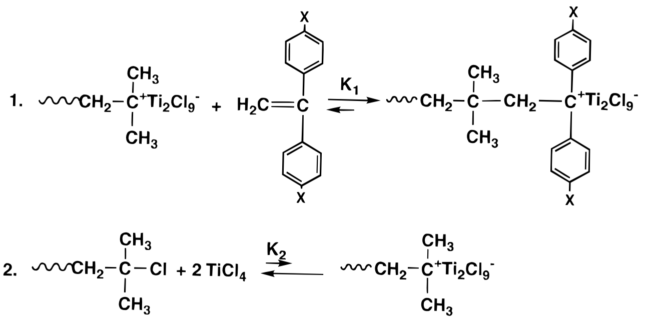
$$K_2 = \frac{[\mathrm{PIB^+Ti_2Cl_9^-}]}{[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2} \qquad (2)$$

It is well-known that $[PIB^+Ti_2Cl_9^-] \ll [PIBCl]$, i.e., K_2 is very small. $[PIB^+Ti_2Cl_9^-]$ can be obtained from K_2 and substituted into eq 1. Rearrangement gives the product of the two equilibrium constants, K_1K_2:

$$K_1K_2 = \frac{[\mathrm{PIBDPE^+Ti_2Cl_9^-}]}{[\mathrm{PIBCl}]}\,\frac{1}{[\mathrm{TiCl_4}]^2[\mathrm{DPE}]} \qquad (3)$$

According to eq 3 the capped/uncapped ratio is determined by K_1, K_2, and the equilibrium concentration of

Scheme 2[a]



[a] When capping with DPE substituents, X are hydrogen atoms. When capping with DTE substituents, X are methyl groups.

the Lewis acid and DPE. Although we have not yet determined K_1K_2 for the CH_2Cl_2/hexanes (60/40 v/v) −80 °C system, from the K_1K_2 value for the CH_3Cl/hexanes (60/40 v/v) −80 °C system ($K_1K_2 = 1.4 \times 10^7$ M^{-3})[24] we estimate K_1K_2 to be at least 5×10^7 M^{-3}. Using the $[TiCl_4] = 6.4 \times 10^{-2}$M and $[DPE]_{eq} = 4.0 \times 10^{-3}$ M concentrations, at equilibrium about 0.1% uncapped PIBCl remains. When $Ti(OEt)_4$ is introduced, ionization of PIBCl and therefore the equilibrium concentration of PIB^+ decrease. (This is supported by the observation that the polymerization of IB is practically absent with the $TMPCl/TiCl_n(OR)_{4-n}$ initiating system, when $n \leq 3$.) With this decrease, due to mass law action, the capping equilibrium will shift and decapping will occur until a new equilibrium is reached. It can be shown that a decrease in K_2 by a factor of 10, even if we neglect the Lewis acid concentration increase, will lead to a new equilibrium where the uncapped PIBCl increases to only ~1%. However, a 250-fold decrease would lead to a new equilibrium where ~25% of chain end is uncapped. Thus the effect of Lewis acidity on the capped/uncapped ratio is rationalized.

With DPE as capping agent it appears that the $[Ti(OEt)_4]/[TiCl_4] = 0.6{:}1.0$ ratio is the most effective for the synthesis of PIB-PMeVE block copolymers. With this ratio, 100% MeVE conversion was reached in 13 h and the solutions remained colorless. With longer time (15−20 h), however, the solutions became strongly colored, from light yellow-brown to dark wine red, indicating decomposition of the chain ends. Using the $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ ratio, the polymerization solution remained colorless even after 20 h.

b. Sequential Block Copolymerization of IB with MeVE Using DTE as a Capping Agent. According to the above rationalization, decapping can be minimized by using capping agents for which K_1 is very high. Higher K_1 is obtained when the diphenyl carbenium ion is better stabilized, i.e., for which ΔH is higher. In agreement with this reasoning a much higher K_1K_2 was obtained for DTE (Scheme 2, X = Me).[24] The capping−decapping equilibrium was investigated at −80 °C by capping PIB with DTE under identical experimental conditions used for DPE capping, followed by the introduction of $Ti(OEt)_4$ to obtain the $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ and 0.6:1.0 ratios. Fifteen minutes later the reactions were quenched with methanol. ^1H NMR analysis of the samples taken before and after the addition of $Ti(OEt)_4$ verified that capping was complete and decapping was absent. The crossover reaction to MeVE was also studied. Samples were quenched with methanol at −80 °C, 10 min after the addition of MeVE, and analyzed by ^1H NMR. Complete disappearance of the peaks at ~2.5 and ~3.0 ppm and appearance of new peaks due to the presence of the PMeVE block at 3.3−3.6 and 1.5−2.0 ppm indicated that the crossover was ~100% at −80 °C.

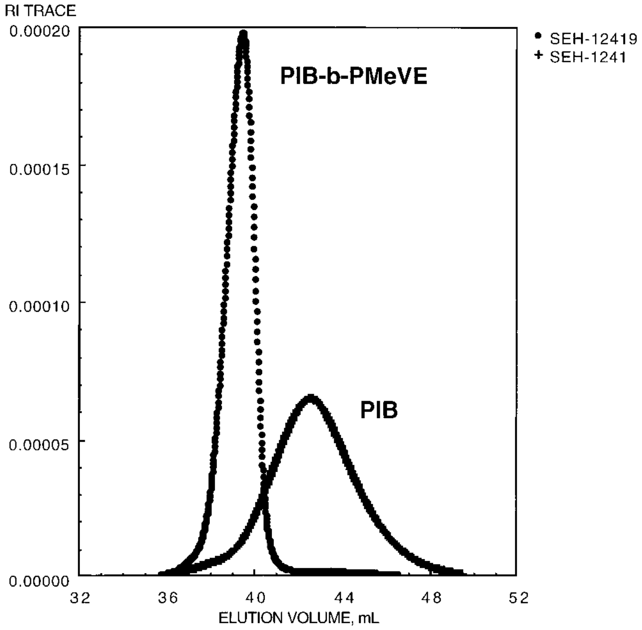


Figure 6. GPC RI traces of the original PIB and the PIB-PMeVE diblock copolymer. Reaction conditions: $[TMPCl] = 4 \times 10^{-3}$ M, $[DTBP] = 6 \times 10^{-3}$ M, $[TiCl_4] = 6.4 \times 10^{-2}$ M, $[DTE] = 8 \times 10^{-3}$ M, [IB] = 0.32 M, [MeVE] = 1.43 M, $[Ti(OEt)_4] = 3.8 \times 10^{-2}$ M, $[nBu_4N^+Ti_2Cl_9^-] = 4 \times 10^{-3}$ M, solvent system CH_2Cl_2/Hex (60/40v/v), $M_{nPIB} = 5700$, $M_w/M_n = 1.6$, $M_{nPIB-b-PMeVE} = 24\,500$, $M_w/M_n = 1.08$.

We proceeded to the synthesis of the diblock with designed blocks of $M_{nPIB} = 5000$ and $M_{nPMeVE} = 20000$. Both $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ and 0.6:1.0 ratios were used. Close to theoretical diblock M_n and narrow molecular weight distributions have been obtained with both $[Ti(OEt)_4]/[TiCl_4] = 1.0{:}1.0$ ($M_n = 25\,500$, $M_w/M_n = 1.1$) and $[Ti(OEt)_4]/[TiCl_4] = 0.6{:}1.0$ ($M_n = 24\,500$, $M_w/M_n = 1.08$) ratios ($M_{nPIB} = 5700$, $M_w/M_n = 1.6$). Using the 1.0:1.0 ratio, the blocking efficiency was found to be ~92%. ^1H NMR analysis of the minute amount of homoPIB separated by column chromatography confirmed the absence of decapping (absence of peaks at ~1.7 and ~2.0 ppm, presence of peaks at 7.0−7.5, 2.5, and 2.3 ppm due to the presence of DTE at the chain end).

Close to ~100% blocking efficiency was obtained when the $[Ti(OEt)_4]/[TiCl_4] = 0.6{:}1.0$ ratio was used. The GPC RI traces of the diblock and the starting PIB are shown in Figure 6. The ^1H NMR of a representative diblock is shown along with the assignments in Figure 7.

c. Characterization of PIB-PMeVE Diblock Copolymers. The purified diblocks were characterized by DSC. The two T_gs (Figure 8) at −64.6 and at −37.9 °C for the 50/50 wt % PIB/PMeVE diblock indicate the presence of two microphases. A sample of homoPMeVE ($M_n = 7500$) prepared under identical conditions exhibited a $T_g = -32.5$ °C, while for homoPIB ($M_n = 9000$), also prepared under the same conditions as in the diblock synthesis, a $T_g = -75.5$ °C was obtained. The T_gs of the homopolymers are close to the values listed in the literature[25] ($T_{gPIB} = -73$ °C and $T_{gPMeVE} = -31$ °C). The two T_gs observed with the diblock are somewhat different, which could be due to partial phase mixing. For the 20/80 w/w PIB/PMeVE diblock the two T_gs are closer to the values for the two homopolymers, possibly indicating better phase separation.

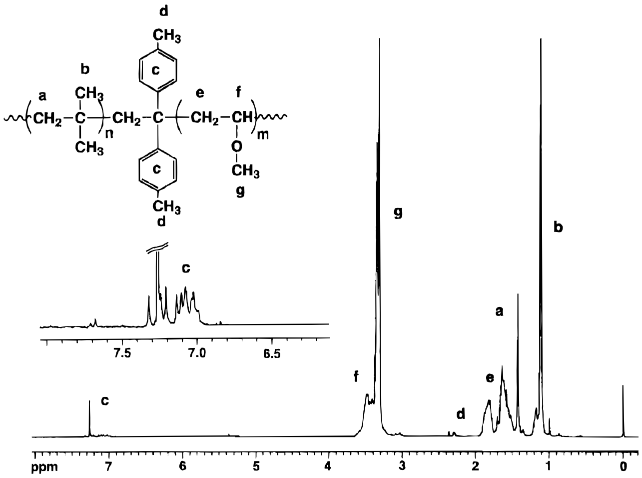


Figure 7. The ^{1}H NMR spectrum of a representative diblock copolymer along with the peak assignments. Solvent $CDCl_3$. The peak cut at 7.25 ppm in the inset corresponds to the traces of $CHCl_3$ that are present in $CDCl_3$ (99.8% D, Cambridge Isotope Laboratories, CIL).

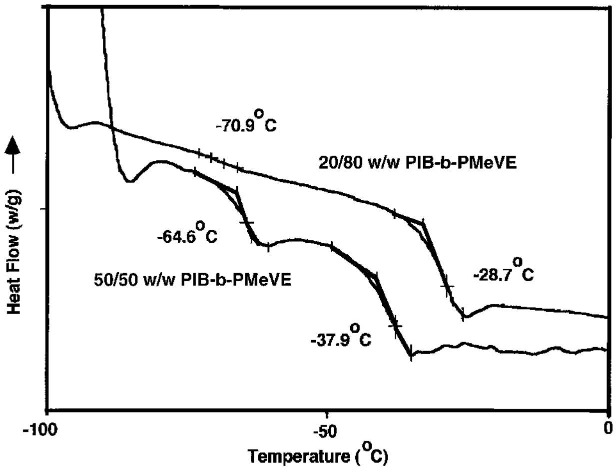


Figure 8. DSC scans of PIB-PMeVE diblock copolymers.

The diblock with 50/50 wt % PIB/PMeVE swelled, but was not soluble in deionized water. In contrast the diblock with 20/80 wt % PIB/PMeVE was soluble in deionized water. The solution (at 0.4% w/v) was reminiscent of a soap solution. The addition of 0.07 g of pump oil to 6.0 mL of this solution and stirring resulted in a stable emulsion having an average particle size of ~200 nm.

The surface tension of aqueous solutions of the diblock at different concentrations was measured at 25 °C. From the plot of surface tension versus concentration (Figure 9), the critical micelle concentration (CMC) of the diblock was determined to be ~2.3×10^{-5} M, typical of nonionic surfactants.

Conclusions

The living polymerization of MeVE was achieved using a designed $TiCl_n(OEt)_{4-n}$ coinitiator at 0 °C, the highest reported to date. The design was based on reverting complexation of the Lewis acid and PMeVE, by increasing the temperature to 0 °C, while still preventing chain end decomposition. Well-defined PIB-PMeVE diblock copolymers with controlled molecular weight and narrow molecular weight distribution ($M_w/M_n < 1.1$) have also been obtained, with the virtual absence of homopolymer contaminants. Efficient crossover was obtained by capping the living PIB chain ends with DPE or DTE followed by moderating the Lewis acidity by the introduction of $Ti(OEt)_4$. While both DPE and DTE may be used under controlled conditions, the use of DTE is preferred, since the high equilibrium constant of capping with DTE prevents substantial decapping when the Lewis acidity is decreased.

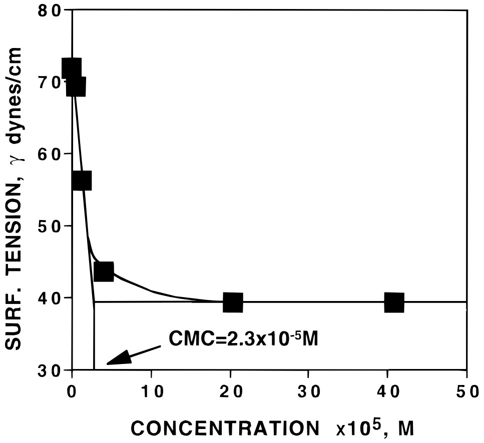


Figure 9. Surface tension versus concentration plot at 25 °C. Critical micelle concentration = 2.3×10^{-5} M.

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