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Novel Epoxide Initiators for the Carbocationic Polymerization of Isobutylene

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Summary: We recently reported the synthesis of polyisobutylene (PIB) via direct initiation by epoxycyclohexyl isobutyl polyhedral oligomeric silsesquioxane (POSS®) (Figure 1) in conjunction with titanium tetrachloride ($TiCl_4$). This system successfully initiated the living carbocationic polymerization of isobutylene (IB) in hexane/methyl chloride (Hx/MeCl -60/40, v/v) at $T = -80\ ^\circ C$, yielding an asymmetric telechelic PIB with one POSS® cage head group and one *tert*-Cl end group.[1] This paper will discuss IB polymerizations initiated by 1,2-epoxycyclohexane and *bis*[3,4-(epoxycyclohexyl) ethyl]-tetramethyl-disiloxane, in conjunction with $TiCl_4$.

Keywords: functionalization of polymers; living cationic polymerization; polyisobutylene; telechelics; siloxane

Introduction

Functional PIBs are of great interest due to their potential applications as macro-initiators, compatibilizers, surface modifiers, etc. Direct functionalization by the use of either a functional initiator or a functional terminator is the simplest and most convenient method in living polymerizations[2,3] though it is limited by the availability of both functional initiators and functional terminators for carbocationic polymerizations. In living carbocationic polymerization of IB, the modification of chloro-functional PIBs is the most frequently used method to obtain functional PIBs; however, it involves a number of steps[4] and is rather cumbersome. In 2000, Puskas et al.[5] discovered that substituted epoxides, in conjunction with $TiCl_4$, initiate the living carbocationic polymerization of IB to yield a telechelic PIB carrying an *α-primary* OH and an *ω-tertiary* Cl group in an one-step polymerization. Later, Kim and Faust[3] reported that a series of chlorosilyl functional initiators were used to obtain PIBs carrying mono-, di-, and tri-chlorosilyl head-group and a *tert*-chloro end group. Recently, the synthesis of telechelic PIB via direct initiation by epoxycyclohexyl isobutyl POSS® with $TiCl_4$ as reported by our group.[1] The incorporation of one epoxy-POSS® per polymer chain was demonstrated by ^1H nuclear magnetic resonance (NMR) spectroscopy. The POSS®-PIB samples showed aggregates by light scattering and transmission electron microscopy (TEM) analysis.

This paper will present other novel initiators for the synthesis of functional PIBs by the use of 1,2-epoxycyclohexane and *bis*[3,4-(epoxycyclohexyl)ethyl]-tetramethyl-disiloxane, in conjunction with $TiCl_4$, and discuss the initiation mechanism.

Experimental Part

Materials

1,2-Epoxycyclohexane (Fluka, ≥ 98%, GC) was vacuum distilled prior to use. *bis*[3,4-(epoxycyclohexyl)ethyl]tetramethyl-disiloxane (SIB1092.0, Gelest Inc.) was used as received. MeCl (99%) and IB (99%) were supplied by LANXESS Inc., Canada and were dried by passing the gases over drying columns packed with $CaCl_2$ and BaO before condensing them from the gas phase. Hx (Aldrich) was dried by distillation

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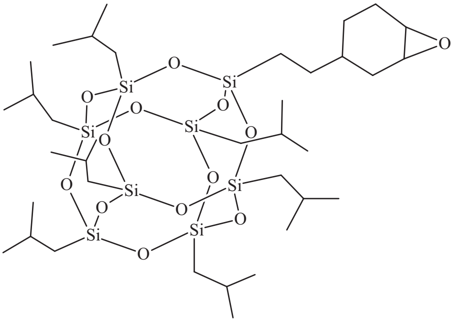


Figure 1.
Epoxycyclohexylisobutyl POSS®.

from Na/Benzophenone prior to use. $TiCl_4$ (99.9% Aldrich), di-*t*-butylpyridine (D*t*BP, Aldrich), d-chloroform (d, 98.9%, Cambridge Isotope Laboratories) and methanol (MeOH, EMD) were used as received.

Polymerization Procedures

Polymerizations were carried out in an MBraun LabMaster 130 glove box under dry nitrogen atmosphere; moisture <1 ppm and oxygen <5 ppm contents were continuously monitored and maintained. A 250 mL three-neck round bottom flask equipped with an overhead stirrer was immersed in a Hx bath maintained at −80 °C using coils through which liquid nitrogen was passed for cooling. The flask was charged with the solvent mixture of Hx/MeCl (60/40, v/v) followed by D*t*BP, the initiator and IB. The reaction was started by the addition of pre-chilled $TiCl_4$ solution. The colorless reaction mixture turned yellow upon the addition of $TiCl_4$ and became colorless again with white solid residue upon termination. Exact reaction conditions are specified in the text, table and figure captions. The reactions were terminated by the addition of MeOH/NaOH. After the evaporation of all volatiles, the samples were dissolved in hexane and washed with distilled water until they were neutral, dried over $MgSO_4$ and filtered. The PIB was recovered by precipitation into methanol. MeOH was expected to dissolve polyether side products, if any. Samples were dried in a vacuum oven until reaching a constant weight. Final conversions were determined gravimetrically.

Polymer Characterization

Real-time fourier transform infrared spectroscopy (FTIR) monitoring was performed during the polymer synthesis using an attenuated total reflectance (ATR) probe (REMSPEC Inc.) interfaced with a Bio-Rad FTS 175C, later replaced by a Varian 3100-Excalibur Series FTIR unit (source cable), and a MID-IR fiber optic detector module (a liquid nitrogen cooled 0.5×0.5 mm MCT detector, receiver cable). The fiber optic cables with a probe were fed into the glove box through a port and immersed into the reactor, which was a three-necked, round-bottom flask equipped with an overhead stirrer. The reactor was immersed in a hexane bath maintained at the specified reaction temperature using either a Flexi-Cool chiller (FTS Systems) or coils through which liquid nitrogen was fed. For best signal output the attached cable ends were aligned manually. Optimum signal/noise ratios (>10) were obtained when the center burst maximum (negative peak on the on-screen display) was about −5 to −7 V at a sensitivity (amplifier gain) between 1 and 3 within the ±10 V signal range. To cool the infrared probe to the reaction temperature, the sensor was kept above the surface of the solvent/solvent mixture for 15 min before immersing it into the cold liquid. Background scans of the solvents and D*t*BP, proton trap, were taken at a resolution of 8 cm^{-1}.

NMR analysis was performed in deuterated chloroform ($CDCl_3$). Spectra were recorded on a Varian NMRS 500 spectrometer (acquisition parameters: number of transients = 64, acquisition time = 2.0486 sec, relaxation delay = 10 sec, receiver gain = 20, temperature = 30 °C.).

Molecular weights (MW) and molecular weight distributions (MWD) of polymers were determined by Size Exclusion Chromatography (SEC) using a Waters system equipped with six Styragel-HR columns (HR0.5, HR1, HR3, HR4, HR5 and HR6) thermostated at 35 °C, a Dawn EOS 18 angle laser light scattering (MALLS) detector (Wyatt Technology), an Optilab DSP refractive index (RI) detector (Wyatt Technology) thermostated at 40 °C, a 2487 Dual Absorbance UV detector (Waters), a quasi-elastic light scattering (QELS) detector (Wyatt Technology), and a Viscostar viscosity detector (Wyatt Technology).

Tetrahydrofuran (THF), freshly distilled from CaH_2, was employed as the mobile phase and was delivered at 1 mL/min. ASTRA (Wyatt Technology) was used to obtain absolute MW data with $dn/dc = 0.108$ for PIB in THF or assuming 100% recovery on the columns.

TEM imaging was performed using a Philips Tecnai 12 (120 kV) electron microscope. For film casting, a carbon-coated copper TEM grid was floated over a bath of boiling water, and a droplet of the polymer solution was carefully dropped over the floating grid. The TEM grid with the polymer film was first kept in a vacuum oven overnight at room temperature. After that, staining was performed on the grid using the vapors of aqueous ruthenium tetraoxide (RuO_4) solution (0.67 wt%) for 30 min. Finally, the grid was again kept in vacuum overnight to remove toxic vapors before TEM imaging.

Results and Discussion

IB Polymerization with 1,2-epoxycyclohexane/$TiCl_4$

The polymerization conditions are given in the caption of Figure 2, which shows the ^1H NMR spectrum of the product. PIB formation is demonstrated by the presence of characteristic PIB methyl and methylene protons at 1.1 and 1.4 ppm. The signals of the $-\mathbf{CH_3}CCl$ and $-\mathbf{CH_2}C(CH_3)_2Cl$ protons at 1.70 and 1.98, respectively, were present in a ratio of 6/2 as expected. The $-\mathbf{CH}OH$ proton of the *sec*-OH head group at 3.13–3.20 ppm split due to vicinal coupling of protons attached to the neighboring carbons.

The ratio of the signal intensities of the proton of the hydroxyl head group ($-\mathbf{CH}OH$, **e**) to the *gem*-dimethyl protons of the *tert*-chloride end groups ($-\mathbf{CH_3}CCl$, **c**) confirmed one hydroxy functionality per polymer chain. Thus the polymerization yielded a PIB containing *α-secondary* OH and *ω-tertiary* Cl chain ends with $M_n = 11{,}000$ g/mol, and $M_w/M_n = 1.05$ by SEC ($I_{eff} = 48\%$; $I_{eff} = M_{n,theo}/M_n$ where M_n and $M_{n,theo}$ were measured and theoretically expected (g PIB/mol initiator) number-average molecular weights, respectively). $M_n = 12{,}000$ g/mol ($I_{eff} = 44\%$) was obtained

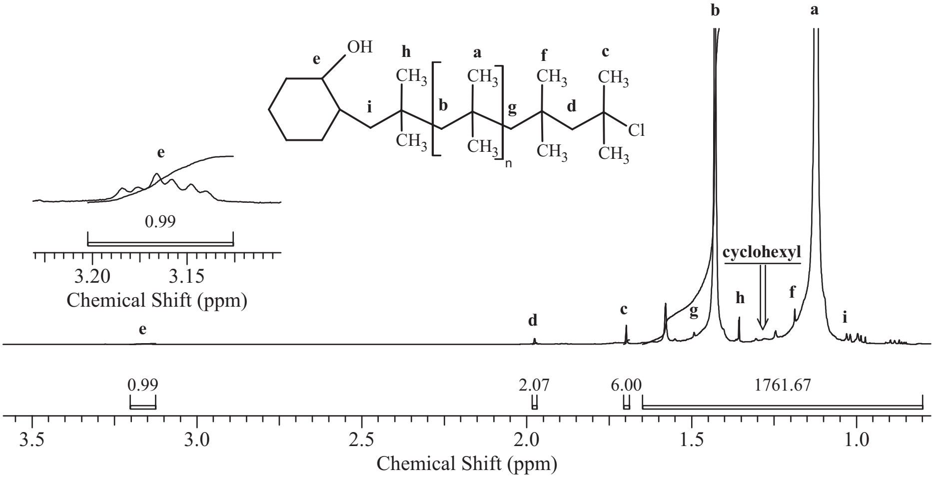
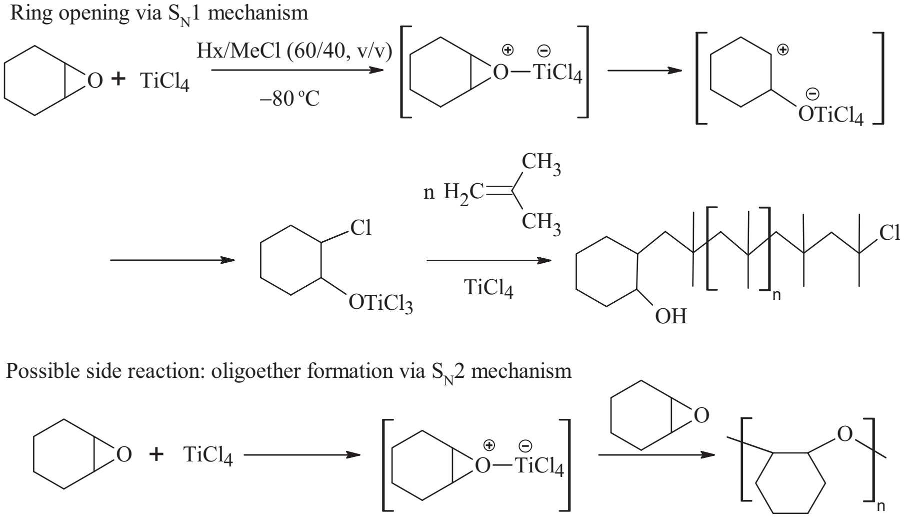


Figure 2.
^1H NMR spectrum of PIB synthesized by 1,2-epoxycyclohexane/$TiCl_4$. $[\text{1,2-epoxycyclohexane}]_0 = 0.004$ M, $[IB] = 1.7$ M, $[TiCl_4] = 0.057$ M, $[DtBP] = 0.007$ M, Hx/MeCl (60/40, v/v), $T = -80$ °C, $t = 24$ min, conversion = 22%.



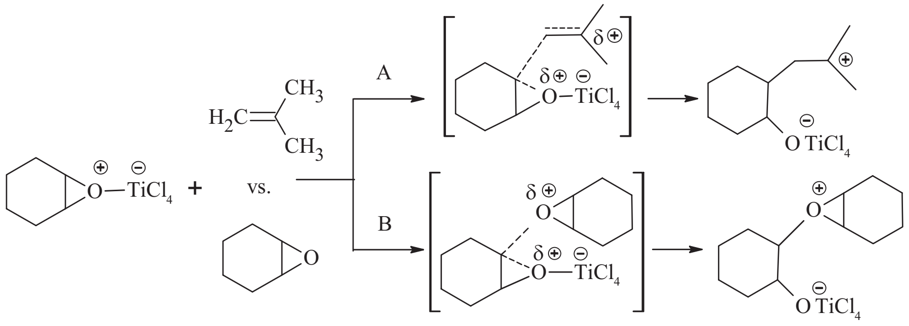
Scheme 1.
S_N1 vs. S_N2 mechanism of the ring-opening of 1,2-epoxycyclohexane with $TiCl_4$ in the presence of IB.

by ^1H NMR from the ratio of the intensities of the *gem*-dimethyl protons of the *tert*-chloride end groups (c) to the intensity of the main chain protons (8) at 0.70–1.65 ppm.

Based on the mechanism of initiation of IB polymerizations by epoxide/$TiCl_4$ systems,[5] from 1,2-epoxycyclohexane a *secondary* carbocation would form as shown in Scheme 1.

The initiation of IB polymerization from epoxycyclohexane that yields a *secondary* carbocation was thought to be less likely compared to an epoxide that yields a *tertiary* carbocation, for example 1,2-epoxy-2,4,4-trimethylpentane, 2,3-epoxy-2,4,4-trimethylpentane or α-methylstyrene epoxide.[5] However, the I_{eff} with 1,2-epoxycyclohexane was higher than with those initiators. This led us to the proposal of a modified mechanism, as given in Scheme 2.

The competitive reactions in Scheme 2 both proceed by S_N2 mechanism. In Pathway A, the oxonium ion reacts with the nucleophilic IB, forming a *tertiary* carbocation. Pathway B represents polyether formation by the reaction of the oxonium ion with another epoxy ring. Based on the $I_{eff} = 48\%$ found experimentally, the two pathways have similar probability. Indeed, the enthalpy difference (ΔH, calculated



Scheme 2.
The proposed modified mechanism of initiation of IB polymerization by 1,2-epoxycyclohexane/$TiCl_4$.

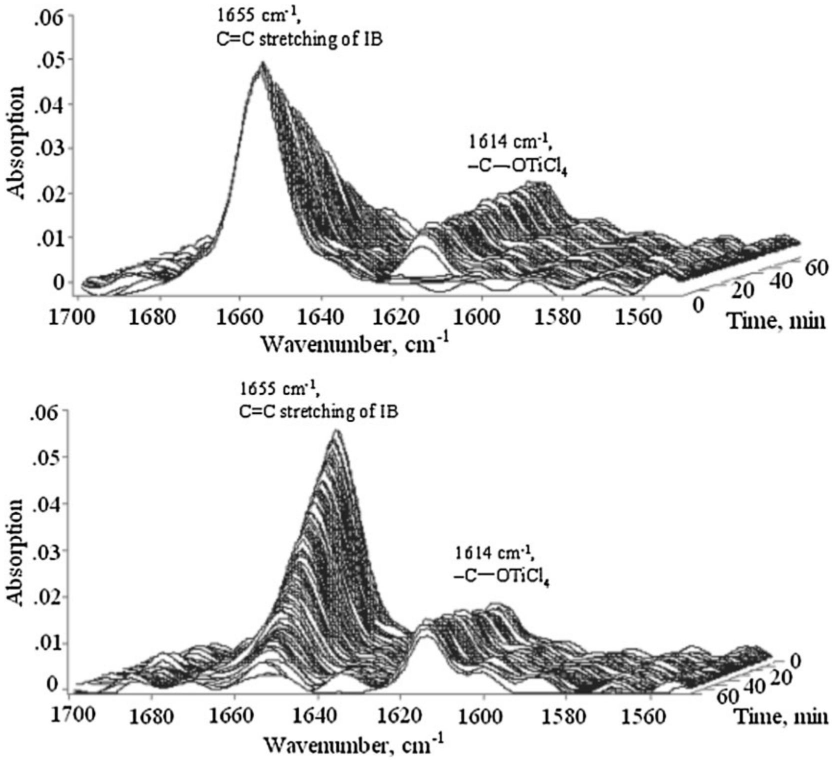


Figure 3.
Real-time FTIR monitoring of IB polymerization initiated by SIB1092.0/$TiCl_4$ with an ATR probe: 1550–1700 cm^{-1} region. (SIB_121207) [SIB1092.0] = 0.004 M, [IB] = 2.1 M, [D*t*BP] = 0.007 M, [$TiCl_4$] = 0.069 M, Hx/MeCl (60/40, v/v), T = −80 °C.

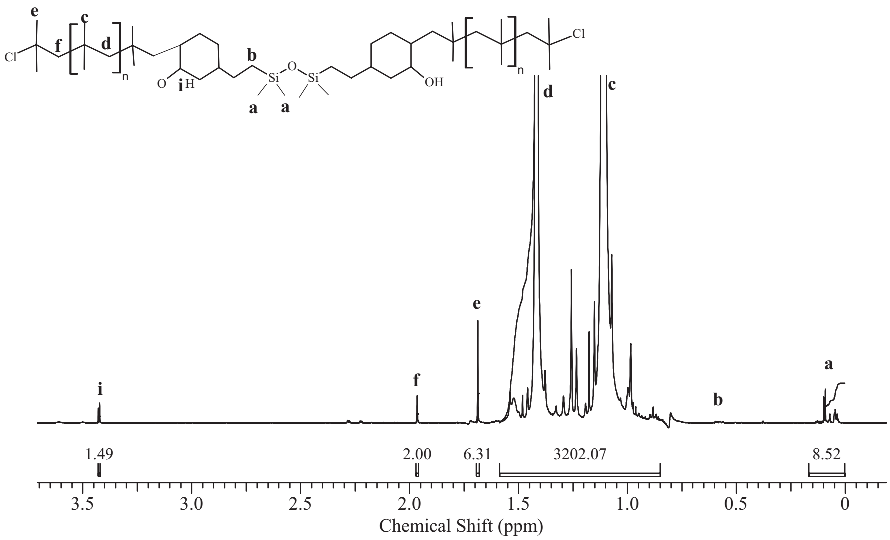


Figure 4.
^1H NMR spectrum of a PIB synthesized by the SIB1092.0/$TiCl_4$ system (SIB_121207). First aliquot.

Table 1.
SEC analysis of PIB synthesized by SIB1092.0/$TiCl_4$ (SIB_121207).

Aliquots	Time (min)	Conv. (%)	$M_{n,\ theor.}$ (g/mol)	M_n by SEC (g/mol)		M_w/M_n	I_{eff} (%)
				dn/dc = 0.108	100% mass recovery		
1	15	5	1,700	22,300*			8*
2	30	39	12,300	50,400	56,200	1.16	25
3	45	61	19,200	77,200	82,600	1.16	25

*by ^1H NMR

using density functional theory (DFT) with B3LYP/6-31G(d) theory level, courtesy of D. Modarelli UA) was found to be only 1.32 kcal.mol^{-1}, slightly favoring Pathway B. This agrees with the experimental observation. Additional support is the fact that I_{eff} was found to be influenced by [IB] concentration; higher the [IB] led to higher I_{eff} values.[6] More investigations are needed to verify the initiating mechanism.

IB Polymerization by *Bis*[3,4-(epoxycyclohexyl)ethyl]-tetramethyl-disiloxane/$TiCl_4$

This siloxane epoxide that possesses two epoxycyclohexyl groups (SIB1092.0) was also investigated as an initiator for IB polymerizations. The reaction was monitored by *in situ* FTIR by using an ATR probe. Upon the addition of $TiCl_4$, a new band was observed at 1614 cm^{-1}, which was assigned to $-COTiCl_4$ group (Figure 3). This band stayed steady until the end of the polymerization. A gradual decrease of the C=C stretching (1655 cm^{-1}) of IB demonstrated monomer conversion.

The ^1H NMR spectrum (Figure 4) of the product demonstrated the incorporation of SIB1092.0 into the PIB chains by the presence of the proton signals of methyl groups attached to the Si at 0.05 ppm. The ring-opening of the epoxide was confirmed by the disappearance of $-C\mathbf{H}O$ protons at 3.12–1.16 ppm. In addition, a new chemical shift appeared at 3.42–3.43 ppm which is assigned to the $-C\mathbf{H}$ proton attached to the $-OH$.

The ratio of the integral of the $-C\mathbf{H_3}$ protons of the *tert*-Cl chain ends (**e**) to the integral of the $-C\mathbf{H_3}$ protons attached to Si (**a**), and that of the $-C\mathbf{H}$ proton attached to the $-OH$ group (**i**) indicated that the average number of PIB chains per SIB1092.0 molecule was 1.4 and 1.3, respectively. This means that more than 50% of the polymer had only one "arm" (no bidirectional growth). The SEC results are summarized in Table 1.

The SEC traces showed a high molecular weight shoulder for both samples (Figure 5). Also a very small amount of high MW polymer was observed with peak MW of 4.0×10^6 g/mol (Aliquot 1) and

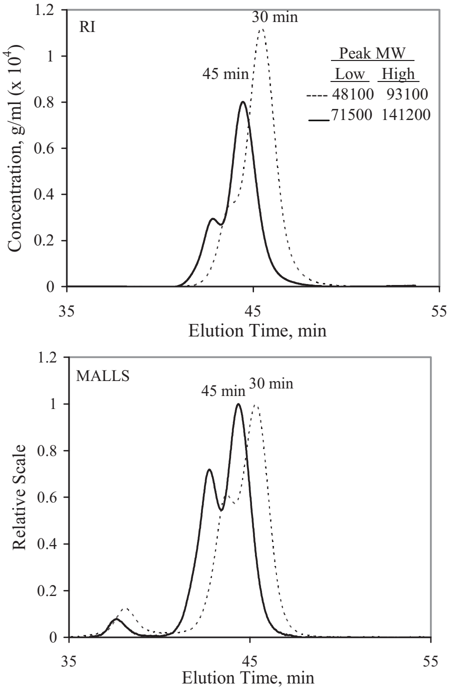


Figure 5.
SEC traces of the last two samples of PIB synthesized by SIB1092.0/$TiCl_4$ by RI and MALLS (SIB_121207).

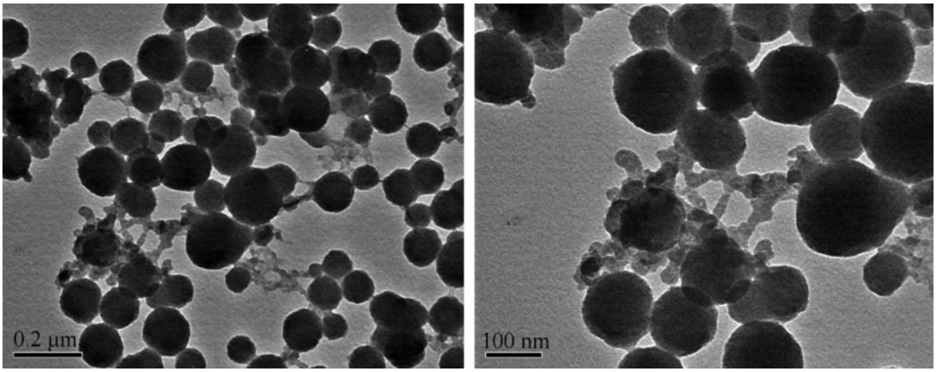


Figure 6.
TEM images of SIB_121207.

2.0×10^6 g/mol (Aliquot 2), only detectable by light scattering. Bimodal distribution indicates the presence of two polymer chain populations, with the higher peak MW being approximately twice as much as the lower peak MW. Most likely one population contains one PIB with one arm while the other one has two PIB arms per initiator molecule.

The final product, examined using TEM, showed a tendency to form aggregates (Figure 6). These aggregates were more dispersed than those of POSS®-PIB.[1] Most of the aggregates were found to have a size of ~100 nm, which is about 8 times larger than the radius of gyration of the PIB (SIB_121207, $R_g \sim 12.2$ nm).

Conclusion

In summary, 1,2-epoxycyclohexane initiated IB polymerization in conjunction with $TiCl_4$ and yielded 48% initiator efficiency. Based on the results presented here, a new initiation mechanism based on two competitive S_N2 pathways was proposed. With the difunctional cyclohexane epoxide initiator, *bis*[3,4-(epoxycyclohexyl)ethyl]tetramethyldisiloxane yielded ~1.4 PIB arms per initiator, and formed well-defined aggregates.

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