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Synthesis of Poly(cyclohexyl vinyl ether-*b*-isobutylene-*b*-cyclohexyl vinyl ether) Triblock Copolymer by Living Cationic Sequential Copolymerization

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Summary

The living cationic polymerization of cyclohexyl vinyl ether (CHVE) and sequential block copolymerization of isobutylene with CHVE were carried out by the so-called capping-tuning technique in hexanes/CH_3Cl solvent mixtures at –80 ºC. It involves capping the initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), or the living polyisobutylene (PIB) chain end with 1,1-ditolylethylene in the presence of titanium(IV) ($TiCl_4$), followed by fine-tuning of the Lewis acidity with the addition of titanium(IV) isopropoxide ($Ti(OIp)_4$) to match the reactivity of CHVE. Well-defined PCHVE, PIB-*b*-PCHVE and PCHVE-*b*-PIB-*b*-PCHVE with predesigned molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$) were thus prepared with $[Ti(OIp)_4]/[TiCl_4]$ ratios of 1.6–1.8. Differential scanning calorimetry of the triblock copolymers showed two T_gs (–62 ºC for PIB and 61 ºC for PCHVE) suggesting a microphas-separated morphology of the triblock copolymers and the potential use of them as thermoplastic elastomers.

Introduction

ABA type linear triblock copolymers consisting of polyisobutylene (PIB) rubbery center block and glassy outer blocks (e.g. polystyrene) are novel thermoplastic elastomers (TPEs) with improved thermal and oxidative stability compared to diene based TPEs. Styrenic TPEs, however, exhibit high melt viscosity due to the highly segregated structure even in the melt. Another incentive for the synthesis of new PIB based TPEs is their excellent biocompatibility and biostability. Most recently poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymer has been employed as a polymer drug carrier for the TAXUS™ Express2™ Paclitaxel-Eluting Coronary Stent system (Boston Scientific Corp.) because of its superior anti-inflammatory properties in the vascular system. By replacing polystyrene with other hard segments the drug release rate may be tailored.

Besides polystyrenes [1-6], poly(alkyl vinyl ether)s are attractive as end segments as poly(alkyl vinyl ether-*b*-isobutylene-*b*-alkyl vinyl ether) triblock copolymers could be prepared in a one-pot process by living cationic sequential block copolymerization. Most poly(alkyl vinyl ether)s exhibit glass transition temperatures (T_gs) far below

0 ºC, but some poly(alkyl vinyl ether)s, especially with a bulky alkyl group, exhibit T_gs well above room temperature and may be utilized as hard segments in PIB based TPEs. For example, poly(*tert*-butyl vinyl ether-*b*-isobutylene-*b*-*tert*-butyl vinyl ether) triblock copolymers have been prepared, which exhibited typical TPE properties [7]. The glass transition temperature of poly(cyclohexyl vinyl ether) (PCHVE) is also higher than room temperature [8,9], indicating that this polymer may be used as the hard segment in PIB based TPEs. Recently a series of vinyl ethers with tricyclic pendant groups were polymerized by living cationic polymerization [10]. The polymers exhibited T_gs as high as 100 ºC. So far the highest T_g was reported for poly(neopentyl vinyl ether) (T_g = 151 ºC) [8], but the monomer is not available commercially.

In living cationic polymerization, sequential block copolymerization is difficult when the reactivity of the two monomers is quite different. When the second monomer is much more reactive than the first monomer, the crossover is usually slow compared to propagation resulting in low crossover efficiency. The solution to this problem is the so-called capping-tuning technique, which involves capping the living chain end with a non-homopolymerizable monomer such as diarylethylenes or furan derivatives followed by lowering the Lewis acidity to match the reactivity of the second monomer [11].

In a recent study on the block copolymerization of isobutylene (IB) with *tert*-butyl vinyl ether (*t*BVE) by the capping-tuning technique, 1,1-ditolylethylene (DTE) was employed as the capping agent and titanium(IV) isopropoxide ($Ti(OIp)_4$) was used to tune the Lewis acidity of titanium(IV) chloride ($TiCl_4$) [7]. By simply tuning the ratio of $[Ti(OIp)_4]/[TiCl_4]$, the Lewis acidity could be fine-tuned in a wide range without retro-addition of DTE and as a result, well-defined PIB-*b*-P*t*BVE could be prepared by this simple one-pot method.

In this work, the living cationic polymerization of cyclohexyl vinyl ether (CHVE) and its block copolymerization with isobutylene was studied employing DTE as the capping agent and $Ti(OIp)_4$ as the Lewis acidity tuning agent.

Experimental

Materials

Cyclohexyl vinyl ether (98 %, Aldrich) was washed with water, dried over KOH overnight, vacuum distilled over CaH_2. The purified CHVE was stored at -20 ºC under nitrogen. The syntheses of 2-chloro-2,4,4-trimethylpentane (TMPCl) [12], 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*-BuDiCumCl) [13] and 1,1-ditoylethylene (DTE) [14] have been described. Titanium(IV) chloride ($TiCl_4$) (99.9 %, Aldrich), 2,6-di-*tert*-buylpyridine (DTBP) (97 %, Aldrich), and Titanium(IV) isopropoxide (97 %, Aldrich) were used as received. CH_3Cl (MeCl) and isobutylene (IB) were dried by passing the gas through in-line gas purifier columns packed with BaO/Drierite and condensed at –80 ºC prior to polymerization. Hexanes (Hex) was rendered olefin free by refluxing it over sulfuric acid (95-98 %, VWR) for 48 hours. It was washed first with 10 % KOH aqueous solution and then with distilled water until neutral, and was stored over $NaSO_4$ for at least 24 hours. It was distilled before use after refluxing over CaH_2 overnight.

Polymerization procedures

All polymerizations were carried out under a dry nitrogen atmosphere in an MBraun 150-M glove box (Innovative Technology Inc.) using Hex/MeCl (60/40 v/v) solvent mixtures. The total volume of the polymerization system was ~25 mL, and 75 mL test tubes were used as reactors. In a representative procedure IB, initiated by TMPCl in conjunction with $TiCl_4$, was polymerized for 1 hour in the presence of DTBP as a proton trap. Next DTE was charged to cap the living PIB chain end. One hour later when capping was completed, $Ti(OIp)_4$ was added, followed by addition of CHVE ~5 minutes thereafter. Finally the reactions were quenched with prechilled methanol at predetermined time intervals. The reaction mixtures were poured into excess 10 % ammoniacal methanol. The polymers were purifed by repeated dissolution in Hex and precipitation in methanol, and then dried in vacuo for 24 hours.

In the homopolymerization of CHVE, TMPCl was directly capped with DTE, followed by sequential introduction of $Ti(OIp)_4$ and CHVE. In synthesis of PCHVE-*b*-PIB-*b*-PCHVE triblock copolymers, *t*BuDiCumCl was used as the initiator instead of TMPCl.

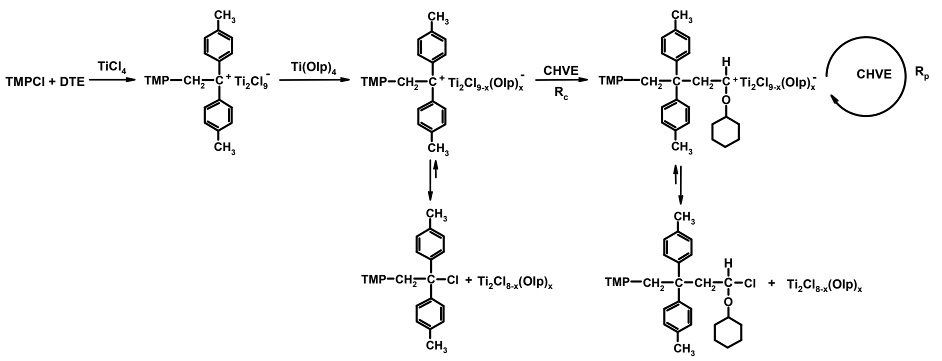
Characterizations

NMR spectroscopy was carried out on a Bruker 250 or 500 MHz instrument. Molecular weights were measured with a size exclusion chromatography system consisting of a Model 510 HPLC pump, a Model 486 tunable UV/visible detector (Waters), a Model 250 RI/viscosity detector (Viscotek) and five ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5 and 100 Å. Samples were eluted in THF at a flow rate of 1 mL/min and analyzed using Viscotek version 3.0 universal and conventional calibration software. Refractive index increments (dn/dc) used for absolute molecular weight determinations were calculated from the individual dn/dc values of PIB (0.11 mL/g) and PCHVE (0.101 mL/g), as determined by a laser interferometer (Optilab, Wyatt Technology Inc.) in THF, based on their relative composition. The glass transition temperatures of the triblock copolymers were determined by a DuPont 910 differential scanning calorimeter. The samples were heated at 20 ºC/min under nitrogen and the second thermogram was recorded.

Results and discussion

Living polymerization of CHVE

Since CHVE and *t*BVE have similar reactivity in cationic polymerization [15], experimentation started with a similar procedure found successful in the living cationic polymerization of *tert*-butyl vinyl ether (*t*BVE) (hexanes/CH_3Cl = 60/40 v/v; [2,6-di-*tert*-butylpyridine (DTBP)] = 0.004 M; [$TiCl_4$] = 0.036 M; [2-chloro-2,4,4-trimethylpentane (TMPCl)] = 0.002 M; [DTE] = 0.004 M; [$Ti(OIp)_4$]/[$TiCl_4$] = 1.6; [CHVE] = 0.522 M) [7]. Thus as shown in Scheme 1, TMPCl was capped with DTE in the presence of $TiCl_4$, and $Ti(OIp)_4$ was added to reach [$Ti(OIp)_4$]/[$TiCl_4$] = 1.6 to decrease the Lewis acidity. After 5 minutes CHVE was charged into the reactor. Under these conditions the conversion of CHVE was complete in ~30 minutes. It was found earlier that under the same conditions, the polymerization of *t*BVE was completed in 40 min [7], which corroborated the similar reactivity of *t*BVE and CHVE.



Scheme 1. Capping-tuning process for homopolymerization of CHVE.

The linear semilogarithmic kinetic plot of $\ln([M]_0/[M])$ vs. time shows that the polymerization proceeded without termination (Figure 1). According to the linear increase of M_n with conversion, which is close to the theoretical line assuming the formation of one polymer chain per initiator molecule, chain transfer was not detected (Figure 2**)**. However, the living nature of polymerization does not guarantee narrow molecular weight distributions. When the conversion was below 30 % the molecular weight distribution (MWD) was broad. Narrow MWD (PDI ≤ 1.1) was obtained only at high conversion (> 70 %), which suggested that the Lewis acidity was still too high at a $[Ti(OIp)_4]/[TiCl_4] = 1.6$, resulting in high concentration of reactive species and very rapid polymerization.

Better polymerization control may be achieved by further decreasing the Lewis acidity to slow down the polymerization. Thus, the next series of polymerizations were conducted at $[Ti(OIp)_4]/[TiCl_4] = 1.8$. As expected, the polymerization was slower and completed in 3 h. The polymerization also exhibited a living character as shown by the linear plots of $\ln([M]_0/[M])$ vs. time (Figure 1) and M_n vs. conversion (Figure 2). The polymerization was better controlled, as the MWD was unimodal even at a low conversion of 6 % and very narrow MWDs (PDI < 1.1) were obtained at conversions higher than ~40 %.

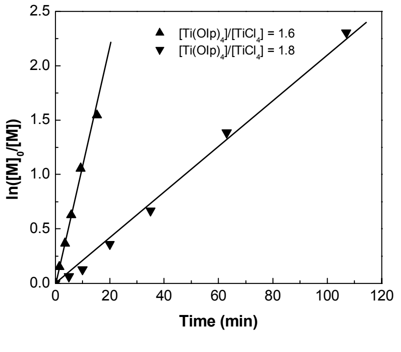


Figure 1. $\ln([M]_0/[M])$ vs time plots for homopolymerization of CHVE at different $[Ti(OIp)_4]/[TiCl_4]$ ratios.

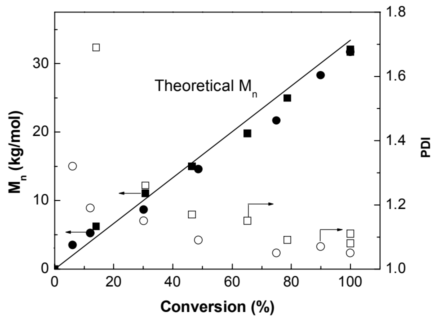


Figure 2. M_n and M_w/M_n vs conversion plots for polymerization of CHVE at different $[Ti(OIp)_4]/[TiCl_4]$ ratios: $[Ti(OIp)_4]/[TiCl_4]$ = (■, □) 1.6, (●, ○) 1.8.

Block copolymerization of IB with CHVE

The homopolymerization is essentially the model block polymerization, since TMPCl in conjunction with $TiCl_4$ is equivalent to the living dimeric IB. As a result, the block copolymerization of IB with CHVE can be carried out with the same procedure except that the living PIB instead of the TMPCl is capped with DTE. Block copolymerization was carried out in Hex/CH_3Cl = 60/40 v/v at –80 ºC using $[Ti(OIp)_4]/[TiCl_4]$ ratios varied in the range of 1.2–2.0 under the following conditions: [TMPCl] = 0.002 M; [IB] = 0.1 M; $[TiCl_4]$ = 0.036 M; [DTBP] = 0.004 M; [DTE] = 0.004 M; [CHVE] = 0.191 M. All samples were quenched 2 hours after the addition of CHVE. The results are shown in Table 1. For all samples 100 % crossover efficiency was obtained, as indicated by the smooth shift of GPC traces of the diblock copolymers from that of the starting PIB (Figure 3). Structural analysis of the block copolymers by ^1H NMR spectroscopy also proved the 100 % crossover efficiency for all $[Ti(OIp)_4]/[TiCl_4]$ ratios, as DTE-capped homo-PIB carrying the methoxy end group was not detected at ~2.5 and ~3.0 ppm (Figure 4) [7,16].

Table 1. Effect of $[Ti(OIp)_4]/[TiCl_4]$ ratio on block copolymerization.

Sample	$[Ti(OIp)_4]/[TiCl_4]$	Conversion of CHVE (%)	Crossover efficiency (%)	M_w/M_n
A	1.2	99	100	1.54
B	1.4	100	100	1.15
C	1.6	99	100	1.08
D	1.8	94	100	1.06
E	2.0	75	100	1.07

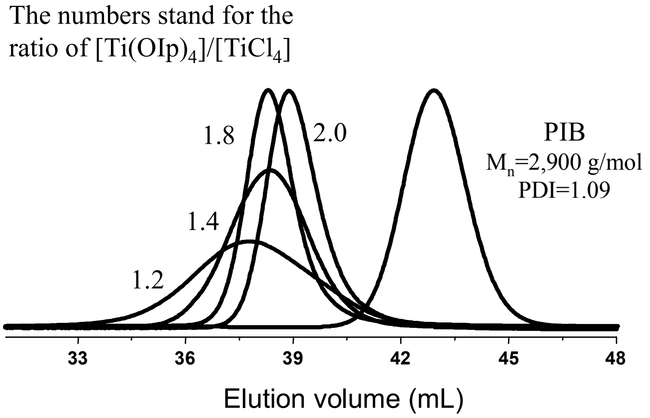


Figure 3. GPC traces of PIB-*b*-PCHVE block copolymers and starting PIB synthesized at different [Ti(OIp)$_4$]/[TiCl$_4$] ratios.

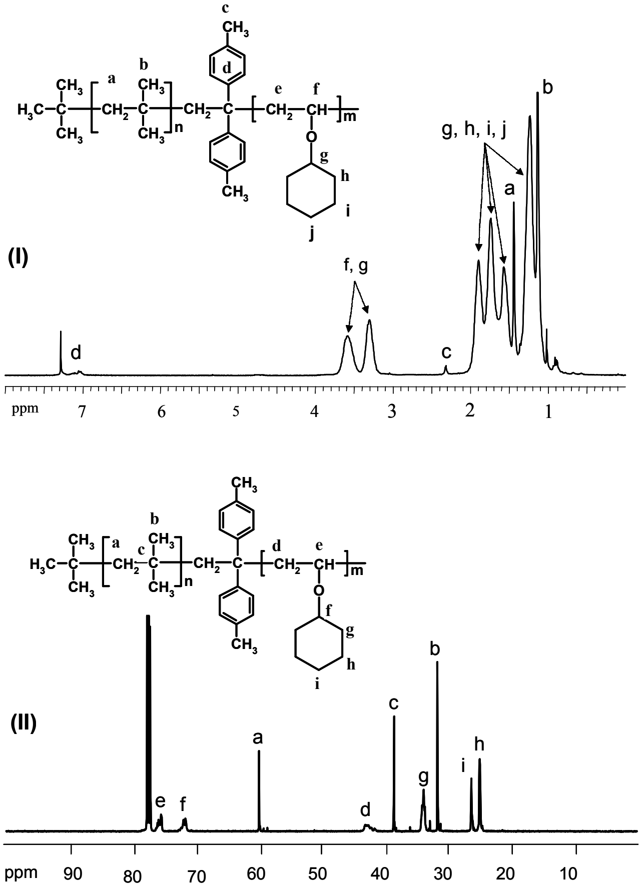


Figure 4. (I) ^{1}H and (II) ^{13}C NMR spectra of a PIB-*b*-CHVE copolymer in $CDCl_3$.

At a high [Ti(OIp)$_4$]/[TiCl$_4$] ratio of 1.2, however, the block copolymer exhibited a PDI of 1.54, indicating poor control of polymerization. Well-defined PIB-*b*-PCHVE diblock copolymers with narrow molecular weight distributions were prepared at [Ti(OIp)$_4$]/[TiCl$_4$] = 1.4–2.0. However, at [Ti(OIp)$_4$]/[TiCl$_4$] > 1.8 quantitative conversion was not reached in 2 h, indicating slow polymerization of CHVE.

Triblock copolymers were synthesized by the capping-tuning technique using 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*-BuDiCumCl) as a difunctional initiator. A [Ti(OIp)$_4$]/[TiCl$_4$] ratio of 1.7 was adopted for both good control over MWD and reasonable polymerization rate. The GPC traces of a representative PCHVE-*b*-PIB-*b*-PCHVE triblock copolymer (14,600-72,000-14,600) and the PIB precursor are shown in Figure 5. The smooth shift of the traces and narrow MWDs indicate that well-defined triblock copolymers were prepared. A DSC scan of the representative triblock copolymer is shown in Figure 6. The two glass transitions at –62 °C and 61 °C suggest a microphase separated morphology of the triblock copolymer with a PCHVE wt % of 29. The T_g of the PCHVE segment is lower than that of P*t*BVE segment (T_g = 74 °C) in P*t*BVE-*b*-PIB-*b*-P*t*BVE [7], but higher than room temperature. The stretchy material may be another useful PIB-based TPE with poly(alkyl vinyl ether) as side segments.

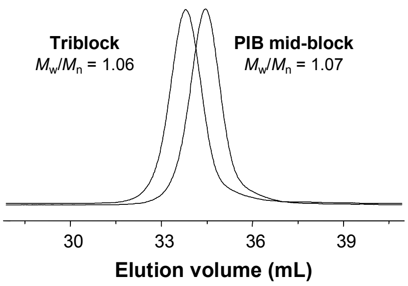


Figure 5. GPC traces of PCHVE-*b*-PIB-*b*-PCHVE triblock copolymer (molecular weight 14,600-72,000-14,600) and starting PIB mid-block.

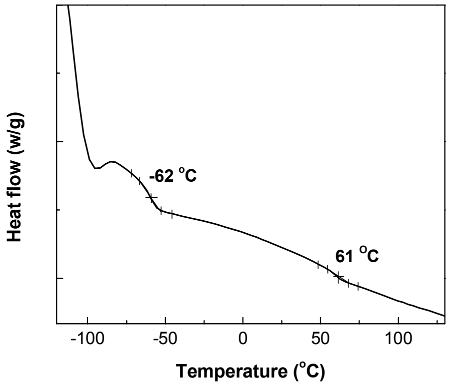


Figure 6. DSC scan of a representative PCHVE-*b*-PIB-*b*-PCHVE triblock copolymer (molecular weight 14,600-72,000-14,600).

Conclusions

Well-defined PCHVE, PIB-*b*-PCHVE and PCHVE-*b*-PIB-*b*-PCHVE with predesigned molecular weights and narrow molecular weight distribution ($M_w/M_n < 1.1$) were prepared, employing the so-called capping-tuning technique which involves capping the initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), or the living polyisobutylene (PIB) chain end with 1,1-ditolylethylene, followed by fine-tuning of the Lewis acidity with the addition of titanium(IV) isopropoxide ($Ti(OIp)_4$). CHVE was found to be slightly more reactive than *t*BVE in cationic polymerization under identical conditions. The two T_gs of the PCHVE-*b*-PIB-*b*-PCHVE triblock copolymers suggested the microphase-separated morphologies and the possible application as thermoplastic elastomers.

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