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STRUCTURAL CHARACTERIZATION OF POLY(ϵ -CAPROLACTONE) AND POLY(ϵ -CAPROLACTONE-*b*-ISOBUTYLENE-*b*- ϵ -CAPROLACTONE) BLOCK COPOLYMERS BY MALDI-TOF MASS SPECTROMETRY

R. F. Storey^a; L. Bryan Brister^a; John W. Sherman^a

^a University of Southern Mississippi, School of Polymers and High Performance Materials, Hattiesburg, MS, U.S.A.

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STRUCTURAL CHARACTERIZATION OF POLY(ϵ -CAPROLACTONE) AND POLY(ϵ -CAPROLACTONE-*b*-ISOBUTYLENE- *b*- ϵ -CAPROLACTONE) BLOCK COPOLYMERS BY MALDI-TOF MASS SPECTROMETRY

R. F. Storey,* L. Bryan Brister, and John W. Sherman

University of Southern Mississippi, School of Polymers and High
Performance Materials, Hattiesburg, MS 39406-0076

ABSTRACT

Poly(ϵ -caprolactone) (PCL) and PCL-polyisobutylene-PCL (PCL-PIB-PCL) block copolymers were synthesized in anhydrous toluene by in situ conversion of 2-methyl-1-propanol (2M1P) and α,ω -dihydroxy PIB, respectively, to the corresponding aluminum alkoxide by reaction with a stoichiometric amount of triethylaluminum (TEA) followed by the addition of ϵ -caprolactone. Structural characterization of 2M1P-initiated PCL by gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry (MS) demonstrated the presence of cyclic oligomers, which are produced by intramolecular transesterification reactions that become significant at high monomer conversions. A minor fraction of chains bearing carboxylic acid termini was also observed in the MALDI-TOF mass spectrum; however, carboxylic acid chain ends could not be detected by ^{13}C NMR analysis. Thus, the likely origin of the carboxylic acid termini is fragmentation of the initiator residue from the chain end during MALDI-TOF analysis. For PCL-PIB-PCL block copolymers, two different α,ω -telechelic PIB diols were used as macroinitiators, one derived from allyl and one from isopropenyl terminated PIB. Terminal olefins were converted to primary alcohols via regioselective hydroboration followed by alkaline hydrogen peroxide oxidation. After reaction with ϵ -caprolactone, formation of a block copolymer

*Corresponding author.

was evidenced by a shift of the polymer peak to lower elution volume in GPC analysis. Block copolymers possessed molecular weight distributions ≤ 1.4 , and molecular weights of the PCI blocks calculated from GPC were in excellent agreement with those found using MALDI-TOF MS. Structural analysis indicated that the PCI end blocks were severed from the crude block copolymer during MS analysis, for both allyl- and isopropenyl-derived materials. For allyl-derived materials the PCI blocks were found to predominantly carry a C₂ residue at the point of detachment of the PIB block; however, the isopropenyl-derived block copolymers showed a complex mixture of different residues suggesting a complex fragmentation mechanism during loss of the PIB block.

Key Words: MALDI-TOF mass spectrometry; Polyisobutylene; Poly(ϵ -caprolactone); Block copolymer.

INTRODUCTION

Matrix-assisted laser desorption ionization–time of flight (MALDI-TOF) mass spectroscopy (MS) is a relatively newly developed soft-ionization technique that allows for desorption and ionization of large macromolecules (1, 2). It was initially developed for analysis of biopolymers such as proteins (3–5), oligonucleotides (6–8), and polysaccharides (9,10). Recent advances in the application of MALDI-TOF MS to synthetic polymers with narrow molecular weight (MW) distributions have allowed for the determination of MW and molecular weight distribution (MWD), and identification of polymer end groups (11–15). Characterization of end groups within a homologous series of polymer molecules yields valuable information regarding polymerization mechanism and is one of the greater advantages afforded by MALDI-TOF MS. However, successful analysis of synthetic polymers requires complete dispersion of the analyte within a suitable matrix; thus, sample preparation is critical.

Unfortunately, application of MALDI-TOF MS to aliphatic hydrocarbon polymers has met with a significant degree of difficulty (16) due primarily to a lack of ionizable sites along saturated hydrocarbon polymer chains. For example, polyethylene is not amenable to this type of analysis (16), and likewise we have been frustrated in attempts to analyze polyisobutylene (PIB) by this technique. Conversely, heteroatom-containing synthetic polymers inherently possess ionizable sites, and their analysis by MALDI-TOF MS has been more easily achieved. For example, a very successful technique for analysis of poly(ϵ -caprolactone) (PCI) by MALDI-TOF MS has recently been developed in our laboratory (17). Because the technique proved successful for homo-PCI, we theorized that PIB-PCI block copolymers could be analyzed in a similar manner, where the presence of the PCI block would facilitate MALDI-TOF analysis. Accordingly, linear A-B-A block copolymers of the type PCI-PIB-PCI were synthesized and analyzed by MALDI-TOF MS.

EXPERIMENTAL

Materials

5-*tert*-Butyl-1,3-di(2-chloro-2-propyl)benzene (bDCC) was prepared from 5-*tert*-butyl-isophthalic acid (Amoco Chemical Co.) through esterification with methanol followed by a Grignard reaction to form the tertiary alcohol, which was subsequently reacted with HCl using previously described procedures (18,19). Hexane (Hex) was freshly distilled from CaH₂ before use. Isobutylene (IB) and methyl chloride (MeCl) (BOC gases) were dried by passing the gaseous material through a column packed with CaSO₄ and molecular sieves. TiCl₄ (99.9%, packaged under nitrogen in SureSeal bottles), 2,4-lutidine (99%, 2,4-dimethylpyridine, DMP), allyltrimethylsilane (99%, ATMS), hydrogen peroxide (30 wt.-% in H₂O), triethylaluminum (1.9 M in toluene, TEA), 9-borabicyclo[3.3.1]nonane (0.5 M in tetrahydrofuran, 9-BBN), anhydrous toluene, tetrahydrofuran, anhydrous 2-methyl-1-propanol (99%, 2M1P), and methanol were used as received from Aldrich Chemical Co. ϵ -Caprolactone monomer (Union Carbide) was freshly distilled from CaH₂ under reduced pressure before use.

Polymer Synthesis

Table 1 identifies the various polymer samples synthesized and lists results of MW characterization.

2M1P-Initiated PCI

Polymerization of ϵ -caprolactone from a 2M1P-derived aluminum alkoxide was carried out under dry nitrogen in a glove box in anhydrous toluene at 25°C. The synthetic procedure used to create sample PCI-1 was as follows: 0.73 mL of a 1.9 M solution of TEA (1.4×10^{-3} mol TEA) in anhydrous toluene was charged to a 100-mL round-bottom flask equipped with overhead mechanical stirrer. The

Table 1. Poly(ϵ -caprolactone) and Poly(ϵ -caprolactone-*b*-isobutylene-*b*- ϵ -caprolactone) Block Copolymers Synthesized

Sample	Type	Initiator	M_n (GPC) (g/mol)	MWD (GPC)	M_p (MALDI-TOF) (g/mol)
PCI-1	Homopolymer	2M1P	2,450	1.3	2,500
PCI-2	Homopolymer	2M1P	3,800	1.2	
BPCI-1	Block copolymer	PIB Diol 1	14,400	1.4	2,200
BPCI-2	Block copolymer	PIB Diol 2	15,600	1.5	3,800

PIB Diol 1: $M_n = 10,000$ g/mol, MWD = 1.1 (GPC); derived from allyl-terminated PIB.
 PIB Diol 2: $M_n = 7,000$ g/mol, MWD = 1.2 (GPC); derived from isopropenyl-terminated PIB.

TEA was diluted by addition of 4 mL anhydrous toluene and this mixture was chilled to -80°C . Aluminum alkoxide formation was begun by the dropwise addition of 0.1 g (1.4×10^{-3} mol) 2M1P, prechilled to -80°C , to the TEA/toluene solution with stirring. The solution was allowed to react for 65 min before being removed from the cold bath and warmed to 25°C . After 1 h at 25°C , a solution consisting of 3.42 mL (3.1×10^{-2} mol) ϵ -caprolactone in 25 mL anhydrous toluene was charged to the TEA/toluene solution. Polymerization was allowed to proceed for 3 h, and was then quenched by pouring the reactor contents into vigorously stirring MeOH containing 30 mL of 0.5 N aqueous HCl.

Solvents were allowed to evaporate overnight and the remaining polymer was dissolved in MeCl_2 . This solution was washed three times with de-ionized water (DIH_2O) and then dried over MgSO_4 . The MgSO_4 was subsequently removed by filtration, and the MeCl_2 was removed by rotary evaporation. The semicrystalline PCl homopolymer was dried in a vacuum oven at 50°C for a period of 24 hs before subsequent analysis.

Synthesis of α,ω -Diallyl PIB (PIB 1)

Polymerizations of IB were carried out at -80°C in a dry box using dry 1,000 mL three-necked, round-bottomed flasks equipped with overhead mechanical stirrers. Synthesis of difunctional PIB 1 (10,000 g/mol) was as follows: to a 1,000 mL round-bottomed flask were charged sequentially 1.5 g bDCC (5.22×10^{-3} mol), 334 mL MeCl, 502 mL hexane, 72 mL IB (0.91 mol), and 0.26 mL DMP (2.26×10^{-3} mol). The mixture was stirred for 30 min to ensure thermal equilibrium before commencing polymerization with the rapid injection of 11.7 mL of TiCl_4 (0.107 mol, neat and at room temperature). After 10 min reaction time, 8.3 mL allyltrimethylsilane (5.22×10^{-2} mol) was charged to the reactor. After an additional 5 minute reaction time, 60 mL prechilled MeOH was added to the reaction vessel to neutralize the remaining coinitiator. Polymer cleanup and recovery are described below. ^1H NMR analysis of the product revealed exclusively allyl end groups with a number average functionality of 2.0.

Synthesis of α,ω -Di-*tert*-Chloride PIB (PIB 2)

Difunctional PIB 2 (7000 g/mol) was synthesized at -80°C as follows: to a 1,000 mL round-bottomed flask were charged sequentially 1.64 g bDCC (5.71×10^{-3} mol), 252 mL MeCl, 378 mL hexane, 54.2 mL IB (0.69 mol), and 0.197 mL DMP (1.71×10^{-3} mol). The mixture was stirred for 30 min to ensure thermal equilibrium, and then polymerization was initiated by the rapid injection of 12.74 mL TiCl_4 (0.116 mol, neat and at room temperature). Polymerization was allowed to proceed for 10 min before termination by injection of 30 mL anhydrous methanol.

PIB Clean-Up and Recovery

Reactors were removed from the dry box and allowed to stand open to the atmosphere overnight to allow for solvent evaporation and slow precipitation of the PIB from the methanol. The methanol was then decanted, and the PIB was redissolved in a minimum amount of hexane. The hexane/PIB solution was washed repeatedly with methanol and then dried with MgSO_4 . The MgSO_4 was removed by filtration, and the hexane was removed by rotary evaporation. The PIB was then brought to constant weight in a vacuum oven at 50°C .

Dehydrochlorination of PIB 2

PIB 2 was dehydrochlorinated according to the method developed by Kennedy *et al.* (20). ^1H NMR analysis of the product revealed exclusively isopropenyl (methyl vinylidene) end groups with a number average functionality of 2.0 after dehydrochlorination.

Synthesis of α,ω -Dihydroxy PIB (PIB Diols) Primary Alcohol Macro-Initiators

PIB diols were produced by the regioselective hydroboration of a terminally unsaturated PIB followed by alkaline hydrogen peroxide oxidation. A representative hydroboration/oxidation procedure was as follows: 22.19 g of the isopropenyl terminated PIB was dissolved in 750 mL anhydrous THF. This solution was added dropwise to 19.4 mL of a 0.5 M solution of 9-BBN (9.68×10^{-3} mol 9-BBN) in anhydrous THF. The mixture was allowed to react for 5 h. A solution of 0.387 g NaOH in 129 mL DIH_2O was then charged to the reactor, followed immediately by 43.88 g of a 30 wt.-% $\text{H}_2\text{O}_2/\text{DIH}_2\text{O}$ solution. This was allowed to react for an additional 2 h before the addition of 250 mL hexane followed by saturation of the aqueous phase with potassium carbonate. The aqueous layer was removed, and the polymer was washed four times with 500 mL of an 80/20 MeOH/ DIH_2O solution, four times with a 50/50 MeOH/ DIH_2O solution, and finally, six times with pure DIH_2O . The hexane/HO-PIB-OH solution was dried with MgSO_4 , followed by filtration and removal of the hexane by rotary evaporation. The product, PIB 2 Diol, was brought to constant weight under vacuum for several days at room temperature. ^1H NMR analysis indicated a number average functionality of 2.0. PIB 1 Diol was produced simply by substitution of the isopropenyl terminated PIB with the allyl-terminated PIB and adjusting the molar ratio of reactants accordingly, based on MW of the starting olefin.

Synthesis of PCI-PIB-PCI Block Copolymers (BPCI)

A representative polymerization procedure was as follows: 4.06 g of PIB 1 Diol (4.06×10^{-4} mol) was dissolved in 70 mL toluene. In a separate flask, $8.93 \times$

10^{-4} mol TEA was dissolved in 1 mL toluene. Both solutions were cooled to -80°C before dropwise addition of the PIB/toluene solution to the TEA/toluene with vigorous stirring. A mineral oil bubbler was attached to the reaction vessel, and reaction progress was monitored by observing ethane gas evolution. Once ethane evolution ceased, the reaction was warmed to room temperature and allowed to stand for an additional hour.

Blocking of ϵ -caprolactone was affected by direct addition to the preformed PIB-alkoxide of a solution comprised of 1.75 mL (0.016 mol) ϵ -caprolactone and 12.25 mL anhydrous toluene. Reaction was allowed to proceed for 3 h before termination was affected by pouring the reactor contents into 150 mL of MeOH, which had been acidified by the addition of several drops of concentrated aqueous HCl. Solvents were then allowed to evaporate, resulting in slow precipitation of the block copolymers from MeOH. The MeOH was decanted and the remaining polymers were dissolved in a minimum amount of MeCl_2 . The resulting solution was washed four times with DIH_2O , dried over MgSO_4 , filtered, and then vacuum stripped. Block copolymers were freed of solvents under vacuum at 50°C for a period of 24 h before subsequent analysis.

Isopropenyl-derived PCI-PIB-PCI was produced in a similar manner from PIB Diol 2. Specific reaction conditions are given in the appropriate figure caption.

Gel Permeation Chromatography (GPC)

MW and MWD were determined using a GPC system consisting of an Alcott model 728 autosampler, a Waters model 510 solvent delivery system, a Waters model 410 differential refractometer (RI detector), a Waters model 484 tunable ultraviolet detector operating at 256 nm, a Wyatt Technology miniDAWN[®] on-line multiangle laser light scattering (MALLS) detector, and two Polymer Laboratories 5- μ mixed-D columns thermostated to 30°C . Tetrahydrofuran (THF), freshly distilled from CaH_2 , was used as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 4 mg/mL with an injection loop of 111 μL . MWs of block copolymers given in Table 1 are absolute MWs determined by MALLS using a dn/dc value calculated from the RI detector response and assuming 100% mass recovery through the columns. Conversely, absolute MWs of PIB homopolymer were determined from MALLS by using the known dn/dc for PIB in THF of 0.11 mL/g.

¹³Carbon Magnetic Resonance Spectroscopy (¹³C NMR)

Spectra were obtained on a 300 MHz Bruker AC-300 spectrometer using 5-mm outside diameter tubes. Sample concentrations were 20–25% (w/v) in chloroform-*d* containing 0.03% (v/v) TMS as an internal reference (0 ppm).

MALDI-TOF MS

A PerSeptive Biosystems Voyager-RP MALDI-TOF Biospectrometry Workstation equipped with 1.3-meter vertical flight tube, tunable two-stage ion source, nitrogen laser operating at 337 nm with a 3 ns pulse delay, dual differential turbomolecular pump for ultra-high vacuum, and positive ion detection was used to analyze both homo-PCI as well as PCI-PIB-PCI block copolymers. All samples were dissolved in THF, freshly distilled from CaH₂, to a final concentration of 8 mg/mL. Separately, a THF solution of 2,5-dihydroxybenzoic acid (DHBA) (40 mg/mL), used as matrix material, was prepared; a 1.5 μL sample of a 1:1 mixture of block copolymer/matrix solution was applied to a polished gold target plate and allowed to air dry immediately before analysis. Each MALDI spectrum was the average of 256 laser shots.

RESULTS AND DISCUSSION

Control Experiments in the Absence of Initiator

Control experiments were conducted in the absence of any added alcohol; the polymerization procedure was identical to the 2M1P-initiated PCI polymerization except that the alcohol was not present. In line with previous reports from other laboratories (21), we were able to confirm that direct initiation of ε-caprolactone does not occur in the presence of TEA. Further, the conventionally dried solvents used for this study were suitably dry to prevent moisture initiation of the caprolactone. Thus, any formed polymer must arise from purposefully added alcohol.

2M1P-Initiated PCI

Before using the PIB diol macro-initiators, ε-caprolactone was initiated from anhydrous 2-methyl-1-propanol to provide homo-PCI for analysis by ¹³C NMR and MALDI-TOF MS. This particular alcohol was selected due to its structural similarity to the end group of PIB Diol 2. The generalized synthetic scheme is illustrated in Figure 1. GPC analysis of the resulting material (Fig. 2) revealed a number-average MW (M_n) = 2450 g/mol and a somewhat broad MWD of 1.3. A minor, low MW contaminant was also observed as a small peak at an elution volume of ~18 mL. The MS obtained by MALDI-TOF analysis (Fig. 3) revealed a primary homologous distribution (I) centered ~2,500 g/mol, which is in good agreement with the GPC results. Thus, distribution I was assigned to the target molecules carrying a 2M1P initiator fragment at one end and a hydroxyl group at the other end (see Fig. 1). A secondary distribution (II) with much lower MW was also observed in the MS.

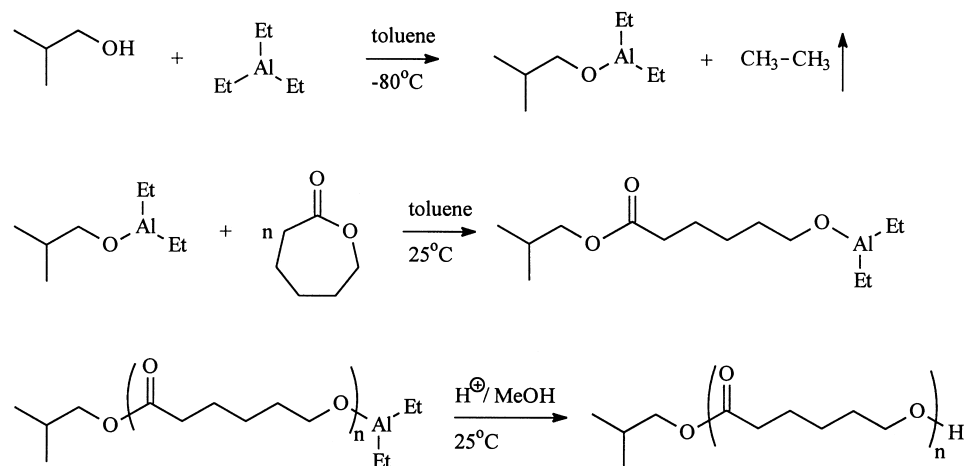


Figure 1. Generalized synthetic scheme for the synthesis of poly(ϵ -caprolactone) from 2-methyl-1-propanol (2M1P).

Figure 4 shows an expansion of the MALDI-TOF spectrum within the range of overlap of the two distributions. Peaks within each individual distribution are separated by exactly 114 g/mol, i.e., the MW of an individual ϵ -caprolactone repeat unit. The mass difference between the two distributions is 74 g/mol, exactly the MW of the 2M1P initiator. Thus, distribution II comprises homologues that contain no initiator fragment and is assigned to cyclic oligomers arising from

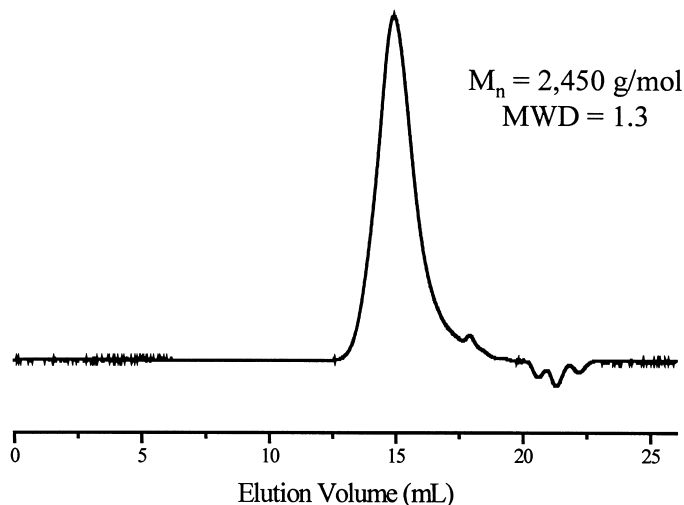


Figure 2. RI detector response for GPC chromatogram of sample PCI-1 (2M1P-initiated PCI) after 3 hour reaction time. For alcohol conversion to aluminum alkoxide, reaction conditions were: $[\text{2M1P}] = 0.3 \text{ M}$; $[\text{TEA}] = 0.3 \text{ M}$. The final reagent concentrations were as follows for the caprolactone polymerization: $[\text{alkoxide}] = 4.2 \times 10^{-2} \text{ M}$; $[\epsilon\text{-caprolactone}] = 0.94 \text{ M}$.

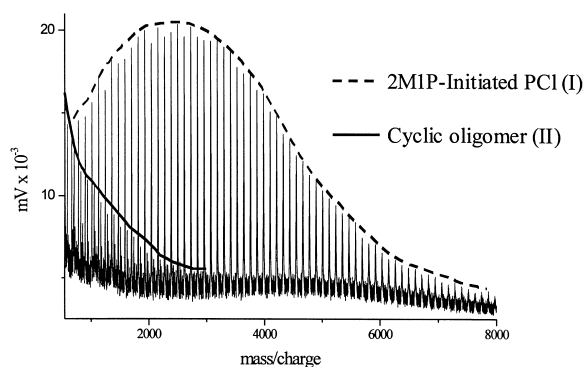


Figure 3. MALDI-TOF MS for sample PCI-1 (2MIP-initiated PCI). Reaction conditions are given in Figure 2 caption.

intramolecular chain transfer to polymer (back-biting). This finding corroborates work by Teysié *et al.* (22) who reported cyclic oligomer formation at reaction times corresponding to high monomer conversion. The corresponding intermolecular chain transfer reactions would also be expected to occur but do not produce cyclic oligomer; however, they probably are responsible for the observed broadening of the MWD.

Closer examination of the mass spectrum in Figure 4 revealed the presence of an additional minor distribution (III). Calculation of the average mass differences between III and the other two distributions (I-III = 56 g/mol; III-II = 18 g/mol) showed III to be carboxylic acid-terminated PCI. This finding prompted us to perform ^{13}C NMR analysis of the crude sample to attempt to observe carboxylic acid end groups (Fig. 5). As expected, a line for the carbonyl carbon of

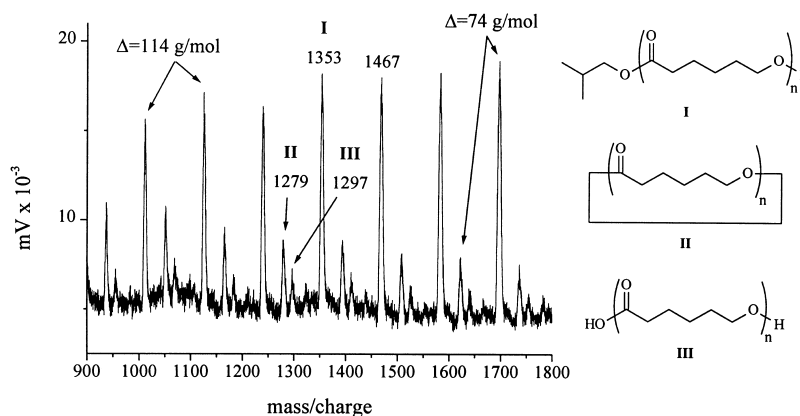


Figure 4. Expanded MALDI-TOF MS for sample PCI-1 (2MIP-initiated PCI) illustrating the mass differences among the three distinct MWDs present.

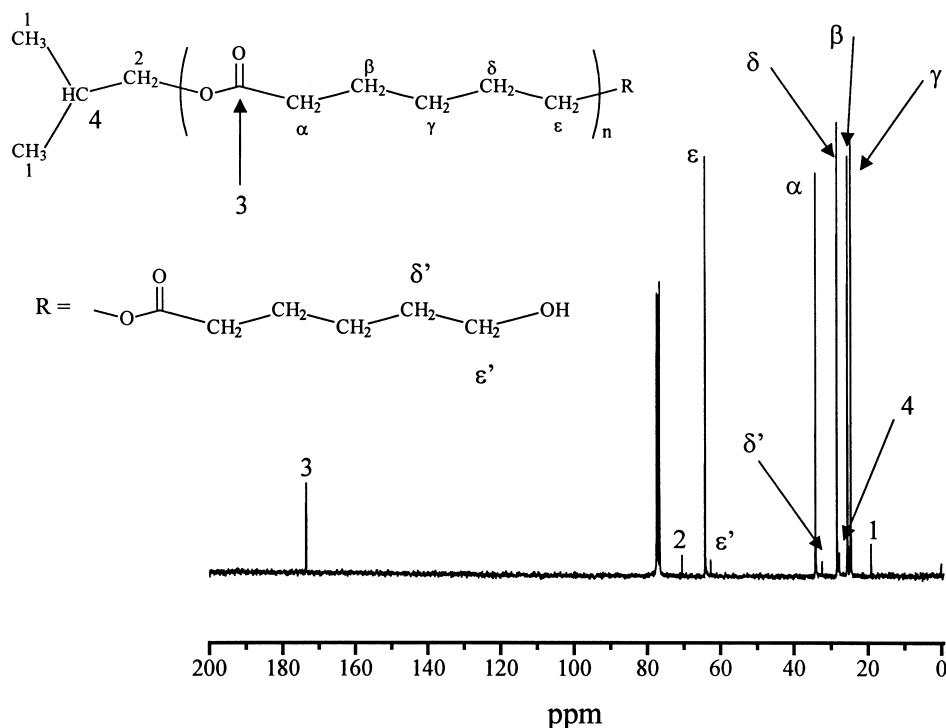


Figure 5. ^{13}C NMR spectrum of sample PCI-1 (2M1P-initiated PCI).

internal repeat units within the PCI backbone was readily observed at 173 ppm; however, there was a conspicuous absence of a carboxylic acid resonance at 178 ppm. Thus, it is proposed that the carboxylic acid end group observed in MALDI-TOF arises from fragmentation and loss of the 2M1P initiating moiety from the PCI block, resulting in liberation of an isobutylene unit with concomitant formation of a carboxylic acid head group.

Allyl-Derived PCI-PIB-PCI Block Copolymers (BPCI-1)

Having established that direct initiation is not operational under these conditions and that an aliphatic primary alcohol readily initiates polymerization of ϵ -caprolactone, the approach was extended to the allyl-derived PIB macro-initiator, PIB Diol 1 ($M_n = 10,000$ g/mol and MWD = 1.1).

Scouting experiments using 2M1P initiator were performed to determine the reaction time required to reach a given monomer conversion under reaction conditions similar to the synthesis of block copolymers from PIB macro-initiators. Figure 6 illustrates the GPC chromatogram of a sample reacted for 3 h under the conditions listed in the figure caption; this sample is designated PCI-2 in Table 1. Comparison of the MW determined from GPC ($M_n = 3,800$ g/mol, MWD = 1.2)

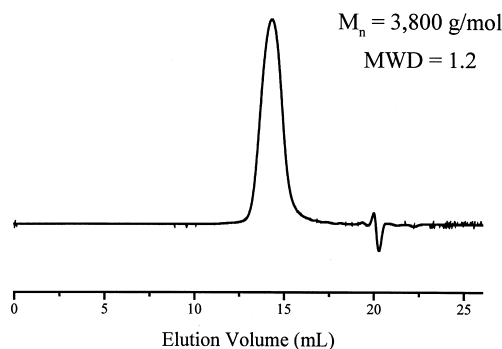


Figure 6. RI detector response for GPC chromatogram of sample PCI-2 (PCI initiated by 2M1P under conditions similar to block copolymer formation). Alkoxide formation proceeded with [TEA] = 0.01 M and [2M1P] = 0.01 M. Polymerization conditions were as follows: [alkoxide] = 5.1×10^{-3} M; [ϵ -caprolactone] = 0.2 M.

to the theoretical MW revealed 85% monomer conversion. It is noteworthy that the GPC trace shows the polymer to be free of cyclic oligomer contaminants, indicating that this side reaction can be minimized by limiting the monomer conversion.

Using this information, block copolymer was produced from PIB Diol 1 macro-initiator using a reaction time of 3 h. GPC chromatograms for PIB Diol 1 and the final block copolymer (BPCI-1) are illustrated in Figure 7; reaction conditions are given in the figure caption. The M_n determined from GPC analysis, 14,400 g/mol, was identical to the theoretical target MW, and indicated that on average, the 10,000 g/mol PIB center block is flanked on either side by 2,200 g/mol PCI outer blocks. The ^{13}C NMR spectrum of the block copolymer is illus-

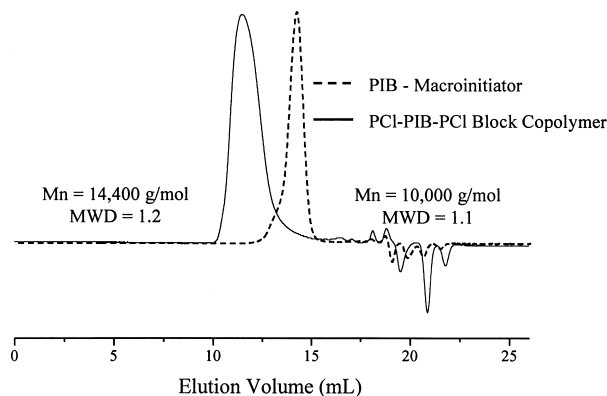


Figure 7. RI detector response for GPC chromatograms of allyl-derived PIB macro-initiator (PIB Diol 1) and resulting PCI-PIB-PCI block copolymer (BPCI-1). Alkoxide formation proceeded with [TEA] = 0.01 M and [PIB-OH] = 0.01 M. Polymerization conditions were as follows: [alkoxide] = 9.1×10^{-1} M; [ϵ -caprolactone] = 0.18 M.

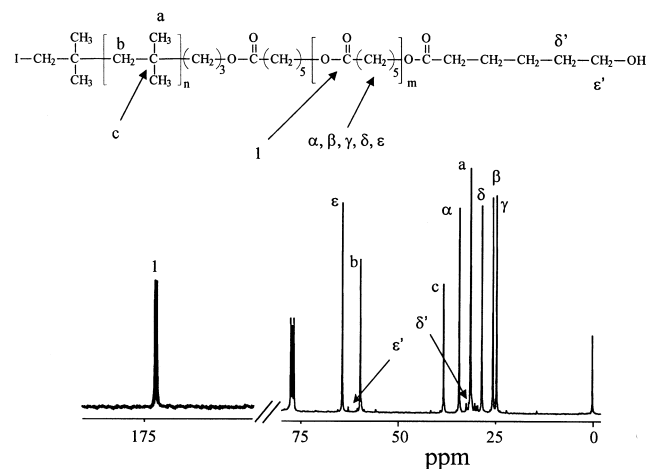


Figure 8. ^{13}C NMR spectrum of allyl-derived PCI-PIB-PCI block copolymer (BPCI-1) from Figure 7.

trated in Figure 8. Again, no carboxylic acid peak was observed at 178 ppm; thus, in agreement with the 2M1P-initiated polymer, initiation proceeded only from the *in situ*-produced alkoxide groups. Peaks due to the trimethylene connecting group between the PIB block and the PCI block could not be positively identified. We speculate that the structural similarity of these three carbons to the γ , δ , and ϵ carbons of PCI caused these small peaks to be buried under the resonances of the main-chain ϵ -caprolactone repeating units.

The MS obtained for allyl-derived PCI-PIB-PCI is shown in Figure 9. Interestingly, a single mass distribution centered about a MW of 2,200 g/mol was observed. The GPC chromatogram also indicated a single distribution of material,

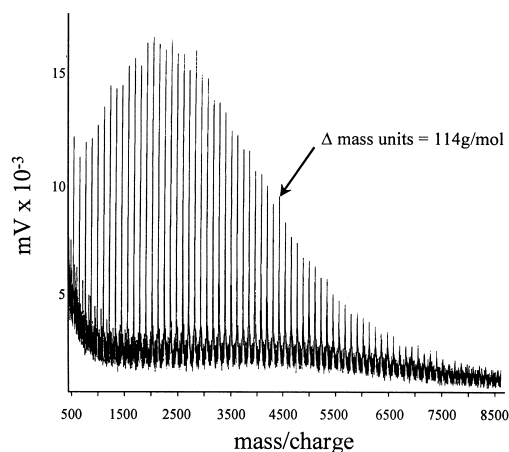


Figure 9. MALDI-TOF MS for allyl-derived PCI-PIB-PCI block copolymer (BPCI-1) from Figure 7.

but with a $M_n = 14,400$ g/mol. Because GPC and MALDI-TOF MS yielded MWs that were in excellent agreement for homo-PCI, it was surprising that MALDI-TOF analysis of the block copolymer did not yield a distribution of MWs centered $\sim 14,400$ g/mol. Rather, the MWD obtained from the MS was consistent only with the PCI end blocks.

It was concluded that the PCI blocks were fragmented from the PIB center block. This was consistent with the previous finding that some of the homo-PCI chains were fragmented from the 2M1P initiator. Determination of the end group after fragmentation of the block copolymer became of critical interest. To make a positive identification, the block copolymer sample was mixed with the homo-PCI sample previously analyzed (Fig. 3). As expected, three major distributions were observed in the spectrum (Fig. 10); they correspond to PCI carrying a 2M1P head group (I), cyclic oligomer (II), and the PCI blocks that were fragmented from the copolymer (IV). An expanded view of a portion of this MS is shown in Figure 11. From the average mass differences between the distributions (I-IV = 28 g/mol; IV-II = 46 g/mol) it was concluded that the PCI fragments from the block copolymer possess an ethyl, or possibly vinyl, head group. Because PIB has a relatively low ceiling temperature, it was hypothesized that the PIB undergoes cationic depropagation with the liberation of IB monomer during MALDI analysis.

Isopropenyl-Derived PCI-PIB-PCI Block Copolymer (BPCI-2)

Having determined the head group remaining after fragmentation of allyl-derived PCI-PIB-PCI, it was of interest to determine the fragmentation pattern for a block copolymer synthesized from an isopropenyl-derived PIB diol macro-initiator. Thus, BPCI-2 was subjected to MALDI-TOF analysis using sample PCI-1 as an internal reference to allow for end group determination (Fig. 12).

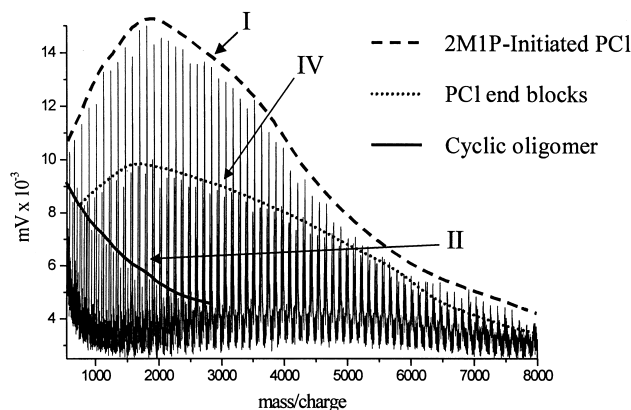


Figure 10. MALDI-TOF MS for PCI-PIB-PCI block copolymer (BPCI-1) from Figure 7 containing PCI-1 as internal reference.

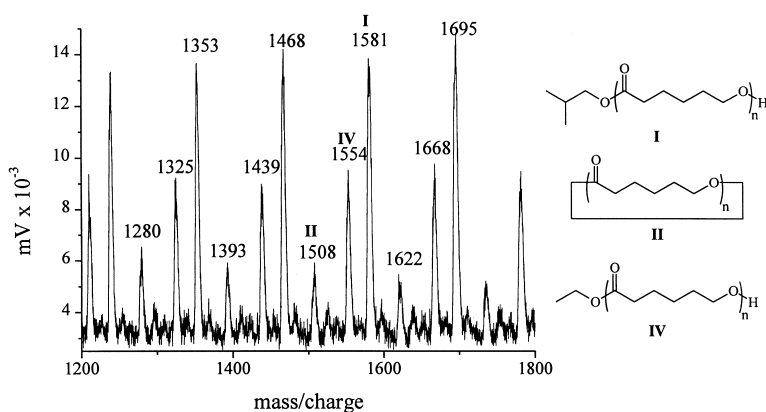


Figure 11. Expanded view of Figure 10 showing molecular structure and molecular mass differences among the three distinct MWDs present.

Compared with the allyl-derived block copolymer, a more complex fragmentation pattern was observed for the isopropenyl-derived block copolymer. The 2M1P-initiated homo-PCI internal reference and its cyclic oligomer contaminant are labeled I and II, respectively. For the block copolymer, one main distribution, labeled IV, was accompanied by several minor distributions. Precise identification of the head groups associated with the minor distributions was not possible due to the poor mass resolution of each peak. However, the head group of the main distribution, IV, was determined by comparison to the known end group of the homo-PCI, and interestingly, it was again found to be ethyl.

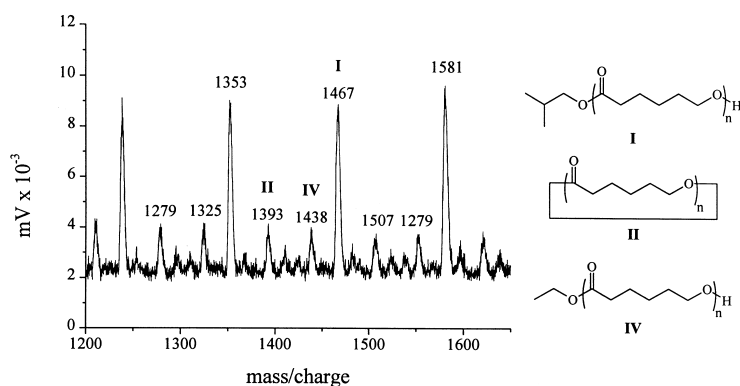


Figure 12. MALDI-TOF MS for isopropenyl-derived PCI-PIB-PCI block copolymer (BPCI-2) mixed with PCI-1. Reaction conditions for block copolymerization were as follows: alkoxide formation proceeded with [TEA] = 0.02 M and [PIB-OH] = 0.02 M. Polymerization of ϵ -caprolactone proceeded with [alkoxide] = 0.01 M and [ϵ -caprolactone] = 0.25 M. Polymerization was allowed to proceed for 2.75 h.

CONCLUSION

A one-pot synthesis was used for primary alcohol conversion to an aluminum alkoxide followed by *in situ* polymerization of ϵ -caprolactone. Initiation of ϵ -caprolactone by 2-methyl-1-propanol yielded PCI with well-controlled MW and fairly narrow MWD; however, excessive reaction times (very high monomer conversion) caused formation of a minor fraction of cyclic oligomer as determined by MALDI-TOF analysis. The same synthetic approach for PCI synthesis from a primary alcohol was then extended to the production of PCI-PIB-PCI block copolymers from PIB macro-initiators. Both allyl and isopropenyl-derived PIB diol macro-initiators, produced by living cationic polymerization, were used. This approach produced well-defined materials with MWs dictated by the ratio $[\epsilon\text{-caprolactone}]_0:[\text{alkoxide}]$ and relatively narrow MWD. Structural evidence of PIB-PCI block junctions was obtained through ^{13}C NMR and MALDI-TOF analysis.

The MALDI-TOF spectra of PCI-PIB-PCI block copolymers were essentially those of homo-PCI, with peak MWs matching closely those of the PCI outer blocks. Thus, it was concluded that the PCI blocks were severed from the PIB center block during MALDI-TOF analysis. Interestingly, the fragmentation pattern observed for isopropenyl-derived PCI-PIB-PCI block copolymers was more complex than that obtained for allyl-derived block copolymers; although the major product in each case was PCI with a C_2 residue at the point of detachment of the PIB block. A possible mechanism for separation and loss of the PIB center block is cationic depropagation to form isobutylene monomer. This explanation is consistent with the low ceiling temperature of PIB and the MALDI-TOF MS technique, which is believed to involve positively charged species.

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