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# Telechelic Polyisobutylene: A Facile Synthesis via the Cross-Metathesis Reaction and Trialkylborane-Containing Olefins

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ABSTRACT: This paper describes the synthesis of telechelic polyisobutylene through the metathetical degradation of poly(isobutylene-*co*-butadiene) copolymer in the presence of a trialkylborane-containing acyclic olefin. Despite the relatively small amounts of butadiene units in the polymer chain, the degradation reaction proceeded fairly satisfactorily with a concomitant introduction of trialkylborane at the cleaved chain ends. The effects of various reaction times and acyclic olefin concentrations on the molecular weight of the final product were studied. The trialkylboranes thus obtained at the chain ends were quantitatively converted to the primary alcohol and iodo groups. The extent of functionalization at the chain ends was further evaluated by column chromatography and the synthesis of block copolymers of polycaprolactone and polyisobutylene.

## Introduction

The synthesis of telechelic polymers[1] has been an area that has attracted a lot of attention owing to the large number of applications that this special form of functionalized polymers can be employed in. Besides the synthetic challenge of introducing the exact number of functional groups at the two ends of a polymer molecule, they find a number of interesting applications, in both theoretical[2] and industrial areas. Among the most interesting uses of these telechelic polymers is the synthesis of triblock copolymers[3] which find application as thermoplastic elastomers and as emulsifiers or compatibilizers in multiphase systems.

A number of living polymerization systems with difunctional[4] or functionally substituted initiators[5] have been employed for the purpose of synthesizing telechelic polymers, including anionic,[6] cationic,[7] group-transfer,[8] and metathesis[9,10] polymerization systems. Earlier work with metathesis degradation,[11-13] as well as ring-opening metathesis polymerization, has shown that good molecular weight control as well as high degrees of functionalization can also be achieved via well-defined catalyst systems[14] as well as traditional metathesis catalyst systems and the borane approach.[12]

The goal of our research has been to synthesize telechelic polymers via facile generic methods that would permit access to different polymers in telechelic form and thus make available a wide variety of different block copolymers from these telechelic precursors. The interest in polyisobutylene as a saturated hydrocarbon rubber is due to its damping properties over a broad frequency range and its excellent barrier properties, both making it a candidate in a number of interesting applications. On the other hand, polycaprolactone exhibits a remarkable capacity to mix with a number of commercial polymers (poly(vinyl chloride), polycarbonats, styrene acrylonitrile copolymers, etc.), and thus block copolymers containing polycaprolactone enjoy the inherent advantage of finding potential application as compatibilizers in a number of multiphase polymer blend systems. Polycaprolactone has also been shown to improve the ozone resistance of styrene butadiene rubbers, as well as to exhibit good low-temperature adhesion. In this work, we present a synthetic route to telechelic polyisobutylene via metathesis degradation and simultaneous functionalization. The hydroxy group terminated polyisobutylene was then used for block copolymerization with caprolactone.

## Results and Discussion

An equilibrium metathetical degradation of poly(isobutylene-*co*-butadiene) with 3.57 mol % (as determined by $^1$H NMR) of 1,4-butadiene was performed in

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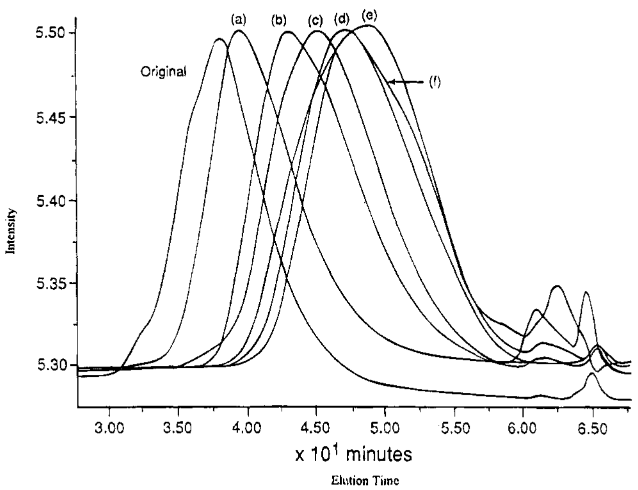
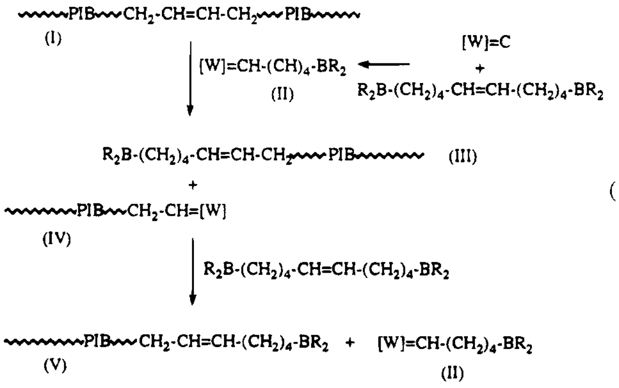


**Figure 1.** GPC chromatograms of original poly(isobutylene-*co*-butadiene) and telechelic polyisobutylene polymers; (a) I-A, (b) I-B, (c) I-C, (d) I-D, (e) I-E, and (f) I-F.

the presence of a trialkylborane-containing acyclic olefin, e.g. 1,10-di(9-BBN)-5-decene. It is known that alkyl-9-BBN (9-BBN = 9-borabicyclononane) compounds are very stable in the presence of most transition metal carbene catalysts and are also very soluble in common hydrocarbon solvents. Both properties are essential for this reaction. The detailed reaction mechanism is illustrated in eq 1. The tungsten carbene generated from the $WCl_6/Me_4Sn$ catalyst system may be expected to react with the acyclic olefin to generate a tungsten carbene with a trialkylborane group as part of the alkylidene ligand (II). The reaction of this tungsten carbene with the olefin units in the polymer chain (I) introduces a trialkylborane at one of the cleaved chain ends (III) and a tungsten carbene at the other (IV). The reaction of this tungsten carbene with another acyclic olefin species functionalizes the other chain end (V) and simultaneously regenerates the tungsten carbene (II). Thus, the reaction progresses with a reduction in molecular weight of the product and simultaneous functionalization of the chain ends. The products thus obtained, with trialkylboranes at the chain ends, can then be functionalized to a wide variety of functional groups.[15] In most cases, the end groups were converted into the alcohol groups via alkaline peroxidation before analysis.



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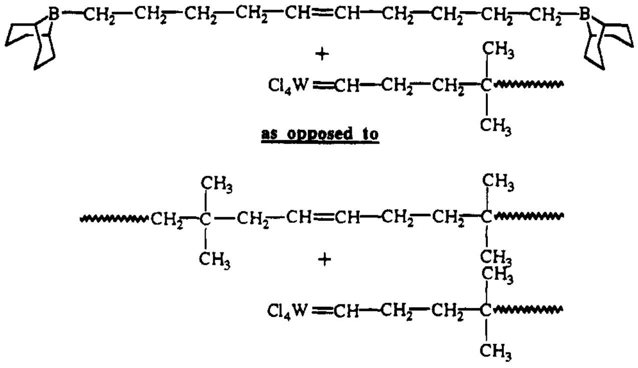
**GPC and $^1H$ NMR Studies.** The efficiency of the reaction can be gauged by monitoring the molecular weight of the product obtained. Figure 1 shows the gel permeation chromatograms (GPC) for various reaction times. The reaction was performed at 54 °C with the mole ratios of [polymer $-CH{=}CH-$]/[$WCl_6$] = 11 and [polymer $-CH{=}CH-$]/[1,10-di(9-BBN)-5-decene] = 1.77. Overall, the degradation reaction is very effective and the polymer molecular weight decreases with reaction time. The molecular weight distribution remains unimodal as the molecular weight decreases, which indicates a homogeneous reaction and a random distribution of the double bonds (butadiene units) along the polyisobutylene backbone. While intermolecular degenerate metathesis reactions may also play a part in the slight alteration in polydispersity, we believe that this reaction is much less likely as opposed to the degradation–functionalization reaction, given the sterics involved in the following two reactions.

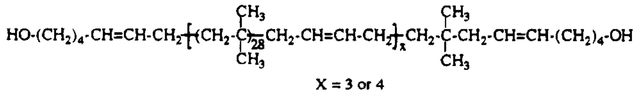
**Table 1. Summary of Telechelic Polyisobutylene Obtained under Different Conditions**

| sample | butadiene/ $WCl_6$ | butadiene/ AO[a] | reacn time (min) | $M_n$[b] | PDI |
|---|---|---|---|---|---|
| original | | | | 140 000 | 3.62 |
| I-A | 11.06 | 1.77 | 5 | 56 700 | 2.82 |
| I-B | 11.06 | 1.77 | 15 | 19 000 | 2.96 |
| I-C | 11.06 | 1.77 | 30 | 14 400 | 3.08 |
| I-D | 11.06 | 1.77 | 60 | 7 900 | 2.88 |
| I-E | 11.06 | 1.77 | 120 | 6 900 | 2.82 |
| I-F | 11.06 | 0.44 | 120 | 5 800 | 3.28 |
| I-G | 11.06 | 0.29 | 120 | 51 100 | 2.89 |

[a] AO: 1,10-bis(9-BBN)dec-5-ene. [b] Estimated from GPC curves. Universal constants[16] for polyisobutylene were employed for the determination of molecular weight.

The detailed results are summarized in Table 1. As seen in sample I-E, the reaction yields a product of $M_n$ of approximately 6900 with a slight narrowing of the polydispersity from the original value of 3.62 to a value of 2.82 within 2 h. This product is envisaged to have an average final structure with three to four unreacted double bonds from the polybutadiene in the original copolymer, as shown.





$$HO\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}\left[(CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}})_{28}CH_2\text{-}CH{=}CH\text{-}CH_2\right]_x\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}OH$$

X = 3 or 4

The monotonic reduction of molecular weight over different reaction times indicates the well-behaved nature of the reaction and suggests that a wide variety of telechelic polymers can be synthesized by this approach. A comparison of the $^1H$ NMR spectra of the starting poly(isobutylene-*co*-butadiene), sample "original" in Table 1 ($M_n$ = 140 000), and telechelic products, sample I-D in Table 1 ($M_n$ = 7900), is shown in Figure 2. Figure 2b exhibits clearly a triplet at 3.65 ppm, corresponding to the protons of the methylene unit adjacent to the hydroxy end groups. The trialkylborane at the chain end was also converted into a primary iodo group. Figure 2c shows the $^1H$ NMR spectrum of iodo-terminated polyisobutylene with a distinct triplet at 3.2 ppm, corresponding to the methylene protons adjacent to iodo groups.

A comparison between samples I-D and I-E in Table 1 shows that the molecular weight, for similar amounts of bis(borane)-substituted olefin, did not alter significantly after a reaction time of about 1 h. Under the assumption that the butadiene units of the initial copolymer were randomly distributed within the polymer chain, the theoretical $M_n$ of the product would be about 3000 for the amount of acyclic olefin employed. This calculated value does not account for the catalytic tungsten carbene species, as the ill-defined nonliving nature of the catalyst system employed does not permit an exact calculation of the number of active species generated, or of the rate of deactivation of the catalyst as the reaction progresses. The discrepancy between the ideal molecular weight and that obtained could be due to three factors. The first being that after a period of about 1 h, the catalyst could become deactivated by the side reactions. Despite the experimental observation that the color of the reaction mixture did not change, deactivation of the catalyst (total or partial) cannot be entirely eliminated for the deceleration of the reduction in molecular weight of the products. A second possibility could be that the acyclic olefin used for the reaction is not purely olefin in nature but contained an impurity in the form of the trihydroborated adduct of decatriene and 9-BBN. The $^1$H NMR spectrum of this acyclic olefin consisted of 82 mol % olefin and 18 mol % trihydroborated adduct of decatriene and 9-BBN. Thus, after a readjustment for this factor, the theoretical molecular weight would be a little higher than the value determined earlier. This value implies that one out of every two acyclic olefin species has reacted. The third possibility might be the fact that while the total amount of unsaturation in the backbones of polymer chains in the reaction system will have remained constant, the concentration of acyclic olefin available for cross-metathesis would have progressively diminished. Consequently, at this late stage along the reaction coordinate, the concentration of the acyclic olefin might be too low to induce further rapid degradation. This hypothesis is supported by the fact that for sample I-F, when the concentration of acyclic olefin in the reaction feed was 4 times that for sample I-E, a lower product molecular weight could be accessed. However, even in the case of sample I-F, the product molecular weight was not the minimum that is theoretically possible.

**Adverse Effect of High Concentration of the Acyclic Olefin.** On attempting to react all olefin units in the polymer backbone by increasing the concentration of the acyclic olefin to 6 times the amount used for the synthesis of I-E, we were surprised to find that the degradation reaction was preempted to a very large extent, as seen for sample I-G. Despite repeated attempts at degradation of all the olefin units in the polymer backbone, by employing this high level of acyclic olefin, the results obtained were unchanged. A comparison between samples I-E and I-G shows that the only parameter that was changed for the reaction was the concentration of the acyclic olefin. Since samples I-E and I-F exhibit molecular weights that are vastly reduced from that of the starting copolymer, for identical reaction conditions, catalyst deactivation with the increased reaction time can be eliminated as the source for this unexpected result. Apparently, the higher concentration of the acyclic olefin seems to have reduced the occurrence of degradative-cum-functionalization attack of a tungsten carbene species on the unsaturation enchained in the poly(isobutylene-*co*-butadiene). A plausible explanation for this phenomenon might lie in the fact that, due to the difference in sterics between the unsaturation enchained in the polymer and that in the acyclic olefin, there is a difference in the reactivities of the two species. It would be obvious to expect that the acyclic olefin would be much more reactive than the unsaturation in the polymer chain.

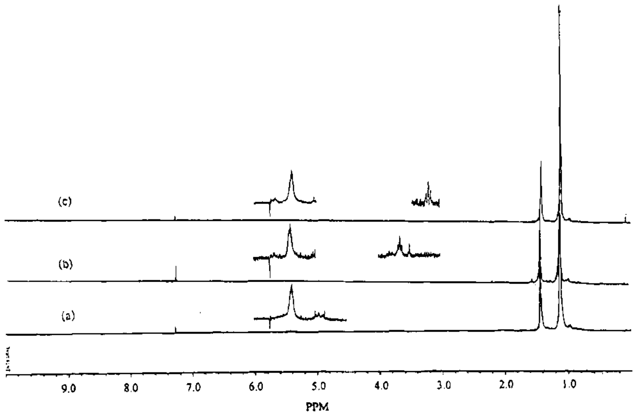
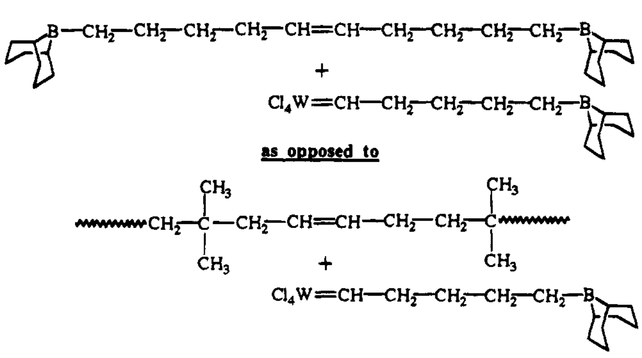


**Figure 2.** $^1$H NMR spectra of (a) poly(isobutylene-*co*-butadiene) and telechelic polyisobutylene (sample I-D) with (b) hydroxyl and (c) iodo terminal groups (peaks at 5.4, 3.65, and 3.2 ppm magnified [32×] to the same extent).



Thus, at a certain rate of catalyst turnovers, the concentration of the acyclic olefin was perhaps too high (the ratio of acyclic olefin to $WCl_6$ was 37.7/1) to permit the carbenes to react to any significant extent with the olefin units in the polymer backbone (the ratio of polymer $-CH{=}CH-$ to $WCl_6$ was 11/1). Since the reaction of the carbene with the olefin units in the polymer backbone is thus precluded, the product has a very high molecular weight. Obviously, the molecular weight of the product obtained is not the equilibrium value of the reaction system. However, with the constraint of a nonliving catalyst system, we did not wish to employ longer reaction times since we had observed, that at this temperature, within a 4 h period, the reaction color changed from burgundy to green, indicating, rather crudely, a change in the oxidation state of the metal and a loss of activity. The employment of the recently described,[9,10] well-defined metal alkylidene and metallacyclobutane catalysts might provide a solution to this problem. This result seems to indicate that one must be careful before attempting to employ extraordinarily high concentrations of each reactant to achieve a desired result, as a nonproductive side reaction might be facilitated to such a large extent that the reaction does not proceed along the desired pathway to any great extent.

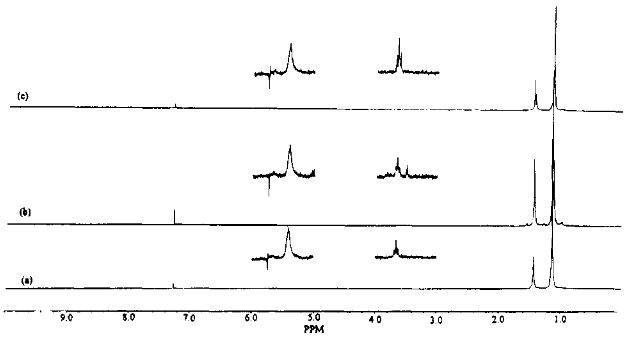


**Figure 3.** Representative $^1$H NMR spectra of telechelic polyisobutylenes, (a) sample I-C, (b) sample I-D, and (c) sample I-F, employed for end group analysis.

**End-Group Analysis.** The functionality number of the products obtained were determined by $^1$H NMR. Since the unsaturation in the starting copolymer is preserved during the reaction, a comparison between the intensity of the peak at 5.4 ppm (due to the unsaturation in the product backbone) and the peak at 3.65 pm (due to the methylene protons adjacent to the primary hydroxy group), coupled with the values of the molecular weight values obtained from gel permeation chromatography, can be used to determine the functionality number of the products. The intensity of this peak (representative spectra shown in Figure 3) for products of different molecular weights, is inversely proportional to the molecular weight of the products, as might be expected when the degradation occurs with simultaneous functionalization. A comparison between the peaks at 3.65 and 5.4 ppm (due to the unsaturation in the polymer backbone) seems to indicate a reasonably high degree of functionalization (functionality numbers ranging from 1.2 to 1.45 for samples I-B through I-F, as determined by $^1$H NMR) of the chain ends. A careful investigation of the $^1$H NMR spectra reveals the presence of peaks corresponding to α-olefin species in the products (at 5.0 ppm and at 5.7 ppm). The source of these imperfections at the chain ends and causes for the reduction in functionality number will be discussed later.

**Column Chromatography Studies.** We were concerned with the possibility of two potential side reactions, mainly due to the 1,2-linked butadiene units (about 10% of the total butadiene units incorporated) in the poly(isobutylene-*co*-butadiene) copolymer and the methylidene unit (=$CH_2$) in the initial catalyst. Both can lead to products without trialkylborane at the chain ends. It can be expected that the 1,4-isomer (especially, cis-isomer) is more reactive toward the metal–carbene than the 1,2-isomer, due to the steric effect. The metathesis reaction involving the 1,2-isomer could result in branched polymers with more than two functional groups per polymer chain. Figure 1 shows a fairly uniform molecular weight distribution throughout the degradation process, which implies that an insignificant amount of branched products has formed. The same result is also obtained from column chromatography and block copolymerization studies (discussed later). On the other hand, it is expected that the tungsten methylidene unit generated from the $WCl_6$/$Me_4Sn$ catalyst system could contribute to the chain ends of the product. The defect thus obtained would be an α-olefin unit at the chain end. In all reactions, the ratio of catalyst to butadiene (=1/11) was relatively high. Therefore, the products inevitably contain some α-olefin chain ends. It is interesting to note that, in our earlier work,[12] on telechelic polybutadiene, we had employed catalyst loadings of much lower concentrations (catalyst/butadiene = 1/100). In that case, no significant amount of α-olefin moieties was detected in the products.

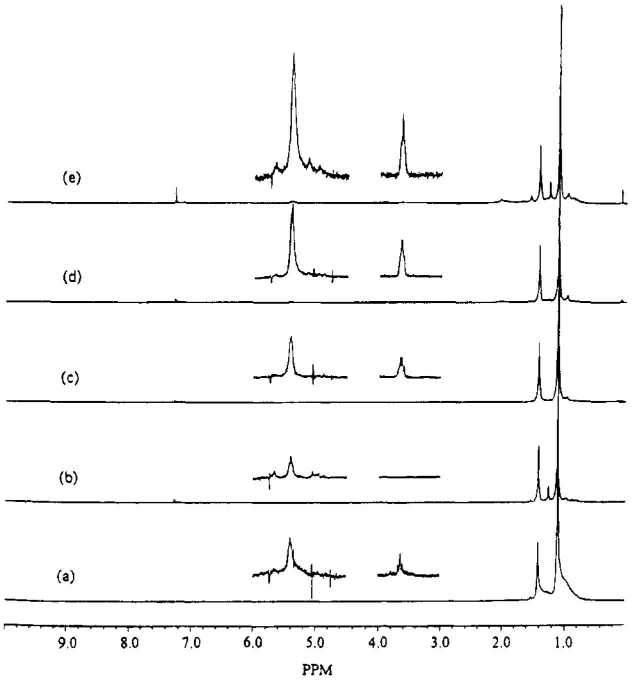
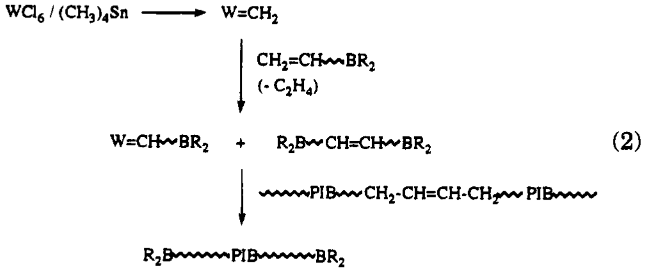


**Figure 4.** Comparison of $^1$H NMR spectra between (a) sample I-D and its fractions eluted by (b) pure hexane, (c) ether/hexane (10/90), (d) ether/hexane (30/70), and (e) pure ether solvent.

An attempt was made to isolate the different fractions of the product obtained from the cross-metathesis of the poly(isobutylene-*co*-butadiene) system via column chromatography. Sample I-D was subjected to a solvent gradient that started with pure hexane as a solvent and gradually increased in solvent polarity to pure ether as the eluting solvent. Figure 4 shows the $^1$H NMR spectra of the starting sample I-D and its fractions. The hexane-eluted fraction shown in Figure 4b contains no functional group, which constitutes about 20% of the reaction product. It is interesting to note the significantly high peak intensities at approximately 5 and 5.7 ppm in Figure 4b, which correspond to α-olefin groups of the unfunctionalized chain ends. Thus, about 20% of the "telechelic" product consists of α,ω-divinylpolyisobutylene. Further attempts to separate more fractions, especially different numbers of functionalities, were not very successful. As shown in Figure 4c–e, there is no significant difference in the $^1$H NMR spectra. There is clearly a need to further investigate the ratio between polymer chains with trialkylboranes at one or two chain ends.

The source of the above mentioned olefin chain ends is mainly from the undesirable reaction of the tungsten carbene generated from the tungsten hexachloride/tetramethyltin catalyst system. An attempt was made to suppress the undesirable side reaction of the catalyst by the dimerization of hexenyl-9-BBN in the presence of the catalyst to yield 1,10-bis(9-BBN)dec-5-ene and a catalyst which already possesses a trialkylborane as part of the alkylidene ligand, as shown in eq 2. However, only about 70% of hexenyl-9-BBN was dimerized under the conditions employed (40 °C and mild vacuum). Obviously, this result would not suffice to preclude the undesirable side reaction but provides hope that an attempt in this direction might yield useful results. This route could be the subject of future attempts to improve



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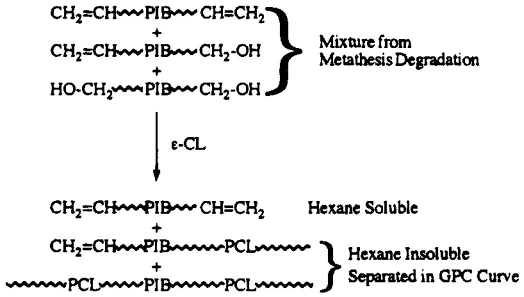
the synthesis of telechelic polyisobutylene via the cross-metathesis reaction.

**Synthesis of Block Copolymers of Polycaprolactone and Polyisobutylene.** To gain a better measure of the efficiency of the cross-metathesis-co-functionalization approach to telechelic polymers, the hydroxy groups at the chain ends of the telechelic polyisobutylene, obtained from the trialkylborane precursors, were employed as initiators for the ring-opening polymerization of $\epsilon$-caprolactone. These block copolymerizations yielded three discrete fractions; homopolyisobutylene which originated from that portion of the metathesis degradation product which had no terminal hydroxyl groups, a diblock copolymer of poly(isobutylene-*b*-caprolactone) from monofunctional polyisobutylene, and a triblock copolymer of poly(caprolactone-*b*-isobutylene-*b*-caprolactone) originating from difunctional polyisobutylene. The overall reaction and separation are illustrated in eq 3. The product was subjected to solvent extraction. The unfunctionalized polyisobutylene was easily separated from the mixture by extraction with hexane. The $^1$H NMR spectrum of this fraction shows a polyisobutylene that has no primary hydroxyl group at either chain end but exhibits the presence of α-olefin groups. This fraction constitutes 20% of the product, corresponding to the amount that eluted as the hexane soluble fraction when column chromatography of "telechelic" polyisobutylene was undertaken. To confirm that the remaining hexane insoluble fraction was a mixture of di- and triblock copolymers, the remaining material was analyzed by GPC measurements with signal detection by UV spectrometry and differential refractometry (RI) in series. Figure 5 compares the GPC/RI chromatograms of the hexane insoluble fraction and the "telechelic" polyisobutylene. The GPC/RI chromatogram (acquired on Baseline software with differential refractometer 410 as the signal detector) shows that while the molecular weight of the product is greater than that of the precursor "telechelic" polyisobutylene, the product consists of copolymers of two different compositions. The UV ($\lambda$ = 210 nm) absorbance chromatogram mirrors the chromatogram obtained from differential refractometry (acquired on Milienium software with photodiode array detector 991 M and differential refractometer 410 as signal detectors connected in series), shown in Figure 6, which gives further evidence for the presence of a mixture of di- and triblock copolymers of polycaprolactone and polyisobutylene. At the wavelength of 210 nm, only polycaprolactone exhibits significant absorbance, with no response from PIB. The presence of polycaprolactone homopolymer was excluded as a possibility after model reactions with identical concentrations of primary hydroxy functionality, under identical reaction condtions, yielded products of much lower molecular weights. All further attempts to separate the diblock and triblock copolymers met with only limited success in each case. A number of different solvents and solvent mixtures were employed to separate the di- and triblock copolymers. A few examples of these are acetone, glacial acetic acid, and acetone/methanol. Separation of the two block copolymers into clean fractions of di- and triblock copolymers could not be achieved. A summary of the product distribution and their molecular weights from two such reactions is presented in Table 2.



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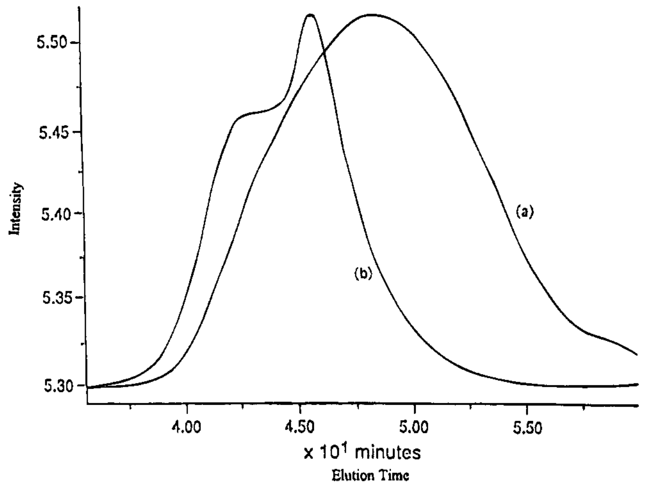

**Figure 5.** Comparison of GPC/RI chromatograms of (a) the hexane insoluble fraction of the block copolymer and (b) precursor telechelic polyisobutylene.

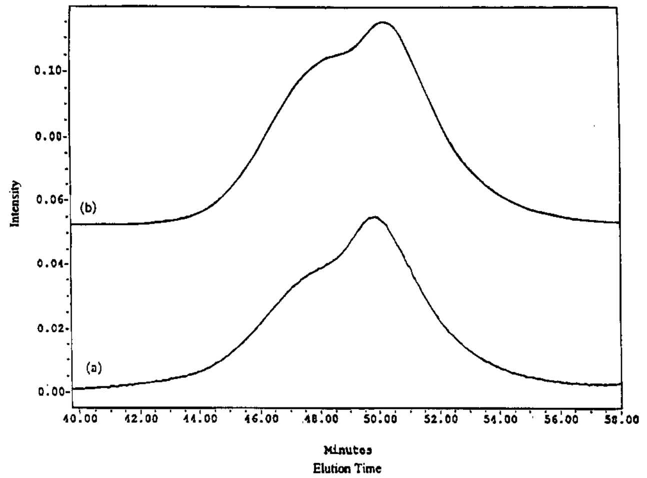

**Figure 6.** Comparison of GPC chromatograms of block copolymer from (a) UV ($\lambda$ = 210 nm) absorbance spectroscopy and (b) differential refractometry.

Figure 7 compares the $^1$H NMR spectra of the starting "telechelic" polyisobutylene and two hexane insoluble products from two independent block copolymerizations. The intensity of the triplet assigned to the methylene protons ($CH_2$—O—C=O) of the caprolactone segment at 4.1 ppm can be compared to the intensity of the peak at 1.1 ppm (assigned to the methyl protons for the isobutylene unit) for the determination of the molar

**Table 2. Summary of the Product Distribution from Block Copolymerization**

| | telechelic PIB | | | wt of | total product | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | hexane soluble | hexane insoluble | | |
| sample | wt (mg) | $M_n{}^a$ | PDI | ϵ-caprolactone (mg) | % yield | % yield | $M_n{}^a$ | PDI |
| II-A | 225 | 8100 | 2.97 | 675 | 8.9 | 91.1 | 21 800 | 2.19 |
| II-B | 225 | 8100 | 2.97 | 1013 | 5.2 | 94.8 | 28 100 | 1.90 |

[a] Estimated from GPC curves. Universal constants[16] for polyisobutylene were employed for the determination of molecular weight.

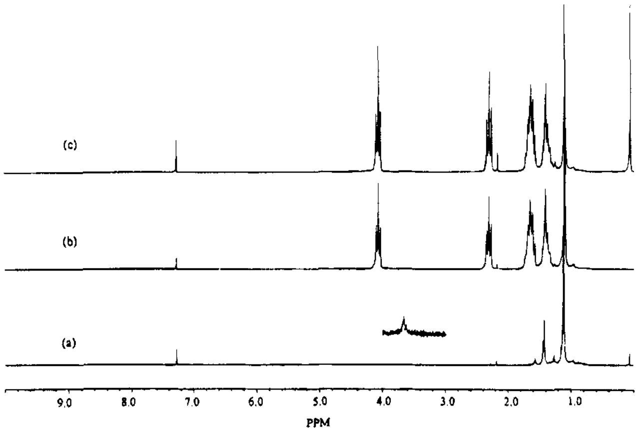

**Figure 7.** $^1$H NMR spectra of (a) precursor telechelic polyisobutylene (sample I-E) and hexane insoluble fractions of block copolymers (b) ϵ-CL/PIB = 3/1 and (c) ϵ-CL/PIB = 4.5/1.

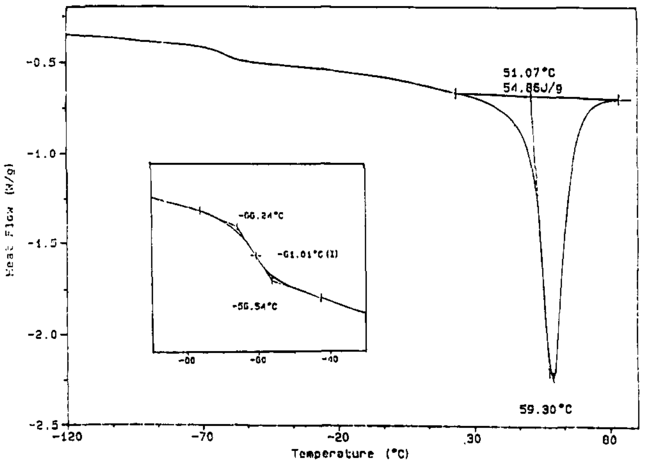

**Figure 8.** DSC thermogram of block copolymer (ϵ-CL/PIB = 4.5/1).

percentage of polycaprolactone in the product. An increased percentage of polycaprolactone in the product was obtained when a higher percentage of ϵ-caprolactone was employed in the starting reaction mixture.

**DSC Analysis of Polyisobutyelene-*b*-Polycaprolactone.** It is very interesting to know the thermal properties of the resulting block copolymers. Figure 8 shows the DSC thermogram for the hexane insoluble fractions of the polyisobutylene–polycaprolactone block copolymers, obtained from ϵ-CL/PIB = 4.5/1. As is immediately apparent, a very distinct glass transition of the polyisobutylene segments at ca. −63 °C, and the melting point of the polycaprolactone segments at ca. 56 °C, was evinced by the thermograms. In addition, the glass transition temperature of the polyisobutylene segments remains unchanged from the homopolymer, indicating that even the amorphous regions of the polycaprolactone segments do not exhibit any miscibility with polyisobutylene. Thus, the method employed for the synthesis of telechelic polyisobutylene would be very effective for the generation of microdomain phase-separated block copolymers.

## Experimental Section

**Materials and Instruments.** 9-Borabicyclononane (9-BBN) crystals were used as received from Aldrich. Reagent grade toluene was purified by stirring over calcium hydride, then transferred into a solvent still containing potassium anthracenide as an indicator, refluxed, and finally collected under inert conditions into a flask, which was then transferred into a Vacuum Atmospheres glovebox and stored therein. Tetrahydrofuran was purified by the same procedure as was toluene. Reagent grade 2-propanol was refluxed with calcium hydride and then transferred, under inert conditions, into another flask containing calcium hydride, which was then sealed off with a vacuum valve. 2-Propanol was degassed prior to each reaction and, as mentioned earlier, distilled directly into the reaction flask at the end of each reaction. 1,10-Bis(9-BBN)dec-5-ene was synthesized as reported earlier.[14] Isobutylene gas was purchased from MG industries and used as received. Butadiene gas was purchased from Aldrich Chem. Co. and used as received.

The molecular weight of the telechelic polyisobutylene and block copolymers were determined using a Waters system consisting of a 600E multisolvent delivery system connected to a 710B auto injector with a 991M photodiode array detector in series with a 410 differential refractometer. The columns used were Phenomenex Phenogel of $10^5$, $10^4$, $10^3$, 500, and 100 Å pore size. A flow rate of 0.7 mL/min of THF was used. Narrow molecular weight polystyrene samples were used as standards. The data obtained were processed on the Waters Baseline or Millenium software employing universal calibration constants[16] for polyisobutylene. Solution NMRs were done on a Bruker WP 200 machine. DSC analysis was performed on the DuPont TA 2000 system.

**Synthesis of Poly(isobutylene-*co*-butadiene).** The poly(isobutylene-*co*-butadiene) was synthesized by cationic polymerization, employing ethylaluminum dichloride as the cocatalyst. Ethylaluminum dichloride (100 mg) was added into a 1000 mL Schlenk flask containing 200 mL of hexane, after which the flask was sealed and brought out of the glovebox. Dichloromethane (30 mL) was then distilled into the flask, via a vacuum line, and the solvents were permitted to thaw and mixed well, via magnetic stirring. This mixture was then frozen and an additional 20 mL of dichloromethane was then distilled into the flask, and the flask was kept frozen in a dewar full of liquid nitrogen. The two monomers (50 mL) were each distilled from a cylinder into a 100 mL flask and then distilled simultaneously into the Schlenk flask, which was then blanketed with a further 20 mL of dichloromethane. The flask was then immersed in a hexane/liquid nitrogen bath maintained at −100 °C. The reaction started as soon as the solvents had thawed sufficiently to permit stirring, as observed by the development of a yellow coloration. The reaction was then terminated after 30 min by the addition of methyl alcohol. The polymer obtained had a large polydispersity. The product was fractionated by dropwise addition of a concentrated solution of the polymer in tetrahydrofuran to 2-propanol in order to isolate the high molecular weight fraction.

**Metathesis Degradation Reaction of Poly(isobutylene-co-butadiene).** Tungsten hexachloride (10 mg, 0.025 mmol) was dissolved in 750 mg of toluene, tetramethyltin (9 mg, 0.05 mmol) was added to it, and the catalyst was allowed to age for 5 min. This catalyst was then added to a flask containing 0.5 g of purified copolymer and the appropriate amount of diborane dissolved in 1.5 g of toluene. A further 250 mg of toluene was used to wash in all the catalyst, and the flask was closed off with a valve, brought out of the glovebox, and immersed in an oil bath maintained at 54 °C. The reaction was then permitted to proceed for a predetermined amount of time, after which the oil bath was removed and the reactants were frozen by immersing the flask in liquid nitrogen. Prepurified 2-propanol (20 mL) was then distilled into the flask, a high vacuum was applied to it, and then it was moved into the glovebox. The polymer was then isolated in the glovebox, redissolved in tetrahydrofuran, brought out of the glovebox, and subjected to alkaline oxidation.

**Block Copolymerization with ε-Caprolactone.** In a typical reaction, 225 mg of telechelic polyisobutylene was dissolved in 2250 mg of toluene, and 675 mg of ε-caprolactone was added to the solution. Stannous octanoate solution (20 mg, 33% in toluene) was then added to it and the reaction flask maintained at 110 °C in an oil bath for a period of 24 h. A blanket of inert gas was maintained above the contents to ensure the exclusion of any atmospheric moisture. The reaction was terminated at the end of 24 h, by the addition of a large amount of methanol to yield the precipitated block copolymer. This copolymer was further purified by redissolution in THF and reprecipitation in methanol and then dried in a vacuum oven overnight to yield 809 mg of product.

## Conclusion

The generic approach described in this work, via the cross-metathesis reaction between borane-containing acyclic olefin and a copolymer containing small amounts of unsaturation in the polymer backbone, appears to be a simple and useful route in the synthesis of telechelic polymers. However, due to the low percentages of unsaturation involved, the method needs to be further refined to produce a highly perfect telechelic polymer. The results from both column chromatography and block copolymerization indicate that up to 80% of the product obtained from the cross-metathesis reaction is either mono- or difunctional. The synthesis of block copolymers via this terminal functionality was also demonstrated to be a very convenient reaction. A number of different block copolymers, as well as multiblock copolymers, are forseeable via this method of synthesis of telechelic polymers. For the synthesis of multiblock copolymers, as well as pure triblock copolymers, the percentage of difunctional product needs to be increased to higher levels. A possible route to increase the percentage of difunctional product is also suggested in the work, and efforts are currently underway to achieve purely difunctional product. Thus, this method should open the door to the synthesis of a wide number of hydrocarbon polymers, in telechelic form, via a facile route.

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