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Communications to the Editor

Novel and Simple Synthesis of Carboxyl-Terminated Polyisobutylenes

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Introduction. Telechelic polymers, i.e., polymers carrying at least two reactive end groups, are in the focus of today's polymer research.[1,2] They can serve as valuable starting materials for a number of polymer analogue reactions as well as building blocks for the synthesis of block copolymers and networks.[3−7] One of the most valuable end groups is the carboxyl group because of its reactivity and versatile convertibility. Carboxyl derivatives, such as anhydrides, nitriles, and acid halides, are easy to prepare and are more reactive than the carboxyl group.

In polymer chemistry two general methods are known for the preparation of the terminal carboxyl group. Because of its simplicity, the more general is the addition method in which the carboxyl group is attached to the polymeric chain end from a small carboxyl-containing molecule. The addition method is easy to carry out as there are a number of possible chain ends and small molecule organic acids to introduce into the polymer. Although the reaction of hydroxyl-terminated PIB with adipic acid gives carboxyl-terminated PIB,[8] the chain end contains an ester bond, which makes the polymer sensitive for the reaction conditions and largely limits the number of expected products. A carboxyl function can be obtained by attaching it through an end-capper, such as 1,1-diphenylethylene,[9] to the main chain; however, the major disadvantage of this method is that it alters the structure of the chain end. By reacting terminal unsaturated C−C bonds with compounds having Al−H bonds, carbon dioxide can add to the chain end, and hydrolysis gives the carboxyl termini.[10]

The other method is the oxidation of the chain ends with strong oxidizing agents. Although there are industrial examples,[11] this procedure is mainly limited to "strong chain" polymers, i.e., monofunctional polyisobutylenes. Butyl rubber is oxidized with O_3 on an industrial scale,[11] but this method destroys the chain end, and no exact end-functionality can be reached (1.09 CO_2H groups/mol). Bi- or trifunctional polyisobutylenes may have an aromatic initiator fragment in the main chain that could result in breaking of the chain when strong oxidizing agents (O_3, $KMnO_4$, peracids) are applied. To avoid chain degradation and solubility problems, organic oxidants such as dioxiranes[12] must be used. The simplest of the dioxiranes is dimethyldioxirane[13,14] (DMD), which is easy to prepare and being a nucleophilic agent offers a high yielding oxidation. DMD is prepared in acetone solution, which is a poor solvent for polyisobutylene; however, DMD can be transferred to chlorinated solvents or even toluene with common extraction techniques.[15] Using DMD, the only byproduct is acetone, which can be distilled off from the reaction mixture; therefore, this very clean process is considered vital for medical applications.

In this paper we report new, simple, and effective synthetic methods for the preparation of carboxyl, namely α,ω-dicarboxyl-, α,ω-di(β-hydroxylcarboxyl)-, and α,ω-di(β-oxocarboxyl)-terminated polyisobutylenes from the corresponding formyl-terminated polymers. Detailed NMR and matrix-assisted laser desorption/ionization mass spectrometric (MALDI-TOF MS) investigations showed the complete conversion of the starting aldehyde termini into the corresponding carboxyl derivative.

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Experimental Section. Materials. CH_2Cl_2 and hexane (reagent grade, Aldrich, Germany) were purified by distillation over P_2O_5. Tetrahydrofuran (HPLC grade, Merck, Germany) was refluxed over sodium in the presence of benzophenone until the mixture turned blue and then distilled. Toluene (technical grade, Aldrich Germany) was distilled and then stored over sodium. *p*-Dicumyl chloride (pDCC) was prepared from *p*-dicumyl alcohol.[6] BCl_3 and dimethyl sulfoxide (DMSO) (99.9%, Merck, Germany) were purified by distillation under diminished pressure. Isobutylene (99.8%, TIFO, Hungary) was dried by passing through a 50 cm column filled with $CaCl_2$ and distilled. Zinc bromide (98%, Aldrich, Germany) was freshly fused before starting the experiments. ^{n}BuLi (1.6 M in hexanes), $LiAlH_4$ (95%), glacial acetic acid (99−100%), HCl (37%), and potassium *tert*-butoxide (*t*-BuOK) (95%) (Aldrich, Germany) were used as received.

1,8-Dihidroxy-9(10*H*)-anthracenone (dithranol) and silver trifluoroacetate (AgTFA) (Aldrich, Germany) were used without further purification.

Dimethyldioxirane (DMD) in acetone was synthesized as described in ref 13. The concentration of the DMD solution was determined iodometrically.

Preparation of Dialdehyde Telechelic Polyisobutylene (OHC-PIB-CHO). Dialdehyde telechelic polyisobutylene was prepared according to ref 16. The M_n values of the starting diolefinic telechelic polyisobutylene determined by ^1H NMR, size-exclusion chromatography, and MALDI MS are 1980/1910/1950 g/mol, respectively. $M_w/M_n = 1.22$ by SEC.

Preparation of α,ω-Dicarboxyl Telechelic Polyisobutylene (HOOC−PIB−COOH). In a separatory funnel 100 mL of DMD solution in acetone (0.082 M) and 100 mL of distilled water were mixed and then extracted with 3 × 15 mL of dichloromethane. The remaining acetone was extracted from the dichloromethane solution by washing five times with 20 mL of a pH = 7 phosphate buffer. The DMD solution was then dried over Na_2SO_4 and filtered. In the dried DMD solution (final volume 40 mL) 1.00 g of the dialdehyde telechelic PIB was dissolved and stirred magnetically overnight, and the solvent was evaporated on a rotary evaporator (yield: 1.00 g, 100%). $M_n = 1940$ g/mol; $M_w/M_n = 1.24$ by SEC.

Preparation of α,ω-Di(β-hydroxylcarboxyl) Telechelic Polyisobutylene. In a three-neck flask, 20 mmol of ^{n}BuLi in 20 mL of anhydrous THF and 0.57 mL (10 mmol) of glacial acetic acid were mixed. The mixture was cooled to −70 °C, and 1.00 g (0.5 mmol) of dialdehyde telechelic PIB in 20 mL of absolute THF was added dropwise over continuous stirring, and the reaction mixture was stirred at −70 °C for 3 h. After the reaction was complete 10 mL of 37% HCl was added, and the mixture was stirred at room temperature for 1 h. The organic phase was separated, and the solvent was evaporated on a rotary evaporator. The resulting polymer was purified by precipitation in a 1:5 (v/v) mixture of hexane and methanol (yield: 0.95 g, 95%). $M_n = 2050$ g/mol; $M_w/M_n = 1.19$ by SEC.

Preparation of α,ω-Di(β-oxocarboxyl) Telechelic Polyisobutylene. In a round-bottom flask 0.50 g (0.25 mmol) of α,ω-di(β-hydroxylcarboxyl) telechelic polyisobutylene was dissolved in 30 mL of DMD solution in dichloromethane (0.078 M) and stirred overnight. The solvent was evaporated on a rotary evaporator (yield: 1.00 g, 100%). $M_n = 2100$ g/mol; $M_w/M_n = 1.22$ by SEC.

Characterization. MALDI-TOF MS. The MALDI MS measurements were performed with a Bruker BIFLEX III mass spectrometer equipped with a TOF analyzer. In all cases 19 kV total acceleration voltage was used with pulsed ion extraction (PIE). The positive ions were detected in the reflectron mode. A nitrogen laser (337 nm, 3 ns pulse width, 10^6-10^7 W/cm^2) operating at 4 Hz was used to produce laser desorption, and 200−250 shots were summed. The samples were prepared with a dithranol matrix dissolved in THF (20 mg/mL). Bulk solutions of the polymers in THF were made in a concentration of 10 mg/mL. To enhance the cationization of the carboxyl-terminated PIBs, silver trifluoroacetate (AgTFA) in THF (2 mg/mL) was added to the corresponding matrix/analyte solutions. The solutions were mixed in a 10:2:1 v/v ratio (matrix: analyte:cationization agent). A volume of 0.5−1.0 μL of these solutions was deposited onto the sample plate (stainless steel) and allowed to air-dry.

Size Exclusion Chromatography (SEC). The M_n and molecular mass distribution (MMD) of the polymers were measured by SEC in THF at 35 °C with a Waters chromatograph equipped with four gel columns (7.8 × 300 mm, 7 μm Ultrastyragel columns: 500, 10^3, 10^4, 10^5 Å), a Waters 600 HPLC pump, and with Waters 490E UV and Waters 410 refractive index detectors. The M_n and M_w/M_n values of the oligomers were calculated relative to polystyrene.

NMR. The ^1H (360 MHz) and attached proton test ^{13}C NMR (90 MHz) spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AM 360 spectrometer with tetramethylsilane as the internal standard.

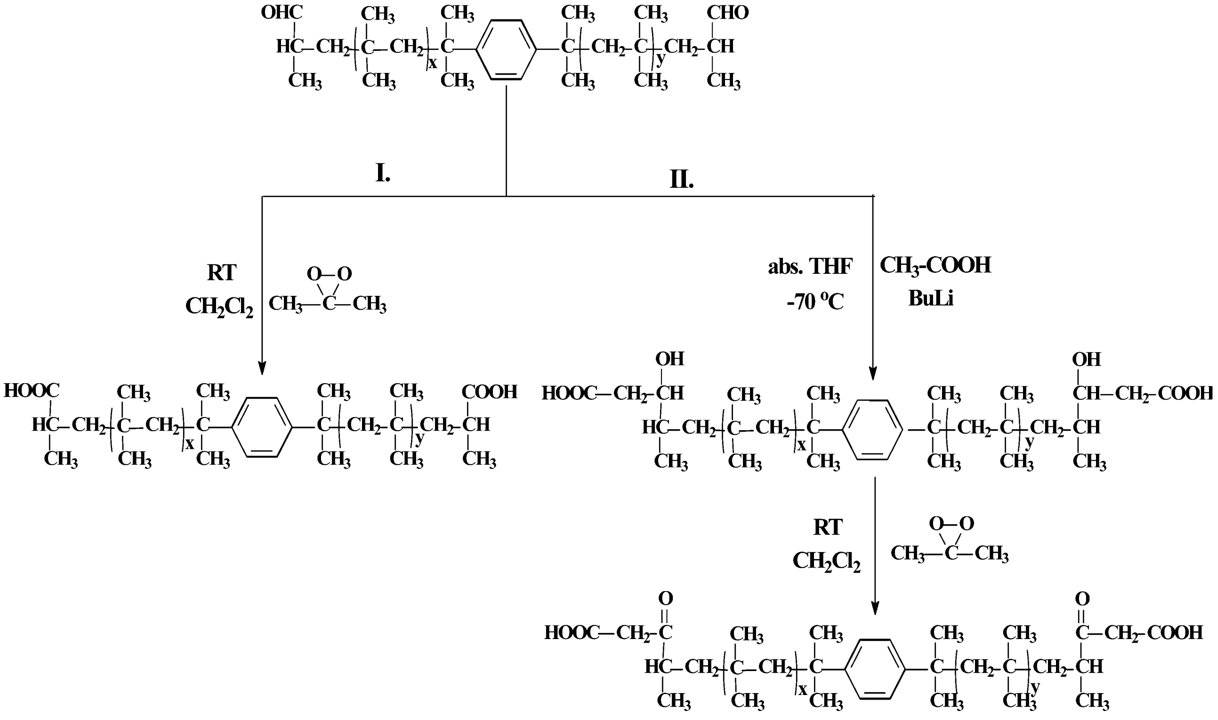
Results and Discussion. The carboxyl-terminated polyisobutylene derivatives were synthesized from the corresponding dialdehyde-terminated polymer as outlined in Scheme 1.

For the preparation of the carboxyl group we used both the oxidation (path I) and the addition (path II) methods. For the oxidation of aldehyde telechelic PIB (path I in Scheme 1) dimethyldioxirane in dichloromethane solution was applied. According to the ^1H NMR spectrum of the dicarboxyl-terminated PIB, the oxidation reaction was complete (Figure 1.).

There is no aldehyde signal at 9.60 ppm, and a large diffuse signal ranging from 13 to 9 ppm appears, indicating the presence of the carboxyl groups. Another proof for the presence of the carboxyl functions is the multiplet signal of the terminal CH groups at 2.55 ppm. According to the signal integral ratios of the methylene protons of the first isobutylene unit next to the initiator fragment (1.83 ppm) and that of the terminal CH groups, the number-average functionality (F_n) was 1.95 ± 0.05. The integral ratios of the protons of the terminal CH groups and that of the CH_3 groups of the first isobutylene unit next to the initiator fragment at 0.80 ppm gave the same F_n value. It should be noted that the protons of the terminal CH_2 group are nonequivalent due to their proximity to the asymmetric CH group. As a result, two peaks appear in the spectrum: the one at 1.93 ppm as a double doublet and the other at 1.28 ppm partially overlapped by the main chain methylene protons. The reaction product is very pure as no byproducts are formed except acetone. The major advantage of this procedure is that the main isobutylene chain remains unchanged.

The β-hydroxylcarboxyl group is more versatile and reactive compared to the carboxyl group, and that is why

Scheme 1. Synthesis Route for the Preparation of α,ω-Dicarboxyl Polyisobutylenes (RT = Room Temperature)



it came into the focus of our interest. The β-hydroxylcarboxyl group can be prepared by addition of acetic acid to the aldehyde end group (path II in Scheme 1). The synthesis involves a two-step reaction: first a double anion[17,18] must be prapared by the reaction of ^{n}BuLi and acetic acid. Then in the second step this carbanion adds to the aldehyde function with the formation of the carbon−carbon bond and the hydroxyl group.

The hydroxylcarboxyl-terminated polyisobutylene was reacted with DMD in order to convert the hydroxyl group to a carbonyl function. By the preparation of an oxocarboxylic acid-terminated polymer, we can increase the number of active groups at the chain end. The carbonyl group can serve as a nucleophilic center for addition reactions since the methylene group is acidic and can be used in oxo-ester synthesis; the terminal carboxyl group is reactive and can be converted to a number of useful derivatives.

The characteristic part of the attached proton test (APT) ^{13}C NMR spectrum of the starting aldehyde telechelic and the carboxyl-teminated polymers mentioned above are shown in Figure 2.

According to the NMR spectra, complete conversion was observed in all three cases. The aldehyde peak at 210 ppm disappeared and the carboxyl signal appeared at 183, 175, and 177 ppm for the carboxyl, β-OH-carboxyl, and the β-oxocarboxyl polyisobutylenes, respectively. In the spectrum of Figure 2d the β-carbonyl signal appears at 215 ppm.

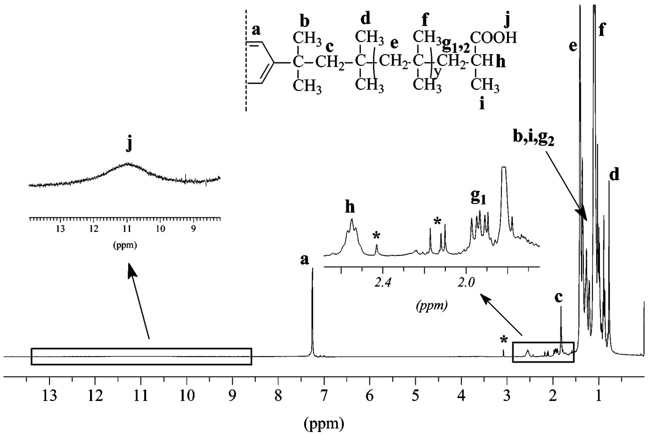


Figure 1. ^1H NMR spectrum of the α,ω-dicarboxyl telechelic polyisobutylene. The insets show the carboxyl and the terminal methylidene regions of the spectrum. The peaks marked with * are unidentified solvent peaks. Experimental conditions: OHC-PIB-CHO = 0.0125 M, DMD = 0.320 M, T = 20 °C, t = 24 h, in dichloromethane.

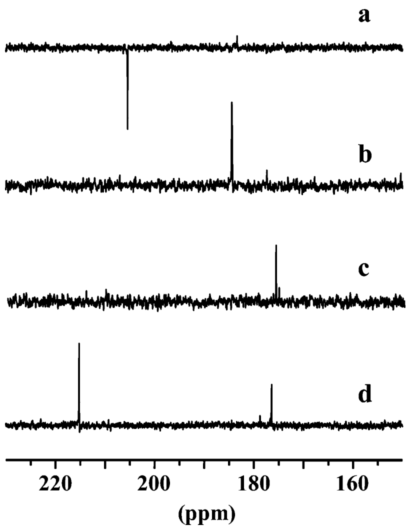


Figure 2. Attached proton test ^{13}C NMR carbonyl region of the carboxyl-terminated polyisobutylenes and that of the starting dialdehyde telechelic PIB: (a) dialdehyde telechelic polyisobutylene (signal has negative phase), (b) α,ω-dicarboxyl telechelic polyisobutylene, (c) α,ω-di(β-hydroxylcarboxyl) telechelic polyisobutylene, and (d) α,ω-di(β-oxocarboxyl) telechelic polyisobutylene.

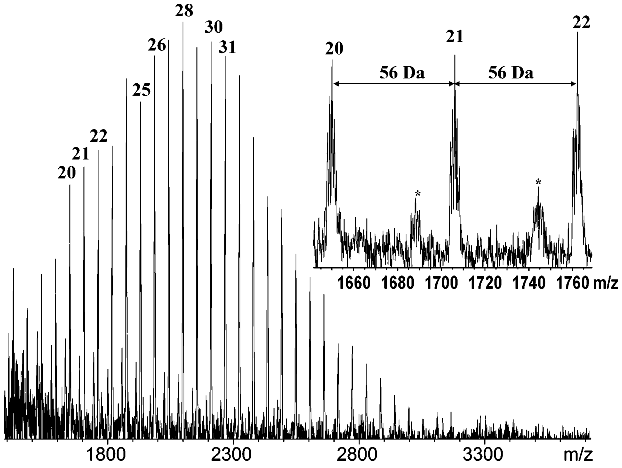


Figure 3. MALDI-TOF MS spectrum of the α,ω-di(β-hydroxylcarboxyl) telechelic polyisobutylene recorded in the reflectron mode. The numbers on the top of the peaks represent the degree of polymerization. The additional peak series (*) can be attributed to the "in-source" fragment ions formed by the loss of a water molecule under MALDI conditions. Experimental conditions: OHC-PIB-CHO = 0.0125 M, HAc = 0.250 M, ^{n}BuLi = 0.500 M, $T = -70$ °C, $t = 3$ h, in absolute THF.

The structure of the resulting polymers was also investigated by MALDI-TOF MS. The representative MALDI-TOF MS spectrum of the β-hydroxylcarboxyl-terminated PIB recorded in the reflectron mode is presented in Figure 3.

The mass of the peaks (M) in Figure 3 can be expressed as

$$M = M_{\mathrm{I}} + M_{\mathrm{end\ groups}} + nM_{\mathrm{m}} + M_{\mathrm{cat}} \qquad (1)$$

where M_{I}, $M_{\mathrm{end\ groups}}$, M_{m}, and M_{cat} stand for the mass of the initiator moiety, the end groups, the isobutylene, and the cation attached to the polymer chain (silver cationized peaks); n represents the number of the repeating units. The molecular weights calculated by eq 1 agree with the molecular weights observed by MALDI MS (Figure 3). As seen in Figure 3, the mass difference between the adjacent peaks is 56 Da, which corresponds to the mass of the repeating isobutylene unit.

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