

New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Initiator-Transfer Agents* (Inifers)

17. Synthesis and Characterization of Acryl and Methacryl Telechelic Polyisobutylenes (Polyisobutenyl Diacrylate and -dimethacrylate)

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Summary

New acryl and methacryl telechelic polyisobutylenes, $\text{H}_2\text{C}=\underset{\text{R}}{\text{C}}-\text{COO}-\text{PIB}-\text{OOC}-\underset{\text{R}}{\text{C}}=\text{CH}_2$, where $\text{R}=\text{H}$ or CH_3 , have been prepared. The syntheses involved reactions between α, ω -di(hydroxy)polyisobutylene, $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$ and excess acryloyl or methacryloyl chloride. Model studies coupled with H^1 NMR and IR spectroscopic analyses of the products indicate quantitative introduction of two $\text{H}_2\text{C}=\underset{\text{R}}{\text{C}}-\text{COO}-$ termini per polyisobutylene chain.

These prepolymers may be useful for the synthesis of a variety of new composites containing a soft polyisobutylene segment.

I. INTRODUCTION

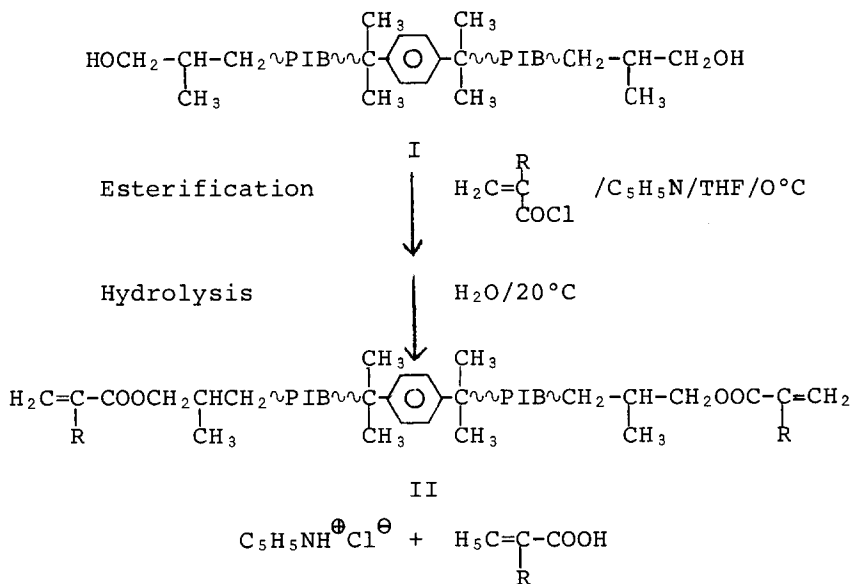
Earlier publications from this laboratory have described the synthesis of di-tert.-chloro telechelic polyisobutylene (KENNEDY, SMITH, 1980) and its dehydrochlorination to di-isopropenyl telechelic polyisobutylene (KENNEDY et al., 1979). Hydroboration of the latter yielded di-hydroxy telechelic polyisobutylene (IVAN et al., 1980) whose esterification with excess adipoyl and/or terephthaloyl chlorides followed by hydrolysis led to di-carboxy telechelic polyisobutylenes (LIAO, KENNEDY, 1981). In the course of these investigations the thought occurred to us that valuable di-acryl and di-methacryl telechelic polyisobutylenes could be obtained from di-hydroxy telechelic polyisobutylene, by esterification with excess acryloyl and methacryloyl chlorides,

Polymers carrying one acryl or methacryl terminus have been prepared by MILKOVICH et al., (1976) by capping "living" polystyrene with ethylene oxide and subsequently reacting with acryloyl or methacryloyl chloride, and by VARGAS et al., (1980), who initiated the polymerization of THF by methacryloyl hexafluoroantimonate. Di-acrylates and methacrylates of poly(ethylene oxide) have been developed as anaerobic adhesives

and sealants (KRIEBLE, 1962).

This paper concerns the synthesis and characterization of di-acryl and methacryl telechelic polyisobutylenes with excess acryloyl and/or methacryloyl chlorides. The synthesis route is shown in Scheme I.

Scheme I
Synthesis of Acryl- and Methacryl-Telechelic
Polyisobutylenes



(IIa): R=H

(IIb): R=CH₃

II. EXPERIMENTAL

A. Materials

The synthesis and purification of α, ω -di(hydroxyl)-polyisobutylene (I in Scheme I) has been described (IVAN et al., 1980); $\bar{M}_n = 3.6000$, $\bar{F}_n = 1.96 \pm 0.07$ (number average terminal functionality). THF (Fisher) was treated with potassium hydroxide and further purified by distilling from lithium aluminum hydride (Foote). Pyridine (Fisher) was treated with potassium hydroxide then refluxed over barium oxide and distilled before use. 2,4,4-Trimethyl-1-pentanol, acryloyl chloride (Aldrich), and methacryloyl chloride (Aldrich), stabilized with 100 ppm phenothiazine, were used without further purification. *n*-Pentane (Eastman) was stirred with sulfuric acid overnight then washed with water and separated.

B. Techniques

Esterification - Esterifications with metha-

cryloyl chloride and acryloyl chloride were carried out in three-neck round bottom flasks equipped with stirrer and dropping funnel under dry N_2 at $0^\circ C$. A solution of acid chlorides in THF (five-fold excess on the polyisobutylene) was added into α, ω -di(hydroxy)polyisobutylene (1 wt% in THF) and pyridine (three-fold excess on the acid chlorides). After five hours stirring at room temperature water (half vol. of THF) was added and the mixture was hydrolyzed for five hours. Subsequently, n -pentane was added, stirred for a few minutes and the organic layer was separated. After washing several times with distilled water the organic layer was dried with anhydrous magnesium sulfate. After filtration the solvent was evaporated and the product dried under vacuum at ambient temperature.

H^1 NMR analysis was carried out by a Varian Associates T-60 NMR instrument, IR spectra were recorded on a Perkin-Elmer 521 grating IR spectrometer by using 0.5 mm KBr cells and CCl_4 solutions. M_n was determined by GPC using a Waters Associates 6000 A (high pressure) pump, dual (UV and RI) detectors, and Microstyrigel columns of 10^6 , 10^5 , 10^4 , 10^3 , 600 A. Elution counts were calibrated by polyisobutylene standards.

Results and Discussion

1. Model Experiments

Orienting experiments have been carried out with 2,4,4-trimethyl-1-pentanol (TMP), a readily available model of $HOCH_2-CH(CH_3)CH_2-PIB-CH_2CH(CH_3)-CH_2OH$. Thus esterifications of TMP were carried out with acryloyl chloride and methacryloyl chloride. The H^1 NMR spectra of the 2,4,4-trimethyl-1-pentyl acrylate and -methacrylate are shown in Figures 1 and 2. The resonances identified and assigned in the figures indicate complete conversion of TMP. Examination of IR spectra of the products also indicate quantitative conversion of the hydroxy end groups to the unsaturated ester end groups. The characteristic absorption of the hydroxy group at 3640 cm^{-1} disappears upon esterification and new peaks associated with the acrylic and methacrylic ester groups appear at 1720 and 1725 cm^{-1} , respectively.

2. Esterification of $HOCH_2CH(CH_3)CH_2-PIB-CH_2CH(CH_3)CH_2OH$ with Acryloyl and Methacryloyl Chlorides.

Scheme I helps to visualize the synthesis steps. The by-products can be readily removed by washing with water. Reaction rates were enhanced by the use of pyridine (SONNTAG, 1953) and the extent of side reactions was minimized by reacting at relatively low temperatures ($0^\circ C$). The free radical polymerization of the chlorides was prevented by the phenothiazine inhibitor. Due to low end group concentrations the reaction time was long (5 hours).

Figures 3 and 4 show H^1 NMR spectra of IIa and IIb.

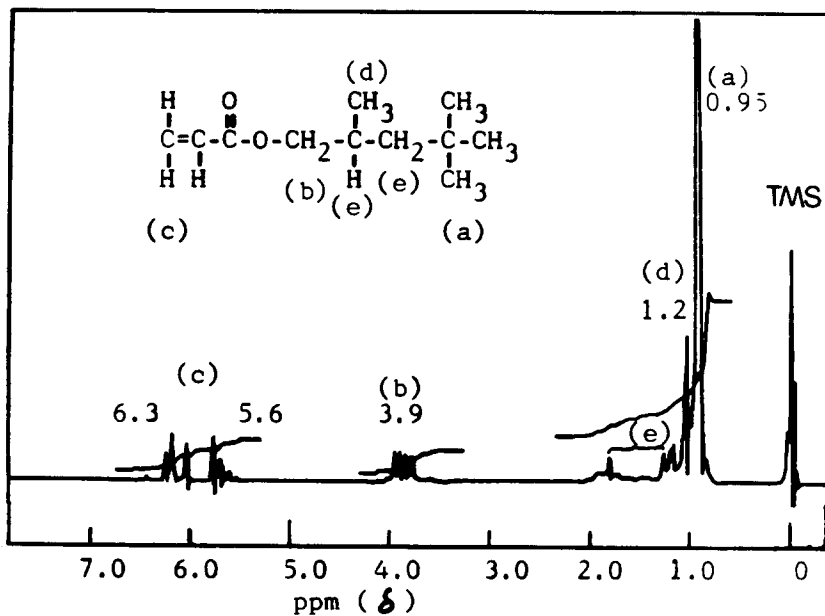


Fig. 1: NMR spectrum of 2,4,4-trimethyl-1-pentyl acrylate (in CCl_4).

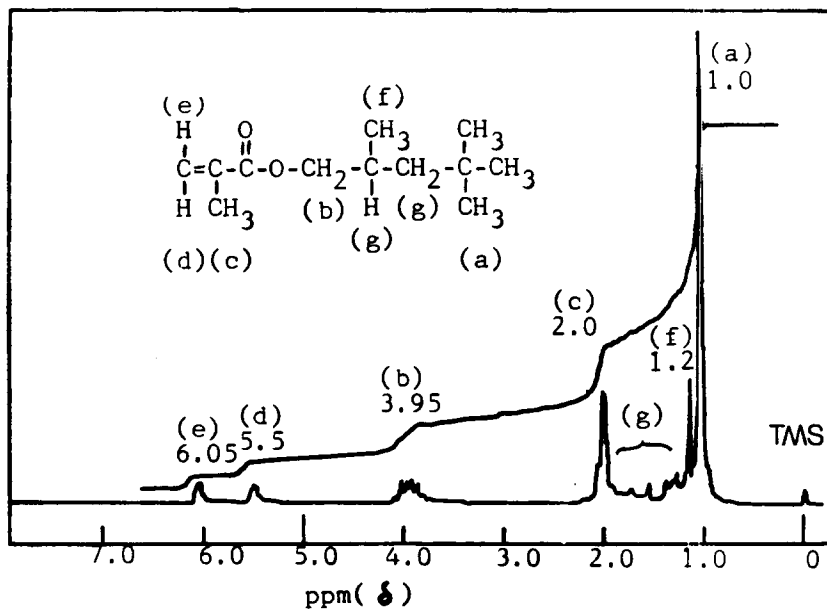
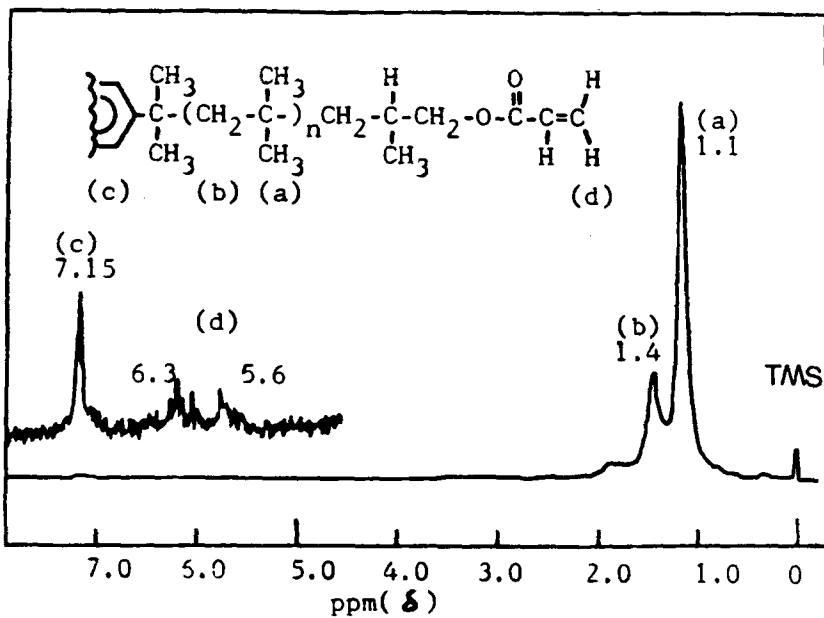
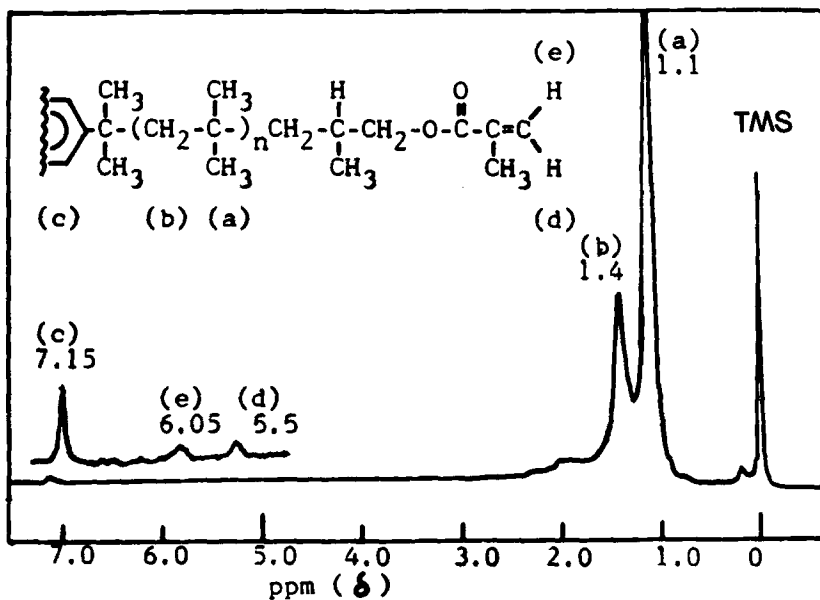


Fig. 2: NMR spectrum of 2,4,4-trimethyl-1-pentyl methacrylate (in CCl_4).

Figure 3. The NMR spectrum of IIa (in CCl_4).Fig. 4. The NMR spectrum of IIb (in CCl_4).

Resonances are identified in the Figures. The aromatic inifer fragment in the products is an internal standard for quantitative end group determination. Thus integration and correlation of the four aromatic inifer protons (6.95-7.35 ppm) with the terminal

$\text{---C} = \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ protons (5.3-5.7 and 5.85-6.25 ppm) in IIb
 and the terminal $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} = \text{C} = \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$ protons (5.6-6.3 ppm) in IIa

yield $\bar{F}_n = 1.95 \pm 0.08$ for IIb and 1.95 ± 0.09 for IIa, respectively.

Major IR absorptions and corresponding structures are shown in Table I. The characteristic absorptions of HOCH₂- termini at 3640 cm⁻¹ (monomer) and 3480 cm⁻¹ (dimer) (LIAO, KENNEDY, 1981) disappear after esterification and strong peaks associated with unsaturated ester groups appear at 1720 cm⁻¹ and 1725 cm⁻¹ for methacrylate and acrylate groups, respectively. The intensity ratios of the C=O to C=C double bonds of the methacrylic or acrylic ester moiety are about 10 which is in agreement with Vargas' result (VARGAS et al., 1980).

TABLE I

Infrared Absorptions of Acryl and Methacryl
Telechelic Polyisobutylenes

cm ⁻¹	Assignments
950 (m), 920 (m)	-CH ₂ -C(CH ₃) ₂ -, skeletal
1250 (s)	-C(CH ₃) ₂ -, skeletal
1360 (s), 1380 (s)	δ CH ₃ (gem-dimethyl)
1470 (s)	ω CH ₂
1630 (m), 1670 (m)	ν C=C
1720 (s)	C=C(CH ₃)-CO-O-
1725 (s)	C=CH-CO-O-
2960 (s), 2870 (m)	ν CH
2925 (s), 2880 (m)	ν CH ₃
3030 (s)	ν CH (arom.)

m = medium

s = strong

Acknowledgement

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