

Tri-*n*-butylborane Oxide-Initiated Homopolymerization of Vinyl Monomers Containing Cyano or Isocyanato Groups

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SYNOPSIS

Homopolymers of 2-isocyanatoethyl methacrylate, ethyl α -cyanoacrylate, and ethyl α -isocyanatoacrylate were prepared in tetrahydrofuran at 22 to 25°C using tri-*n*-butylborane oxide as a free radical initiator. Additionally, ethyl α -isocyanatoacrylate was homopolymerized using 2,2'-azobis(2-methylbutyronitrile) as the initiator. Homopolymers were characterized by photoacoustic FT-IR, DSC, and elemental analysis. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The use of alkylboron compounds and their derivatives as free radical initiators for vinyl polymerization has been reported.¹ One oxidized derivative, tri-*n*-butylborane oxide (TBBO), is currently marketed as the catalytic component of a dental adhesive luting cement kit.² Recently, TBBO has been investigated as an initiator for the neat homopolymerization of isocyanatoacrylate esters³ and used in adhesion studies of isocyanatoacrylates to dentin.⁴

The vinyl homopolymerization of 2-isocyanatoethyl methacrylate (IEM) has been carried out in dry solvents using azobisisobutyronitrile (AIBN) as a free radical initiator.⁵ Copolymers of IEM and ethyl α -isocyanatoacrylate (α -EIA) with selected vinyl monomers have been prepared neat at 60°C using 2,2'-azobis(2-methylbutyronitrile), VAZO 67, as the initiator.⁶

The homopolymerization of ethyl α -cyanoacrylate (α -ECA) has been initiated by triethyl and triphenylphosphine,⁷ pyridine and polyvinylpyridine,⁸ dimethylformamide,⁹ and simple anions, or covalent organic bases.¹⁰ Various mechanisms for the polymerization of cyanoacrylates, depending on the chosen initiator, have been suggested.¹¹

We report here the preparation and preliminary characterization of IEM, α -EIA, and α -ECA homopolymers. Homopolymerizations were conducted in THF at 22 to 25°C using TBBO as a free radical initiator. A homopolymer of α -EIA was also prepared using VAZO 67 as the initiator.

EXPERIMENTAL

Materials

Hexane UV (Baxter Chemical Co.) was used as received; tetrahydrofuran, THF (Taylor Chemical Co.) was dried with LiAlH₄, redistilled, and stored over 4A molecular sieves prior to use except where noted; 2,2'-azobis(2-methylbutyronitrile), VAZO 67 (Du Pont), was used as received; C&B METABOND Catalyst, TBBO (Parkell Biomaterials), was used as received; ethyl α -cyanoacrylate, α -ECA (Sigma) was used as received; 2-isocyanatoethyl methacrylate, IEM (Monomer-Polymer Laboratories) was redistilled at reduced pressure prior to use; ethyl α -isocyanatoacrylate, α -EIA, was synthesized in house¹² and was molecularly redistilled at 0.025 to 0.005 mmHg, collected in an ortho-xylene/liquid N₂ slush bath (-29°C), and equilibrated to room temperature immediately prior to use.

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Characterization

Homopolymers were characterized by infrared spectroscopy (IR), differential scanning calorimetry (DSC), and elemental analysis (ANAL).

IR: 0.05 wt % in KBr disk (2 mm thick); Perkin-Elmer Model 283. DSC: Al pan with inverted lid at a heating rate of 20°C/min under 40 mL/min N₂; Du Pont Thermal Analyzer Model 1090. ANAL: Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Homopolymerizations

The homopolymerization of α -ECA was carried out at room temperature (22 to 25°C) using appropriate solvent-resistant Nalgene[®] labware. Into a 125 mL flask was added 40 mL (35.6 g) THF (used as received) and 4.1 g α -ECA. TBBO catalyst was added to the magnetically stirred mixture in two aliquots, 3 h and 20 min apart. The total catalyst dose was 1.81 wt % based on α -ECA. The mixture was covered with a watch glass and stirred for ~ 21 h. An additional 10 mL THF was added to the clear, viscous mixture to aid in handling and transfer. The reaction mixture was drawn into a plastic syringe and added gradually to 250 mL vigorously stirred hexane in a 500 mL flask. After the precipitated polymer was fully dispersed, it was collected by centrifuging at 10,000 rpm for 10 min and dried at room temperature under vacuum (0.05 to 0.025 mmHg) for 17 h. The yield was 2.9 g (70.8%).

ANAL: calcd. for (C₆H₇NO₂)_n: C, 57.59%, H, 5.64%, N, 11.19%.

Found: C, 56.26%; H, 6.15%; N, 10.37%.

IR: 3000, 2260, 1755, 1475, 1450, 1395, 1375, 1255, 1160, 1115, and 1015 cm⁻¹.

DSC: one endothermic transition; maximum at 278.2°C; heat flow 508 J/g.

The homopolymerization of IEM was carried out at room temperature (22 to 25°C). All glassware was flame dried under nitrogen or argon. Reaction mixture additions and transfers were made in such a way as to minimize exposure to air and moisture. Into a 125 mL flask was added 10.0 g IEM and 100 mL (88.9 g) THF. TBBO catalyst was added to the magnetically stirred mixture at 4.1 wt % based on IEM. The mixture was purged (3 min) with argon, stoppered, stirred for 26.5 h until near the gel point, and transferred in small amounts to a 2-L flask containing 500 mL vigorously stirred hexane. After the precipitated polymer was fully dispersed, it was al-

lowed to settle, and the mother liquor was decanted off. The polymer was washed by stirring in an additional 200 mL hexane, collected by centrifuging at 10,000 rpm for 10 min, and dried at room temperature under vacuum for 21.5 h. The yield was 6.22 g (62.2%).

ANAL: calcd. for (C₇H₉NO₃)_n: C, 54.19%, H, 5.85%, N, 9.03%.

Found: C, 53.56%; H, 6.8%; N, 8.94%.

IR: 2960, 2290, 1735, 1550, 1460, 1390, 1355, 1270, 1150, and 1035 cm⁻¹.

DSC: one exothermic transition; maximum at 311.2°C; heat flow 67 J/g.

The homopolymerization of α -EIA was carried out at room temperature (22 to 25°C) by two methods. All glassware was flame dried under nitrogen or argon. Reaction mixture additions and transfers were made in such a way as to minimize exposure to air and moisture.

Method I

Into a 125-mL flask was added 1.95 g α -EIA and 20 mL (17.78 g) THF. TBBO catalyst was added to the magnetically stirred mixture at 3.47 wt % based on α -EIA. The mixture was blanketed with argon, stoppered, and stirred for 18 h. The reaction mixture was then transferred into a 500-mL flask containing 150-mL vigorously stirred hexane. After the precipitated polymer had been fully dispersed, it was collected by centrifuging at 10,000 rpm for 10 min and dried at room temperature 16–1/2 h under vacuum (0.05 to 0.025 mmHg). The yield was 0.55 g (28%).

ANAL calcd. for (C₆H₇NO₃)_n: C, 51.07%, H, 5.00%, N, 9.92%.

Found: C, 50.40%; H, 5.65%; N, 9.72%.

IR: 2995, 2280, 1745, 1475, 1450, 1375, 1265, 1140, and 1010 cm⁻¹.

DSC: one exothermic transition; maximum at 235.5°C; heat flow 120 J/g.

Method II

Into a 125-mL flask was added 8.0 g α -EIA and 80 mL (71.1 g) THF. Vazo 67 was added to the magnetically stirred mixture at 4.0 wt % based on α -EIA. The reaction mixture was blanketed with argon and stirred for 42 h. The mixture was transferred in several aliquots into a 2-L flask containing 400 mL vigorously stirred hexane. An additional 50 mL hexane was used to transfer residual polymer from

the reaction flask. After the precipitated polymer was fully dispersed, it was collected by centrifuging at 10,000 rpm for 10 min and dried at room temperature under vacuum (0.05 to 0.025 mmHg) for 19 h. The yield was 3.65 g (46.5%).

ANAL: calcd. for $(C_6H_7NO_3)_n$: C, 51.07%, H, 5.00%, N, 9.92%.

Found: C, 49.88%; H, 5.04%; N, 9.86%.

IR: 2995, 2280, 1745, 1475, 1450, 1375, 1265, 1140, and 1010 cm^{-1} .

DSC: two exothermic transitions with the maxima at 133.4°C (heat flow 31.3 J/g), and 227.6°C (heat flow 123 J/g).

RESULTS AND DISCUSSION

General Remarks

All homopolymer reaction mixtures formed easily dispersed precipitates in hexane resulting in fine white powders when dry. Nalgene[®] labware was used in the homopolymerization of α -ECA to circumvent potential problems with monomer reactivity at and polymer adhesion to active glass surface sites. Homopolymerizations of IEM and α -EIA were conducted at room temperature in dried glassware and solvent under argon to minimize the loss of isocyanate groups by hydrolysis to primary amines, and formation of urea crosslinks. The IEM homopolymer appeared to remain in solution until very near the gel point, at which time the reaction mixture became slightly clouded. In contrast, the homopolymer of α -EIA began to appear in a near colloidal state within 5 to 10 min after addition of the TBBO catalyst. The α -ECA homopolymer remained in solution until precipitation in hexane.

Characterization

α -ECA Homopolymer

Elemental analysis yielded lower values for %C and %N and a higher %H value than expected for $(-C_6H_7NO_2-)$, perhaps as a result of occluded residual catalyst. The IR spectrum showed C—H stretching at 3000 cm^{-1} , C=O stretching at 1755 cm^{-1} , and an active C—O stretching region with a maximum at 1255 cm^{-1} . The C=N stretching peak at 2260 cm^{-1} was sharp, but very weak, not unusual for cyano compounds also containing oxygen. DSC

revealed one endothermic transition with the maximum at 278.2°C and heat flow of 508 J/g.

IEM Homopolymer

Elemental analysis yielded a lower value for %C and a higher value for %H than predicted for $(-C_7H_9NO_3-)$, most probably due to some hydrolysis of the isocyanate functionality (NCO). The IR spectra showed C—H stretching at 2960 cm^{-1} , N=C=O stretching at 2290 cm^{-1} , C=O stretching at 1735 cm^{-1} , and an active C—O stretching region with a maximum at 1150 cm^{-1} . DSC revealed one exothermic transition with the maximum at 311.2°C and a heat flow of 67 J/g.

α -EIA Homopolymers

Discrepancies between the values found by elemental analysis for %C, %H, and %N and those calculated for $(-C_6H_7NO_3-)$ are probably due to some hydrolysis of the isocyanate functionality. The IR spectra of both homopolymers were nearly identical showing C—H stretching at 2995 cm^{-1} , N=C=O stretching at 2280 cm^{-1} , C=O stretching at 1745 cm^{-1} , and an active C—O stretching region with the maximum at 1140 cm^{-1} . DSC of the homopolymer prepared by Method I (TBBO catalyst) showed one exothermic transition with the maximum at 235.5°C and heat flow of 120 J/g. DSC of the homopolymer prepared by Method II (VAZO 67 catalyst) showed two exothermic transitions, the first with the maximum at 133.4°C and heat flow of 31.3 J/g, and the second with a maximum at 227.6°C and heat flow of 123 J/g.

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