Synthesis, Characterization and Diels-Alder Extension of Cyclopentadiene Telechelic Polyisobutylene

2. \(\alpha\)-Dicyclopentadienyl-\(\omega\)-t-Chloropolyisobutylene*, **

J.P. Kennedy, G.M. Carlson† and K. Riebel‡

Institute of Polymer Science, The University of Akron, Akron, OH 44325, USA

Abstract

The use of 1-chlorodicyclopentadiene (DCp-Cl) as a minifer for the polymerization of isobutylene leading to asymmetric telechelic polymers having dicyclopentadienyl head groups and t-chloro tail groups, has been investigated. BCl₃ is ineffective, however, diethylaluminum chloride was found to be a suitable coinitiator for the polymerization. According to kinetic investigations chain transfer to monomer is absent and DCp-Cl is an efficient minifer. Polymer characterization indicated a DCp functionality close to 1.0. The t-chloro functionality was 0.27, probably due to side reactions of the t-chloro group with the strong Lewis acids formed during the polymerization.

Introduction

The use of binifers has led to the synthesis of \(\alpha,\omega\)-di(t-chloro)-polyisobutylene¹, \(\alpha\)-Cl-PIB-Cl² whose derivatization has led to numerous novel telechelic polyisobutlenes carrying various useful end groups, e.g., isopropenyl², hydroxyl³, dimethylsilylchloride⁴. These polymers are symmetrically substituted, i.e., they carry the same functions at each terminus. This symmetry is due to the symmetrical binifer, \(p\)-dicumyl chloride, used for the synthesis of the parent compound \(\\alpha\)-Cl-PIB-Cl². Recently experimentation has also been extended to the preparation of asymmetric telechelic prepolymer \(A\\wedge\wedge B\), i.e., telechelics carrying different functional groups A and B at either chain end, by the use of minifers. The principles governing the synthesis with minifers have been discussed and the preparation of \(\alpha\)-phenyl-\(\omega\)-t-chloropolyisobutylene by the cumyl chloride/BCl₃/isobutylene minifer system was described⁵,⁶. This paper concerns an extension of research on minifers, in particular the synthesis and characterization of \(\alpha\)-dicyclopentadienyl-\(\omega\)-t-chloropolyisobutylene DCp-PIB-Cl², a new asymmetric telechelic prepolymer.

It was theorized that DCp-PIB-Cl² could be prepared by 1-chlorodicyclopentadiene, DCp-Cl, as the minifer in conjunction with a suitable Friedel-Crafts acid coinitiator. DCp-Cl is in fact an allylic chloride and as such was visualized to lead to controlled initiation (head group control). Further the DCp head group was thought to lead to the versatile cyclopentadiene, Cp, head group upon thermal cracking:

\[
\begin{align*}
\text{Cl} & \quad \to \quad \text{PIB} \\
\text{Cl} & \quad \to \quad \text{PIB}
\end{align*}
\]

\* Pa~ XXXII of the series 'Yew ~lechelic Polymers and Sequential Copolymers by Poly~n~ional Initiator-Trans~r ~ents (Ini~rs)'.

\** The first part of this series was presented at the Kansas City Am. Chem. Soc. Meeting, September 12-17, 1982, Polym. Prepr., 23, 103 (1982) which is considered Pa~ XXXI of the series 'New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)'.

† Present address: Glidden Coatings and Resins, Strongsville, OH 44136, USA

‡ Present address: Bayer AG, Leverkusen, Federal Republic of Germany
DCp–Cl should also act as a chain transfer agent yielding a new growing chain and a PIB chain having a t-chloro tail group:

$$\text{DCp} \quad \text{CH}_2-\text{C} + \quad \text{DCp} \quad \text{CH}_2-\text{C}-\text{Cl}$$

The resulting polymer (DCp–PIB–Cl) would have a DCp head group formed during initiation or chain transfer to DCp–Cl and a Cl$^-$ tail group. Since PIB's having Cl$^-$ termini have been shown to initiate α-methylstyrene polymerization$^7$, the synthesis of poly(isobutylene-α-α-methylstyrene) was envisioned. Thermal cracking of the DCp head group would yield α-cyclopentadienyl-ω-poly(isobutylene-α-α-methylstyrene) and Diels-Alder dimerization of this diblock would give a most intriguing A-B-A triblock copolymer.

Experimental

Materials

Materials, purification and handling techniques have been described (1-7). DCp–Cl was synthesized by the method of Dilling et al.$^8$

Polymer Synthesis

Equipment and procedures have been described (1-7). Typically the reactors were charged with solvent followed by condensed isobutylene, DCp–Cl, and finally Et$_2$AlCl or BCl$_3$. Polymerizations began immediately. Pre-cooled methanol was added to quench. The polymers were dissolved in n-hexane and washed with aqueous sodium potassium tartrate to remove aluminum oxide residues.

Polymer samples were analyzed using a Waters Associates 6000 A High Pressure Gel Permeation Chromatograph equipped with ultraviolet (UV) and refractive index (RI) detectors and Microstyragel columns of 10$^6$, 10$^4$, 10$^3$, and 500 Å. Approximately 0.2 ml of a 0.2% polymer in tetrahydrofuran solution was used at a flow rate of 2 ml/min. Fractionated samples of polyisobutylene having narrow molecular weight distributions were used as standards to construct a calibration curve.

The DCp head group was analyzed using a Perkin-Elmer 559-A UV/Vis Spectrophotometer. A sample of DCp–PIB–Cl was heated to 160°C at 0.5 mm to crack the DCp head group. The polymer was dissolved in spectrograde n-hexane and the UV absorbance determined using a path length of 1 cm. Using α-propyl cyclopentadiene as a model compound for the cyclopentadiene absorbance, it was possible to determine the DCp functionality of the polymer.

The Cl$^-$ end group concentration was determined by quantitative thermal dehydrochlorination$.^9$ A thin polymer film was coated on the inner surface of a U-shaped glass tube and heated to 180°C while dry nitrogen was passed through this tube. The evolved HCl was swept into water whose conductivity was measured.

Results and Discussion

1. Orienting Experiments with the DCp–Cl/BCl$_3$ System

Initially BCl$_3$ was examined as a coinitiator. BCl$_3$ is preferred for the synthesis of t-chloro telechelic polymers because this end group is formed during termination as well as during chain transfer$^7$. Results are shown in Table I. DCp–Cl did not produce increased conversions beyond those obtained in control runs. Evidently the polymer arises via initiation due to protogenic impurities i.e., water. Conversions increased with decreasing temperature in the control experiments as well as in those containing DCp–Cl because termination is frozen out by lowering the