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Lockmann's Base System

Delocalized Carbanions:
Synthesis and Polymerization of 2,3-Disubstituted-1,3-Butadienes

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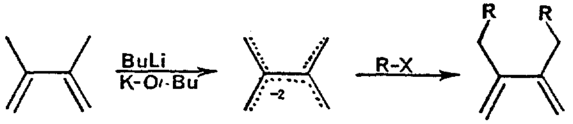
Summary

The 2,3-dimethylene-1,3-butadiene dianion (2) was prepared from 2,3-dimethyl-1,3-butadiene (1) using Lochmann's base (n-BuLi/potassium-t-butoxide in pentane). The dianion was reacted with primary halides to yield 2,3-disubstituted-1,3-butadiene monomers. These monomers were polymerized free radically with AIBN and with Ziegler/Natta coordination catalysts. The resulting polymers were examined by DSC for crystallization of the polymer backbone and alkyl side chains.

Introduction

The synthetic utility of delocalized carbanions resulting from the abstraction of a proton alpha to a double bond has been established(2) using strong metalating agents such as n-butyllithium/tetramethylethylenediamine (n-BuLi/TMEDA)(3,4) or Lochmann's base system (n-BuLi/potassium-t-butoxide in pentane).(5,6,7) Lochmann's base system has been shown to cause allylic metalation of conjugated dienes, with the notable exception of isoprene where the butyl anion adds to the conjugated diene instead of abstracting the alpha proton.(8) However, metalation of 2,3-dimethyl-1,3-butadiene (1) proceeds cleanly and quickly (10 min) to the 2,3-dimethylene-1,3-butadiene dianion (2) in yields of greater than 80%. Dianion 2 reacts with primary halides in an S_N2 manner to yield 2,3-disubstituted-1,3-butadienes (Scheme 1).(9) The synthesis of these compounds has been identified as a desirable goal for the preparation of disubstituted polybutadienes.(11)

Scheme 1: Preparation of 2,3-dialkyl-1,3-butadiene monomers(10)



1 2 3a-e

Compound	R	% Yield
3a	CH_3	78
3b	CH_2CH_3	80
3c	$(CH_2)_3CH_3$	60
3d	$(CH_2)_{11}CH_3$	74
3e	$(CH_2)_{17}CH_3$	78

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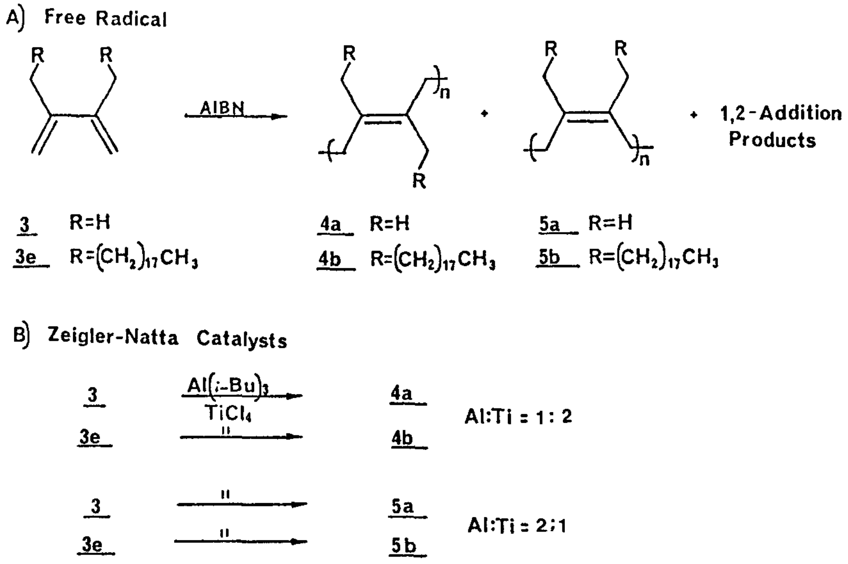
The polymerization of conjugated dienes can be initiated free radically using 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator. In addition, polymerization can be initiated with Ziegler/Natta coordination catalysts $TiCl_4$ and $Al(i\text{-}Bu)_3$ to control the stereochemistry and obtain the desired cis- and trans-1,4-polymers (Scheme 2). The resulting polymers have been examined by DSC to study crystallization of the polymer backbone and alkyl side chains.

Scheme 2: Polymerization of 2,3-Dialkyl-1,3-Butadiene Monomers



Experimental

$Al(i\text{-}Bu)_3$ and $TiCl_4$ were used as received from Alpha Division, Ventron Corp. AIBN was recrystallized twice from methanol and all other reagents were purified by standard methods. DSC endotherms were recorded on a Perkin Elmer DSC 2 instrument. Preparation of anion 2 and monomers 3a-e have been previously described.(10)

Poly-2,3-Dimethyl-1,3-Butadiene: In a clean, dry, 25 ml flask was placed 2.9g (35 mmole) 2,3-dimethyl-1,3-butadiene and 110mg (.067 mmole) AIBN and then flushed with N_2. The flask was degassed by five freeze-thaw cycles, at 0.10 mm, and placed in a constant temperature bath at 65°C under N_2. The polymerization proceeded for 72 hr. The contents of the flask were poured into 25 ml of methanol. Rotary evaporation of the methanol, followed by drying in a vacuum oven gave a tacky polymer in 18% yield.

Poly-2,3-Dinonadecyl-1,3-Butadiene: A clean, dry 25 ml flask was charged with 2.0g (3.5 mmole) 3e and 11mg (.006 mmole) AIBN. The polymerization and isolation were the same as for poly-2,3-dimethyl-1,3-butadiene. A white tacky polymer was obtained in 15% yield.

Trans-Poly-2,3-Dimethyl-1,3-Butadiene (4a): In a dry 250 ml round bottom flask 50 ml heptane was placed under N_2. To the heptane, 0.03g (0.15 mmole) $Al(i\text{-}Bu)_3$ and 0.05g (0.30 mmole) $TiCl_4$ was added via a syringe and stirring was continued for 25 min. To the aged catalyst system, 5.0g (61 mmole) of 3 was added and the polymerization was allowed to proceed for 24 hr. Afterwards, 10 ml of 10% HCl in MeOH was added to terminate the polymerization. The contents of the flask were poured into 50 ml of MeOH and the white polymer was isolated by filtration, washed with MeOH and dried under vacuum in 75% yield.

Trans-Poly-2,3-Dinonadecyl-1,3-Butadiene (4b): In a 500 ml round bottom flask was added 250 ml heptane under N_2. To this, 0.15g (0.75 mmole) $Al(i\text{-}Bu)_3$ and 0.28g (1.5 mmole) $TiCl_4$ was added. After 25 min of stirring, 1.8g (3.1 mmole) 3e was added and the polymerization continued for 24 hr. The purification was the same as for 4a. A white polymer was obtained in 73% yield.

Cis-Poly-2,3-Dimethyl-1,3-Butadiene (5a): In a 250 ml round bottom flask 50 ml heptane was added under N_2. To this, 0.25g (1.3 mmole) $Al(i\text{-}Bu)_3$ and 0.12g (0.64 mmole) $TiCl_4$ was added and stirring continued for 25 min. To the aged catalyst system, 5.0g (61 mmole) of 3 was added and the polymerization continued for 24 hr. The purification was the same as for 4a. A white polymer was obtained in 71% yield.

Cis-Poly-2,3-Dinonadecyl-1,3-Butadiene (5b): In a 500 ml round bottom flask was added 250 ml heptane under N_2. To this, 1.28g (6.5 mmole) $Al(i\text{-}Bu)_3$ and 0.61g (3.25 mmole) $TiCl_4$ was added. After 25 min of stirring, 1.8g (3.1 mmole) 3e was added and the polymerization proceeded for 24 hr. The purification was the same as for 4a. A white polymer was obtained in 70% yield.

Results and Discussions

Generally delocalized carbanions react readily with primary halides, epoxides, primary sulfates and carbonyl groups in an S_N2 manner.(10,12) The reaction of 2 with primary halides and sulfonates goes rapidly and in high yields (60-80%, Scheme 1). The compounds synthesized by this method have been analyzed by ^1H NMR and have been reported in a previous publication.(10) This procedure is a facile preparation of 2,3-disubstituted-1,3-butadiene monomers as compared to a recently published procedure.(11)

The polymerization of compounds 1 and 3e was done free radically using AIBN as the initiator. In each case, a white tacky polymer was produced in low yields (15-18%). Thermal analysis of these polymers showed no well defined endotherms above 0°C. This observation is consistent with other work which has shown substituted butadienes polymerized free radically yield a polymer of mixed microstructure with random placements of 1,4-cis-, 1,4- trans- and 1,2-addition which prevents crystallization of both the polymer backbone and the alkyl side chains.(13)

Stereoregular polymers were synthesized with Ziegler/Natta coordination catalysts. Vogl et al., have shown that the polymerization of 2,3-dimethyl-1,3-butadiene with $Al(i\text{-}Bu)_3$ and $TiCl_4$ coordination catalysts in an Al:Ti ratio of 2:1 forms the 1,4-cis- product. However, when the polymerization was done with an Al:Ti ratio of 1:2, the 1,4-trans- product was obtained (Scheme 2).(13)

Thermal analysis using Differential Scanning Calorimetry was used to study the thermal properties of the disubstituted butadiene polymers. The trans- and cis-polymers (4a and 5a) are high melting crystalline materials with melting points of 280°C and 190°C, the glass transition temperatures are 22°C and 2°C respectively. These results are in agreement with previously recorded results on the same compound,(13) with the higher values corresponding to the trans compound.

It has been observed that small alkyl substituents do not change the T_g of polymers appreciably, whereas bulky substituents, such as isopropyl groups, increase the T_g and long normal alkyl groups as substituents decrease the T_g of the polymers.(14) Polymers with long side chains are comb-like and the effects of the length of n-alkyl side chains on their T_g, T_m and crystallinity has been investigated.(14-16) The polymers studied have been based on alpha olefins(15), polyaldehydes(16) and especially methacrylates(14). Their thermal behavior shows crystallization of the polymer backbone and of the aliphatic side chains as a function of the side-chain length.

In polymethacrylates the polymer is inherently non-crystalline, and it was found that a side-chain length of 12 carbon atoms was necessary to observe side-chain crystallinity.(14) In polyaldehydes, with side chains greater than 11 carbons in length, it is observed that the side-chain crystallization contributes to the crystallinity of the polymer,(16) and in polyterephthalates of 2,3-disubstituted-1,4-butanediols it has been observed that a side-chain length of 10 carbon atoms was needed to produce side-chain crystallization in the polymer.(14)

Thermal analysis of 4b showed two endotherms at 178°C and 192°C while 5b also showed two endotherms at 161°C and 191°C. Since these polymers have side chains of 18 carbon atoms, and side-chain crystallization has been observed for side-chain lengths of $>$ 10 carbon atoms in other systems,(14-16) one endotherm can be assigned to the melting of the crystalline side chains, and the other to the polymer backbone.

Future studies of this work include the synthesis and stereoregular polymerization of 2,3-disubstituted butadiene monomers, with various alkyl side-chain lengths to examine the lower limit of the alkyl group length that will cause side-chain crystallization and the effects of these alkyl groups on the polymer properties.

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