

Synthesis of Polymers with π -Conjugated Molecules Using a Rearrangement Method

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Abstract

π -Polymerization is typically the sole way to make conjugated polymers. Typical conjugated polymer synthesis methods are briefly discussed in this viewpoint article, and a novel way for producing conjugated polymers via rearrangement is given. Many conjugated structures were produced in polybutadiene during the metalation process due to double bond migration. On the product structure, the effects of reaction duration, temperature, and catalyst dose were examined. FTIR, ¹H NMR, and 2D HSQC NMR spectra were also used to validate the structure of the compounds. Thus, a possible reaction mechanism was proposed, in which polybutadiene generates allylic carbanions in the presence of n-butyllithium, and then the double bonds migrate through the carbanions rearrangement to generate many conjugated structures in the backbone chain. π -Polymerization is typically the sole way to make conjugated polymers. Typical conjugated polymer synthesis methods are briefly discussed in this viewpoint article, and a novel way for producing conjugated polymers via rearrangement is given. Many conjugated structures were produced in polybutadiene during the metalation process due to double bond migration. On the product structure, the effects of reaction duration, temperature, and catalyst dose were examined. FTIR, ¹H NMR, and 2D HSQC NMR spectra were also used to validate the structure of the compounds. In the presence of n-butyllithium, polybutadiene forms allylic carbanions, and subsequently the double bonds migrate through the carbanions rearrangement to generate numerous conjugated structures in the backbone chain, according to one probable reaction process.

Keywords: Polymerization; Synthesis; polymers; Carbanion; Conjugated polymers

Introduction

Polymers with conjugated structures in the backbone chain are known as π -conjugated polymers. Chemical and physical characteristics of π -conjugated polymers differ greatly depending on their structure. The use of these various π -conjugated polymers in chemistry and materials research indicates a potentially rich sector. Conjugated polymers have recently gained popularity, and their applications, such as intrinsically conducting polymers, solar cells, and organic light emitting diodes, are becoming increasingly common (OLEDs). Furthermore, because conjugated double bonds have higher reactivity than isolated double bonds, conjugated polymers are commonly utilized as substrates for chemically modifying high-performance materials. Conjugated polymers, for example, may be changed by cycloaddition events to make a variety of functional polymers, and they can also be employed as macro monomers to make polymers with complicated topologies and good hydrodynamic characteristics.

Polymerization, including coordination polymerization and condensation polymerization, is used to make conjugated polymers in general. Natta and colleagues described the synthesis of poly-acetylene using Ti/Al catalysts in 1958, which was a coordination polymerization approach. Researchers have been paying close attention to the use of conjugated polymers in growing industries like solar cells and OLEDs in recent years. Condensation polymerization, particularly Suzuki coupling polymerization, is employed to make most of the innovative π -conjugated materials used in these domains.

A major subject in this sector has been the development of innovative techniques for the production of conjugated polymers. Various palladium- and nickel-catalyzed cross-coupling processes have been developed throughout the years, allowing the coupling of aryl halides with organometallic aryl derivatives, resulting in a flexible tool for the synthesis of conjugated polymers. Direct

Arylation Polymerization (DArP) has lately gained popularity due to its effectiveness and environmental friendliness. The synthesis of monomers in DArP is typically simple, no organostannane or organ boron monomers are required, and the by-products are less harmful, all of which are in accordance with green chemistry standards.

As can be seen from the examples above, one of the aims pursued by researchers in this field is the development of convenient, low-cost, and environmentally acceptable techniques for the synthesis of conjugated polymers. Furthermore, scientists have struggled to develop and manufacture sophisticated conjugated polymers due to a lack of alternate synthesis techniques. A unique technique for the manufacture of conjugated polymers is described in this paper. In the presence of alkyl lithium, the double bonds in polydienes were rearranged, according to our findings. We investigated this phenomenon in depth in this paper and used a rearrangement technique to create a new method for synthesizing conjugated polymers from non-conjugated (separated) polymers.

Preparation of Conjugated Polymers Using a Rearrangement Strategy

The surprising discovery of C=C bond rearrangement and migration of polybutadiene in the presence of n-butyllithium (n-BuLi) and N, N, N', N'-tetramethylethylenediamine spurred this research (TMEDA). To prepare samples for analysis, polybutadiene was dissolved in n-hexane and heated in the presence of butyllithium/TMEDA. The Supplementary Material contains details on the experimental approach. FTIR and NMR spectroscopy were used to examine the products of polybutadiene rearrangement.

The existence of a substantial number of conjugated double bonds in the n-BuLi-treated polybutadiene is confirmed by spectroscopic investigations of the products. The peak at 1,655 cm⁻¹ associated to the C=C stretching vibration gradually migrated to 1,611 cm⁻¹ as the reaction time increased in the FTIR spectra of the treated polybutadiene. The creation of conjugated double bonds causes the electron density to average out, resulting in such a large redshift. Furthermore, the wide signal at 5.7 ppm in the ¹H NMR spectrum of the treated polybutadiene is attributed to conjugated structure protons, which moved to lower fields than unconjugated structure protons (5.4 ppm). The stacking of several conjugated structures causes the electron cloud to disperse even more, explaining the weak signals seen at lower fields (5.8 ppm–6.5 ppm). Rearrangement produces continuous conjugated structures that are comparable to polyacetylene. These low-field indications are consistent with the pioneers' reporting on polyacetylene NMR spectra.

Furthermore, the 2D HSQC spectrum validates the validity of the proposed hypothesis. The signal at 5.7 ppm (¹H) is significantly correlated with the signal at 131.8 ppm (¹³C), and both the signals at 131.8 ppm in the ¹³C NMR spectrum and 5.7 ppm in the ¹H NMR spectrum come from carbons or protons of the conjugated structures, according to the cross-correlation peak I. It may be determined from the aforementioned FTIR spectra, as well as NMR spectrum data, that polybutadiene developed a conjugated double bond after being treated with n-BuLi/TMEDA. As a result of the product structure characterization, we offer a plausible reaction mechanism.

Furthermore, to optimize the reaction conditions, a number of rearrangement processes were carried out at various reaction temperatures, durations, and catalyst doses. With increasing reaction time, the fraction of conjugated double bonds to total double bonds in the products rose. Because the reaction is somewhat slow, the amount of conjugated double bonds in the final product may be controlled by adjusting the reaction time.

Conclusion

The n-BuLi/TMEDA combination can cause polybutadiene to undergo double bond migration, resulting in the formation of π -conjugated structures. Because the reaction's kinetics reveal that the rearrangement happens gradually, the amount of conjugated double bonds in the products may be controlled by adjusting the temperature, reaction time, and catalyst dosage. Furthermore, the reaction mechanism was defined as a process in which carbanion rearrangement leads to the conversion of the double bond to a more stable conjugated structure, based on spectroscopic data.

Because the resultant polymer lacks aromatic rings, it is unsuitable for use as a conductive polymer or in the fabrication of optoelectronic devices. However, because of the conjugated double bonds, it has a high reactivity and may be utilized as a substrate for a variety of reactions.