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Delocalized Carbanions

Linear and Star Polymers by Anionic Initiation

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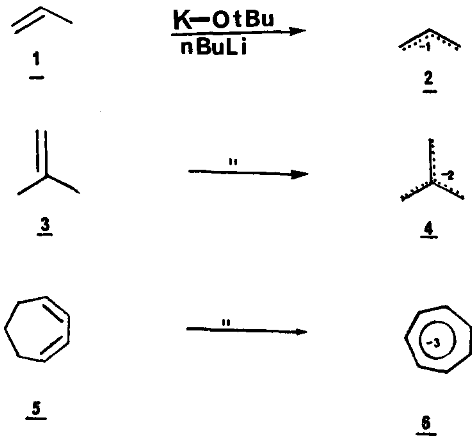
Summary

Anions of propene, isobutylene and cycloheptatriene have been prepared using Lochmann's Base. Star polymers in the form of "one arm star", "two arm star" and three arm star polymers of styrene have been synthesized from the allyl anion (2), 2-methylenepropylenyl dianion (4) and the cycloheptatrienyl trianion (6) respectively, with acid end groups by quenching the living polymers with carbon dioxide. The number average molecular weight has been determined by stoichiometry, HPSEC and end group analysis by titration.

Introduction

The most common procedure for the preparation of telechelic polymers has been via the napthalene anion radical to produce a dianion which propagates from both ends.(1,2)

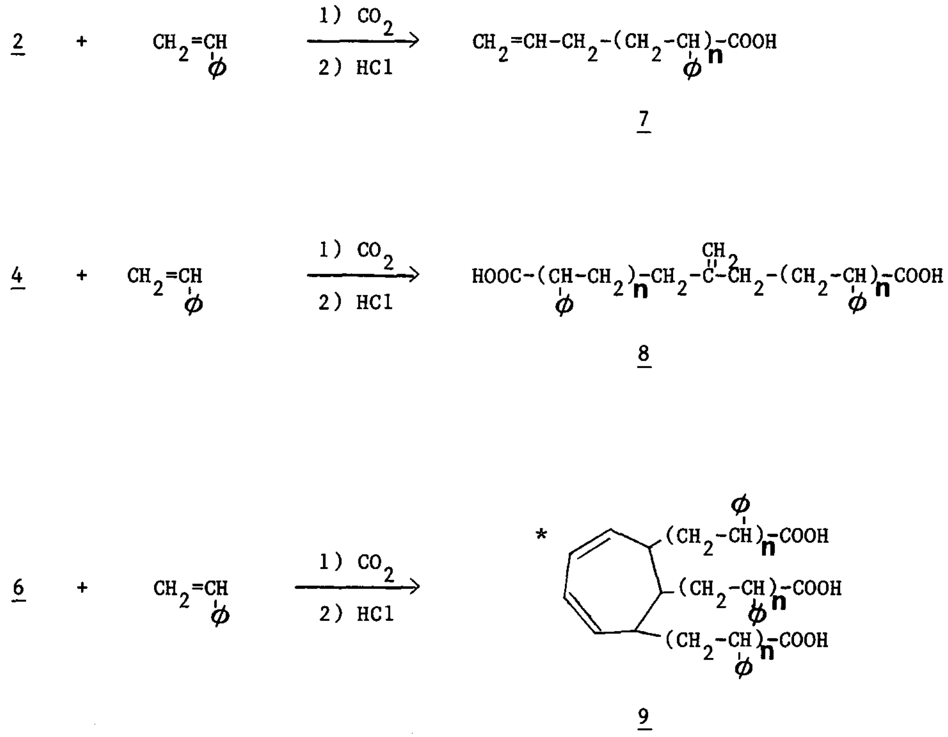


Scheme 1: Preparation of Anions

The telechelic polymers are formed by reacting the living dianion polymer with compounds that leave reactive end groups. The two most common compounds are carbon dioxide and ethylene oxide which yield dicarboxylic acids and diols respectively (3,4). One problem present in this system is the removal of the napthalene initiator which is not part of the polymer and is present in large quantities if low molecular weight polymeric dianion is desired (1). Therefore, to overcome this problem, a well characterized dianion initiator which is incorporated into the polymer should be used.

Star polymers are generally made by anionic initiation of a living monoanionic polymer followed by addition of chlorosilanes to couple the chains (i.e., trichloromethylsilane to prepare a three armed star) (5,6). A star polymer by this procedure is formed by polymerization from the ends of the arm to the center. However, with delocalized carbanions, the propagation would be from the center of the star to the ends of the arms.

The allyl anion (2), (7,8,9) 2-methylenepropylenyl dianion (4), (10,11) and the cycloheptatrienyl trianion (6) (12) have all been prepared in high yields. In this report, anions (2), (4) and (6) have been prepared using Lochmann's Base, K-O-t-Bu and n-BuLi in pentane (see scheme 1). The anions were reacted with styrene and quenched with CO_2, followed by HCl to make end groups of a "one arm star" linear polymer (7), a "two arm star" linear polymer (8), and a three arm star polymer (9). (see scheme 2). These polymers were analyzed by titration with 0.025 M NaOH. The molecular weights of these polymers were determined by stoichiometry, HPSEC and end group analysis by titration.



* Only one of the isomers is shown.

Scheme 2: Reaction of Anions with Styrene Followed by Carbon Dioxide and Neutralization to make Carboxylic Acid Ended Linear and Star Polymers.

Experimental

Potassium tert-butoxide and 2.4M n-BuLi in hexane were obtained from Alfa Chemical Company and used without purification. 1,3-cycloheptadiene was obtained from Aldrich Chemical Company and used without purification. Propene and isobutylene gas were obtained from Air Products. HPSEC data were obtained with a Dupont Instrument 860 HPSEC system with U.V. detector; two Zorbax PSM 60 μ pore and two Zorbax 1000 μ pore columns were used.

Initiator Preparation: Ten mmole of potassium tert-butoxide was suspended in 15 ml of dry pentane with stirring under nitrogen. Ten mmole of n-BuLi was slowly added and stirring continued for 10 min. at room temperature. The flask was then placed in a dry ice/acetone bath and 10 mmole of propene was added, and stirring continued for 20 min. at room temperature. The pentane layer was drawn off and the anion was blown dry under nitrogen. For preparation of the 2-methylenepropylenyl dianion and cycloheptatrienyl trianion, the same reaction flask was prepared using 5 mmole of isobutylene and 3.3 mmole of cycloheptatriene respectively.

Linear Polystyrene 7: For a polymer of molecular weight 5,200 (polymer 7) 0.128 mole, 3.6 ml of allyl anion in THF was used to initiate 5 ml styrene in 15 ml THF.

Linear Polystyrene 8: For a polymer of molecular weight 10,000 (polymer 8) 0.064 mole, 1.8 ml of 2-methylenepropylenyl dianion in THF was used to initiate 5 ml styrene in 15 ml THF.

Three-Arm Star Polystyrene 9: For a polymer of molecular weight 20,000 (polymer 9) 0.0268 mole, 4.5 ml of cycloheptatrienyl trianion in THF was used to initiate 5 ml styrene in 15 ml THF.

Results and Discussion

Delocalized carbanions have been shown to be successful in the preparation of linear and star polymers of styrene. Allyl anion (2) and 2-methylenepropylenyl dianion (4) were used to initiate "one arm star" and "two arm star" polymers and the cycloheptatrienyl trianion was used to initiate a three arm star polymer. The molecular weights of the polymers were determined by stoichiometry, end group titration and HPSEC. These results are summarized in Table 1.

Table 1: Summary of Molecular Weights of the Linear and Star Polymers

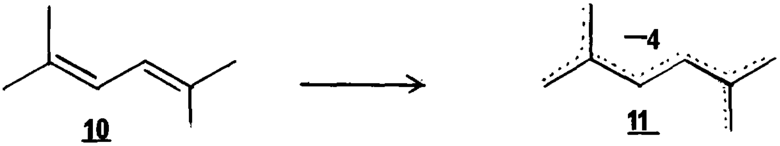
poly.	stoich.	HPSEC		titration
		(M_n)	(M_w)	
7	5200	5900	9000	5100
8	10000	12000	22000	16000
9	20000	16000	23000	**

Note : Poly. 7 = One Arm Star Polymer
Poly. 8 = Two Arm Star Polymer
Poly. 9 = Three Arm Star Polymer
** = Sample Quenched with MeOH

Conclusion

Delocalized mono-, di-, and tri- carbanions have been used to synthesize linear and star polymers of different molecular weights. The molecular weights are in close agreement with the three techniques used for the determination. The low molecular weights obtained are typical for telechelic polymers which are generally used as prepolymers for synthesis of higher molecular weight condensation polymers. Finally, these new anionic initiators allowed for the preparation of telechelic and star polymers with the initiator as part of the polymer, therefore eliminating the need to remove the spent initiator.

Future studies of this work include the preparation of a new tetraanion 2,5-dimethylenehexatrienyl tetraanion (10), from 2,5-dimethyl-2,4-hexadiene for use in making a four arm star (11).



Other work includes the preparation of linear and star polymers with isoprene and butadiene monomers. FT-IR, and NMR will be used to analyze the resulting polymers for incorporation of initiator and microstructure.

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