Macromolecules **1996,** *29,* 3639−3641 **3639**

Notes

Synthesis and Characterization of H-Shaped Polyisoprene

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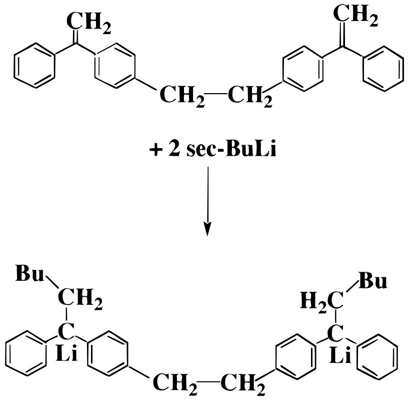
Received June 20, 1995
Revised Manuscript Received February 14, 1996

Introduction

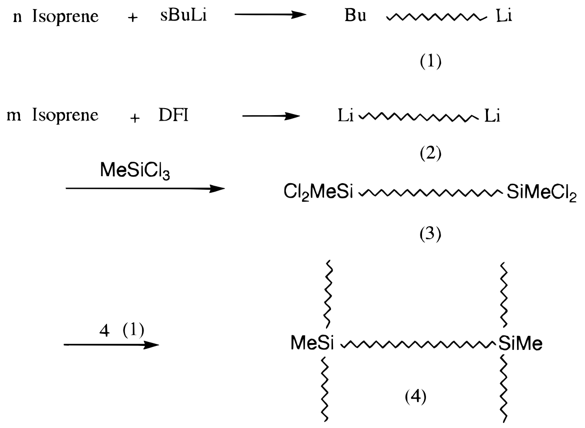
Advances in understanding and predicting relationships between polymer properties (such as their rheology) and their structure require the availability of macromolecules with totally controlled architectures and narrow molecular weight distributions. In particular, branched polymers and copolymers are materials of rapidly growing importance in the formulation of elastomers, compatibilizers for polymer blends, oil additives, etc. Much attention has been given to the synthesis of star polymers in the past 20 years.[1−15] Polymers of different compositions have been studied—including A_2B_2, A_2B, ABC, and ABCD.[16−19] The first H-shaped polymer was synthesized from styrene by Roovers and Toporowski[20] using anionic polymerization; two molecules of poly(styryllithium) were reacted with one molecule of methyltrichlorosilane, and the resulting $(PS)_2Si(CH_3)Cl$ was subsequently condensed with α,ω-difunctional poly(styryllithium).

The route followed for the synthesis of α,ω-dicarbanionic polymers depends upon the monomer concerned. In the case of styrene, sodium naphthalene reacts almost instantly with the monomer by electron transfer to form the styrene dimer dianion which then initiates the polymerization of the rest of the monomer. Unfortunately, this chemistry requires the use of a powerful solvating solvent such as tetrahydrofuran which does not permit the polymerization of isoprene in the predominant cis-1,4-sense that is necessary for elastomeric behavior.[21] Instead, a hydrocarbon-soluble organodilithium species capable of sufficiently rapid initiation must be employed. Organolithium compounds are usually strongly aggregated in hydrocarbon solvents, and the presence of two lithium atoms in the same molecule tends to cause insolubility. However, a considerable variety of soluble dilithium initiators (of widely varying reactivity) has been prepared—generally by locating the lithium atoms such that association is minimized by steric hindrance purposely built into the molecule. A critical study has been made of a wide range of such species.[22] Here we report the synthesis of an H-shaped polyisoprene using anionic polymerization but with a quite different strategy. We use a difunctional initiator derived from a divinyl compound and *s*-BuLi. This choice gives rise to polyisoprene having similar high cis-1,4-microstructure to that obtained using *s*-BuLi.

Scheme 1. Difunctional Initiator Synthesis



Scheme 2. Reaction Mechanism of the Formation of the H-Shaped Polyisoprene



Experimental Procedures

Isoprene (Fluka) was purified by distilling from solvent-free dibutylmagnesium. Just before use, it was distilled onto *n*-butyllithium, kept at −10 °C for at least 1 h, and then distilled into the reactor. Butadiene (Aldrich) was twice distilled onto a sodium mirror under vacuum at −20 °C and then onto solvent-free *n*-butyllithium. Benzene was distilled first from sodium−potassium alloy and then from *n*-butyllithium. *s*-Butyllithium (Aldrich) was distilled in a cold finger apparatus under high vacuum. The pure product was dissolved in dried benzene, and after titrating a sample, the solution was ampulized and stored in the freezer. Methyltrichlorosilane (Fluka) was distilled on the vacuum line: The middle fraction was collected and diluted with dried benzene. The solution was analyzed by titrating an aliquot with sodium hydroxide and then ampulized.

Synthesis of the Difunctional Initiator (DFI). 1,2-Bis(4-(1-phenylethenyl)phenyl)ethane (Scheme 1) was synthesized according to a literature procedure.[23,24] Reaction with *s*-BuLi in a benzene/*n*-heptane (1:2) solution under vacuum generated a red color, and solid DFI precipitated over night at room temperature. This solid and the interior of the reactor were washed several times with *n*-heptane to remove any monofunctional adduct and other soluble contaminants. The DFI

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S0024-9297(95)00863-1 CCC: $12.00

Table 1. Characteristics of the H-Polymers

polymer	M_n arm (SEC)	M_n bridge (SEC)	M_n H-polymer predicted	M_n H-polymer SEC	H-polymer M_w (scattering)	radius of gyration (nm)	10^4A_2 (mL/g)
A	18 000	274 000	346 000	334 000	371 000	32.4	9.0
B	40 000	164 000	324 000	324 000	345 000	26.8	9.6
C	58 700	215 000	450 000	460 000	[a]	[a]	[a]
D	63 000	198 000	450 000	460 000	612 000	39.7	8.5
E	135 000	253 000	793 000	[a]	801 000	50.9	8.8

[a] Not determined.

was dissolved in benzene and, after titration of an aliquot to determine the concentration, was ampulized and stored in the freezer.

Synthesis of the H-Shaped PI. The experimental procedure used high-vacuum techniques throughout. The monofunctional poly(isoprenyllithium) chains were synthesized in one reactor using *s*-BuLi as initiator and benzene as solvent. The α,*ω*-difunctionl poly(isoprenyllithium) chains were similarly prepared using DFI in another reactor to which a little triethylamine (Et_3N:Li = 0.2) was added. Reaction was allowed to proceed for at least 24 h to ensure completion. In the second step, a large excess of $MeSiCl_3$ (ca. 50:1) was added to the difunctional chains to form the α,*ω*-bis(dicholoromethylsilyl) telechelic **3** (Scheme 2). Complete reaction was ensured by allowing it to continue for 24 h, whereafter the excess of trichlorosilane was removed under vacuum together with the solvent. Fresh solvent was distilled into the reactor, the contents were allowed to dissolve, and then the solvent was removed together with any lingering $MeSiCl_3$. In the final stage of the synthesis, the monofunctional chains were added in excess (50%) to the telechelic, and the reaction was allowed to continue for at least 1 week. The reaction was terminated by quenching the excess of living chains with methanol, and the polymer was fractionated as a 1% solution in toluene as solvent and with methanol as precipitant. Molecular weights and molecular weight distributions were measured by SEC and light scattering. SEC was conducted using THF as the solvent at a flow rate of 1 mL/min at 30 °C. Two columns (microstyragel) of 30 cm and one of 60 cm were connected to a differential refractometer (ERC-7512, Polymer Laboratories). The samples were injected at a concentration of 1 mg/mL, and the SEC trace was analyzed by a computer using Polymer Laboratories LogiCal software and polyisoprene standards.

Static light-scattering experiments were conducted using light of 632 nm wavelength given by a vertically polarized laser, and the apparatus was calibrated with benzene. Mother solutions of concentration C_M in THF or cyclohexane (refractive indices 1.402 and 1.4243, respectively) of about 2×10^{-3} g/mL were prepared and split down into further concentrations ($C_M/4$, $C_M/2$, and $3C_M/4$). These were then freed from any suspended material by centrifugation at 18 000 rpm. The measurements were performed at several angles ranging from 30° to 150°. The refractive index increments of the H-polymer were found to be 0.131 mL/g in THF and 0.106 mL/g in cyclohexane. The crude data were analyzed using the method of Zimm.

Results and Discussion

In general, organolithium compounds are strongly associated, and the presence of two such moieties in the same molecule can result in insolubility. Heterogeneity leads to slow, inefficient initiation and a broad molecular weight distribution which would be quite useless for the present purpose. The introduction of bulky substituents such as aromatic rings and the judicious placing of the two lithium atoms with respect to each other can impede aggregation and permit sufficient solubility to allow use as a polymerization initiator. It is important that the two organolithium moieties have equal reactivity: This precludes their belonging to a common delocalized structure. A survey of the literature suggested that DFI might be suitable for the preparation of the H-polymer. Very conveniently, this species precipitates from benzene/heptane (1:2) leaving behind in solution any 1:1 adduct or residual butyllithium. Recovery by filtration, washing with *n*-heptane, and finally dissolution in benzene yielded a pure solution. However, tests showed that in the absence of any solvating agent this solution is not a very rapid initiator of polymerization, and the resulting molecular weight distribution is relatively broad. However, it was found that with the addition of small quantites of triethylamine (Et_3N:Li ca. 20:1) much narrower distribution is obtained at the cost of only a small decrease in the extent of cis-1,4-addition. Quirk and Ma[25] encountered analogous but much more severe problems with molecular weight distribution using the dianionic initiator formed from *s*-butyllithium and another double diphenylethylene—1,3-bis(1-phenylethenyl)benzene. They found it necessary to employ tetrahydrofuran or lithium *s*-butoxide as promotor to eliminate this problem.

The flow plan for the assembly of the H-polyisoprene is summarized in Scheme 2. In summary, α,*ω*-poly(isoprenyllithium) is reacted with a very large excess of CH_3SiCl_3 so as to place a -$Si(CH_3)Cl_2$ functionality at both chain ends while reducing the likelihood of chain extension to negligible proportions. Complete removal of the unreacted and highly volatile CH_3SiCl_3 is readily achieved by pumping under vacuum. Subsequent reaction with an excess of monofunctional poly(isoprenyllithium) attaches the “legs” of the H to the “bridge” formed by the telechelic.

The SEC chromatograms of the α,*ω*-dilithiopolyisoprene before and after reaction with CH_3SiCl_3 were almost indistinguishable, showing that no detectable coupling had occurred. Tests showed that the subsequent reaction of the product with poly(isoprenyllithium) is slow and effectively stops when only three of the four chlorine atoms have reacted. However, the reaction was found to be both quantitative and significantly faster if the living carbanion chains were first capped with some five to seven units of 1,3-butadiene. Figure 1 shows the SEC chromatograms of the crude and the fractionated H-polymer. Peak A represents the excess poly(isoprenyllithium) and B the H-polymer. Also shown in Figure 1 are the traces for the bridge and the H-polymer after fractionation. The molecular weights of the arms, bridges, and H-polymers are reported in Table 1. For the four H-polymers for which data were obtained, there is good agreement between the values obtained by SEC and those calculated according to the relation $M_n(H) = 4M_n(\text{arm}) + M_n(\text{bridge})$. The M_w values obtained by light scattering are also in good agreement in the cases of polymers A, B, and E. In the case of polymer D, the agreement is rather poor, for which there is no obvious explanation since the SEC trace indicated a dispersity similar to that of the other H-polymers (ca. 1.1). The radii of gyration are generally

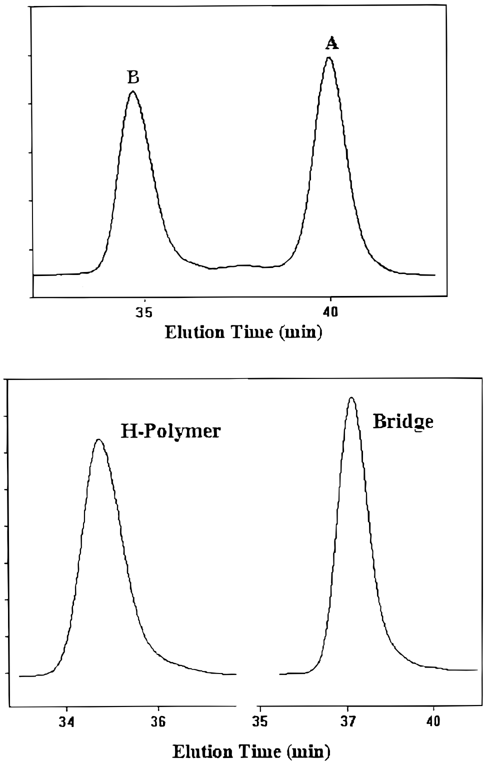

Figure 1. Chromatograms of the bridge polymer and the crude and the fractionated H-shaped PI.

slightly smaller than those of linear polymers of the same molecular weights, reflecting the somewhat more compact shape of the H-polymer.

Conclusion

The dilithium initiator DFI formed by the reaction of *s*-BuLi with 1,2-bis(4-(1-phenylethenyl)phenyl)ethane allows the synthesis of α,ω-difunctional poly(isoprenyllithium) of quite narrow molecular weight distribution. Conversion of the organolithium functionalities into $-SiCl_2CH_3$ by reaction with CH_3SiCl_3 followed by condensation with monofunctional poly(isoprenyllithium) generates an H-shaped polymer. The quantitative nature of the silylation and the subsequent condensation was established by the good agreement observed between the expected and experimental molecular weights of the H-shaped polyisoprene. Light-scattering measurements of the chain dimensions in dilute solutions in a good solvent showed that the radius of gyration scales with the molecular weight with an exponent close to the theoretical value.

Acknowledgment. The authors thank the Science and Engineering Research Council for the grant which supported this work, Dr. Lew Fetters for helpful discussions, and Dr. C. Strazielle of the Institut Charles Sadron for assistance in the light-scattering measurements.

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MA950863Q