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Telechelic Polyisobutenes with Asymmetrical Reactivity

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Summary: 3-Chlorocyclopentene-(1) has been used as initiator in the quasiliving cationic polymerization of isobutene. Polyisobutenes in the molecular weight range Mw = 300 – 60000 Dalton with a molecular weight distribution MWD between 1.17 and 1.34 have been synthesized. The linear polymer was selectively hydrosilated on one or both ends. With a furan coupling agent, the PIB (polyisobutene) was dimerized, yielding polymers with a cyclopentene head- and tail group.

Keywords: cationic polymerization; functionalization of polymers; initiators; NMR; polyolefins

Introduction

In the field of the living cationic polymerization of isobutene, a discrepancy between academical advancement and industrial realization has been noted: The issue is versatility versus cost. Numerous authors[1] have shown the ample opportunities for a "molecular engineer". For many industrial applications, a bifunctional polyisobutene in the molecular weight range Mw = 500 – 5000 Dalton is the educt of choice. Whereas widely used starters like 1,4-bis(1-chloro-1-methylethyl)benzene are well suited from a technical / chemical point of view, their inherent cost structure is a major obstacle for many industrial applications.

Polymerizations with 3-Chlorocyclopentene (CCP)

In the living cationic polymerization of isobutene, well-defined telechelic polymers with reactive end groups may be produced[1]. The reactivity of these functional PIBs together with the stability and elasticity of the polymer backbone makes them versatile and hence attractive macromers for sealants, adhesives or industrial rubbers. On the other hand, the need for an absolutely proton free environment, low temperatures and special initiators in the polymerization puts a burden on the industrial synthesis which the markets often are not willing to bear. In the 1000 – 2000 Dalton

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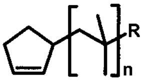
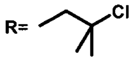
molecular weight range, an economic initiator is the cornerstone of a successful industrial process.

3-Chlorocyclopentene seemed to be a prospective candidate for such an initiator: Allylic activation of the chlorine atom ensures the proper reactivity. It is generated by simple addition of HCl gas to cyclopentadiene according to a procedure in Organic Synthesis[2]. (Reaction of dichlorocarbenes with dicyclopentadiene[3] is an alternative to this route.)

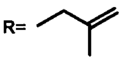
We applied standard polymerization conditions to a CCP / IB (isobutene) system. The polymers **Ia** have been prepared with molecular weights from 300 Dalton to 60,000 Dalton and molecular weight distribution (MWD) between 1.17 and 1.34.



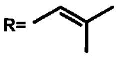
I



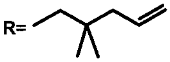
Ia



Ib



Ic



Id

Low concentrations of the catalyst $TiCl_4$ together with elevated temperatures during the work-up procedure[4] directly lead to a 3:1 mixtures of the olefins **Ib** and **Ic**. By end-capping with trimethylallylsilane, a polymer with reactive vinyl end groups **Id** has been obtained.

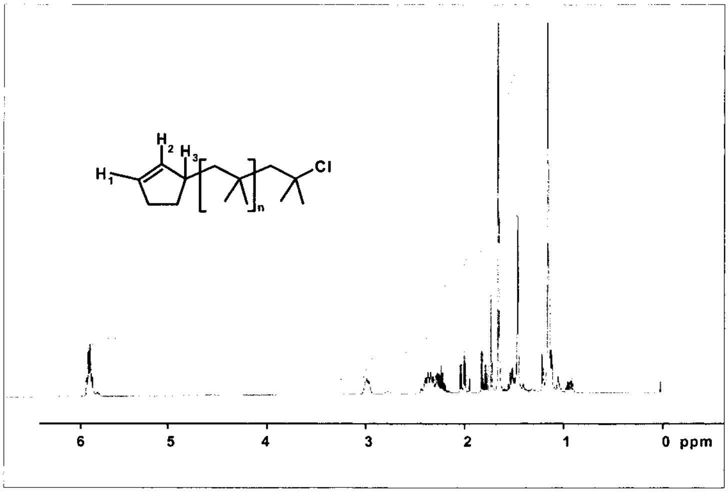


Figure 1: ^{1}H-NMR of Polymer **Ia**, $M_n = 350$, solvent $CDCl_3$, 16 scans at 500 MHz

The structure of the polymers was determined by ^{1}H-NMR. As model component, a 1:1 adduct of IB and CCP (**Ia**, n=0) was prepared according to Mayr[5]. Figure 1 shows the ^{1}H-NMR spectrum of a low molecular weight (M_n = 350) PIB **Ia**. The signals in the olefinic region are attributed to protons H_1 and H_2 , the signal at δ = 2.95 ppm to the allylic proton H_3. Especially this allylic signal is a clear indication for the proposed structure. In the initiator CCP, H_3 is attached to a C-Cl group and it's ^{1}H-NMR signal is significantly shifted to δ = 5.05 ppm.

In Figure 2 the CCP / IB ratio is plotted against the number molecular weight average M_n. As expected from a quasiliving system, the M_n is a linear function of the CCP / IB relation.

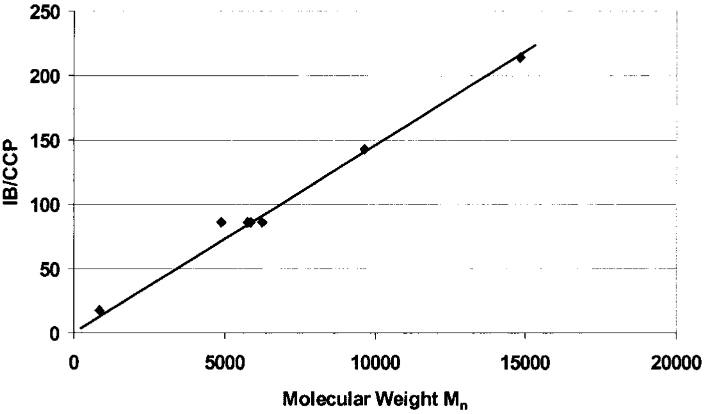
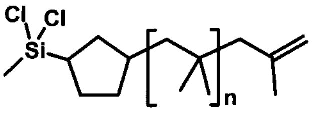


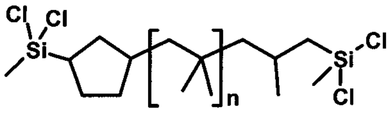
Figure 2: Plot of the IB/CCP relation versus M_n. Typical reaction condition: 4.28 mol IB, 0.05 mol CCP, 300 ml Hexane, 300 ml CH2Cl2, 0.026 mol TiCl4, 0.002 mol DBP (2,6-Di-t.butylpyridine), 2 h -50° – -70°C

Functionalization

The different reactivity of the terminal olefins in the dienes **Ib-Id** has been used to tailor-make new telechelic PIBs. Depending on reaction conditions, both ends can be functionalized. Addition of H_3C-$SiHCl_2$ to PIB **Ib** with H_2PtCl_6 * $6H_2O$ ("Speiers reagent"[7]) as catalyst yielded the bifunctional structure **IIb**[a].



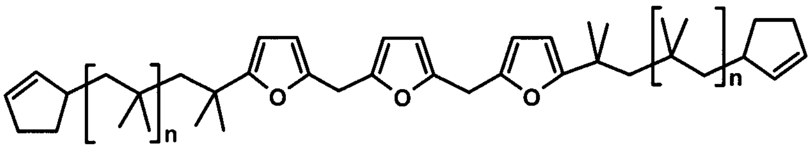
IIa



IIb

Catalyzed by a 1,3-divinyl-1,1,3,3-tetramethyl-disiloxan-Pt(0) complex, the reaction proceeded to the mono addition product **IIa**[a].

A living cationic polymerization of IB may be terminated by a coupling reagent, yielding a polymer with twice the molecular weight.[6] Reaction with 2,5-bis(furanyl(2)-methyl)furan led to the dimerized PIB **III**.



III

The terminal cyclopentene double bonds in structure III are more reactive than a $-CH_2-(CH_3)=CH_2$ or $-CH=C(CH_3)_2$ group and offer an ample synthetic potential. In many cases, the use of an expensive end-capping reagent like allyltrimethylsilane may be avoided.

Conclusion

The use of CCP as initiator in the living cationic polymerization of IB leads to a cost efficient synthesis of the new polyisobutenes I. They are very versatile intermediates for symmetrical and asymmetrical (R-PIB-R') telechelics. The (functionalized) polyisobutenes are useful as macromers e.g. for sealants, adhesives or industrial rubbers.

[a] The cyclopentane ring is shown to be substituted in the 1,3- position. It should be noted however that the polymer is actually a mixture of 1,2- and 1,3-isomers.

Experimental

1. Polymerization (typical experiment)

A 2l 4-necked flask was equipped with stirrer, dry ice condenser, septum inlet and 2 dropping funnels with cooling jackets. Both dropping funnels contained 3 Å molecular sieves over glass wool. A mixture of 300 ml CH_2Cl_2 and 300 ml n-hexane was conditioned at –78°C for 20 min in a funnel, than added to the reaction vessel. IB (400 ml) was treated in the same way. With vigorous stirring, 6 mmol triethoxyphenylsilane, 50 mmol CCP and 26 mmol $TiCl_4$ were injected through the septum at –70°C. The temperature increased to –55°C and was kept between –50°C and –70°C for 2 h. The polymerization was terminated by the addition of 50 ml iso-propanol. The solution was washed three times with water and the solvent was driven off with a rotary evaporator at 180°C until a final pressure of 5 mbar was reached.

The product was 300g of clear polymer, Mn = 4,890; MWD = 1.18

2. Bis-Hydrosilylation

A 2l 4-necked flask was equipped with stirrer, condenser, thermometer and a dropping funnel. Polymer from experiment 1 (200g, 41 mmol) was dissolved in 1200ml toluene. A solution (1ml) of 0.1 M $H_2PtCl_6 * 6H_2O$ in isopropanol and then 11.5 g (100 mmol) dichloromethylsilane were added. The reaction mixture was kept at 90°C for 12h. The solvent was driven off with a rotary evaporator at 180°C until a final pressure of 5 mbar was reached.

The product was 195g of clear polymer. 1H-NMR (500MHz, 16 scans, $CDCl_3$) indicated the absence of olefinic protons. A new signal at $\delta = 0.80$ ppm corresponded to $-Si(CH_3)Cl_2$ groups.

3. Mono-Hydrosilylation

A 2l 4-necked flask was equipped with stirrer, condenser, thermometer and a dropping funnel. polymer from experiment 1 (200g, 41 mmol) was dissolved in 1000ml THF (tetrahydrofuran). A solution (4ml) of 0.1 M 1,3-divinyl-1,1,3,3-tetramethyl-disiloxan-Pt(0) complex in polydimethylsiloxane and then 5.7 g (50 mmol) dichloromethylsilane were added. The reaction mixture was kept at 60°C for 3h. The solvent was driven off with a rotary evaporator at 180°C until a final pressure of 5 mbar was reached.

The product was 200g of clear polymer. ^{1}H-NMR (500MHz, 16 scans, $CDCl_3$) indicated the absence of cyclo-olefinic protons. A new signal at $\delta = 0.80$ ppm corresponded to a $-Si(CH_3)Cl_2$ group.

4. Dimerization

The polymerization was run as in experiment 1, but before termination, 50 mmol 2,5-bis (furanyl(2)-methyl)furan was added to the polymerization mixture. After an additional period of 120 min at –70°C, the mixture was terminated and worked up as described above.

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