Novel Synthesis and Crystal Structure of 1,4-Bis(3-chloro-1,1,3-trimethylbutyl)benzene

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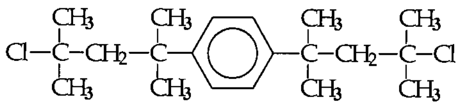
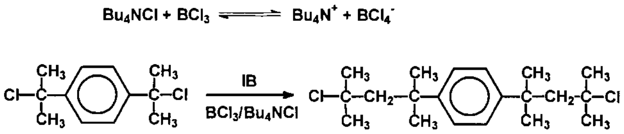
A symmetrical isobutene adduct was synthesized with high yield at −80 °C by means of the 1,4-bis(1-chloro-1-methylethyl)benzene/isobutene system using tetrabutylammonium chloride. The main product under the reaction conditions applied was the symmetrical isobutene adduct, which was crystallized from a hexane/dichloromethane solution and the crystals were analyzed by X-ray crystallography.

Isobutene (IB) in the presence of cumyl chloride derivatives/Lewis acid systems[1–10] can be readily polymerized. Our aim was to suppress the polymerization of isobutylene by adding tetrabutylammonium chloride to the reaction mixture, i.e., to stop the propagation after cationation, and to define conditions for the high-yielding synthesis of 1,4-bis(3-chloro-1,1,3-trimethylbutyl)benzene (**D1**) from 1,4-bis(1-chloro-1-methylethyl)benzene (pDCC) by increasing the counter ion concentration, i.e., BCl_4^-. The **D1** is a potential model compound, it mimics the chlorine-telechelic polyisobutylenes and can be used as initiator for living polymerizations.



D1

Our synthetic strategy is outlined in Scheme 1.



Scheme 1. Schematic Representation of the Synthetic Strategy.

The reactions were performed at –80 °C under dry nitrogen atmosphere in a 500 mL three-necked flask equipped with an overhead stirrer in the mixture of CH_2Cl_2/hexane (60/40) under dry-box conditions. The volume of the solution was 300 mL, 1,4-bis(1-chloro-1-methylethyl)benzene (pDCC, 1–2.7 g), and tetrabutylammonium chloride (0.08–0.3 g) were dissolved in the mixture and then 5 mL of isobutene was introduced. The reaction was started by adding 0.1–1 mL BCl_3 to the solution. After 30 min, the reactions were terminated with 30 mL prechilled methanol and the first generation of the product were prepared. The crude products were dissolved in hexane and filtered to remove Bu_4NCl and the solvent was evaporated. The products were recrystallized from a 9:1 (v/v) mixture of hexane and CH_2Cl_2 and dried in vacuum at ambient temperature. The yields were higher than 95% even at high [IB]/[pDCC] ratio. The ORTEP plot (50% probability displacement ellipsoids) of the synthesized and recrystallized **D1** is shown in Figure 1.

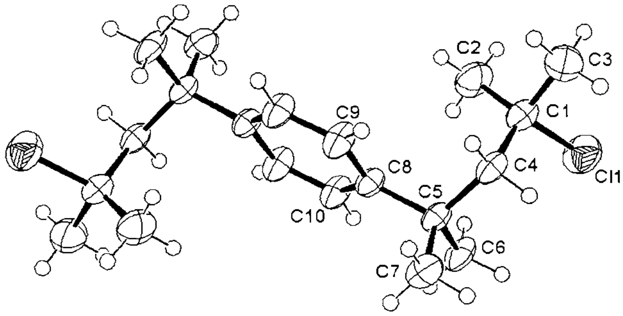


Figure 1. Ortep Plot of D1

Colorless block crystal of 0.65 × 0.4 × 0.32 mm was grown from hexane/dichloromethane (10:1 v/v) (mp = 71 °C, ^{1}H-NMR: methyl: 1.25 (s, 12H) and 1.45 (s, 12H) ppm, methylene: 2.35 (s, 4H) ppm, aromatic: 7.25 (s, 4H) ppm). Data were collected at 293(1) K, Enraf Nonius MACH3 diffractometer, Mo $K\alpha$ radiation λ = 0.71073 Å, ω-2θ motion, $\theta_{max} = 25^o$, 1528 reflections of which 1528 were unique with $I > 2\sigma(I)$, no decay. The structure was solved using the SIR-92 software[11] and refined on F^2 using SHELX-97[12] program, publication material was prepared with the WINGX-97 suite[13], R(F) = 0.0858 and $wR(F^2)$ = 0.2306 for 1528 reflections, 100 parameters. Based on the X-ray experiments M = 343.36 and a composition of $C_{20}H_{32}Cl_2$ could be determined. The crystal structure of **D1** was found to be monoclinic with cell parameters as follows: a = 6.1399(10) Å, b = 10.311(2) Å, c = 15.428(4) Å, β = 92.15(2)°, V = 976.00(8) Å^3 , Z = 2, space group: $P2_1/n$, ρ_{calc}= 1.168 g cm^{-3}.

Polymerizations of isobutene initiated by **D1** and pDCC using BCl_3 and $TiCl_4$ coinitiators were compared under the same experimental conditions.

The polymerization experiments were carried out at –80 °C in dichloromethane (in the case of BCl_3 coinitiator) or in the mixture of hexane and dichloromethane (in the case of $TiCl_4$ coinitiator) (hexane/dichloromethane = 2/1 v/v) in 50 mL glass-tubes. Isobutene (0.0128 mol) and the initiator (pDCC or **D1**) (2×10^{-4} mol) were dissolved in 25 mL solvent. To avoid the initiation by protolytic impurities 2,6-di-*t*-butylpyridine (DTBP, 1×10^{-3} mole) was added to the mixture. The polymerization was started by the addition of the coinitiator (1.2×10^{-3} mole) to the reaction mixture. The polymerizations were terminated by adding 1 mL prechilled methanol to the reaction mixture.

The polymerization rate and the M_n obtained were almost the same: the M_n–s of the samples by **D1**/$TiCl_4$ and pDCC/$TiCl_4$ initiating systems are 3560 (M_w/M_n=1.59) and 3550 (M_w/M_n=1.58) g/mole at 100% conversion, respectively. The M_n–s of the samples by **D1**/BCl_3 and pDCC/BCl_3 initiating systems are 1610 (M_w/M_n=1.27) and 1690 (M_w/M_n=1.26) g/mol at 40% conversion, respectively. With this new effective bifunctional initiator the formation of undesirable indanyl ring formation[8] can be avoided.

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