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Macroazoinitiators for the Preparation of Polymers with Cycloboraziane Units

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MACROAZOINITIATORS FOR THE PREPARATION OF POLYMERS WITH CYCLOBORAZANE UNITS

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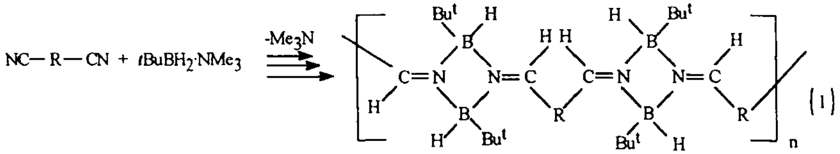
ABSTRACT

Macroazoinitiators containing cyclodiborazane moieties and various amounts of -N=N- units in the main chain were prepared by polyaddition between thexyl borane and adipoyldinitrile (AD) with the addition of 2,2'azobis(isobutyronitrile) (AIBN) at room temperature. These polymers were employed in the polymerization of styrene (St) to afford polystyrene with cyclodiborazane groups.

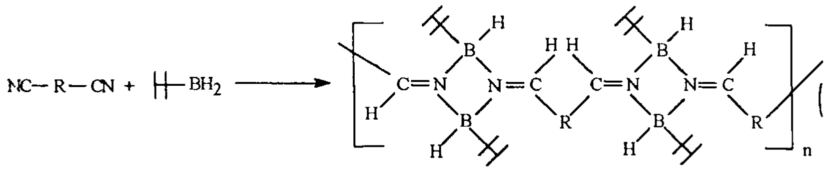
INTRODUCTION

Novel polymeric materials with unique properties are of interest, since available materials generally don't meet requirements for "high tech" applications [1]. One way to achieve macromolecular targets reflecting to improved properties of the available materials is block copolymers. Various methods to synthesize these polymers have been known for a long time. We are interested in preparing block copolymers by using functional initiators which allows multiple combination of monomers. Previously, carboxyl [3,4], hydroxyl [5,6], amine [7], nitrile [8,9], N-acyldibenz [b,f]azepine [10] and trichloroacetyl [11] functional azoinitiators were readily used to synthesize block copolymers of monomers with different chemical nature.

Quite recently, Chujo et.al. [12,13] reported the synthesis of novel boron containing-polymers by hydroboration polymerization. In these polymerizations, α,ω-dicyano alkanes react with t-$BuBH_2{\cdot}NMe_3$ [12] or thexylborane [13] to yield the corresponding poly(cyclodiborazane)s of the following four-membered ring structure.



(1)



(2)

Notably, undesired side reactions leading to the formation of only low molecular weight oligomers [14] are minimized in the latter case due to more sterically hindered structure of thexylborane. We consider that the same reaction principle may be applied to the well known azo initiator, 2,2′-azobis(isobutyronitrile) (AIBN), possesing both thermo-sensitive azo and dinitrile functions.

From such a viewpoint, we propose a new polymeric initiator consisting of boron-nitrogen four-membered rings and azo groups. When radical polymerizations is carried out in the presence of these initiators, polymers having segments with cyclodiborazane units are formed.

EXPERIMENTAL

Materials

Thexylborane was prepared by reacting borane-dimethyl sulfide with 2,3-dimethyl-2-butene according to the described procedure [15]. 2,2′-Azobis(isobutyronitrile) (AIBN) (Fluka) was recrystallized from ethanol. Styrene (St), adipoyldinitrile (AD) (Fluka) and solvents were purified according to conventional drying and distillation procedures.

Hydroboration Polymerization of AIBN with Thexylborane

The room temperature hydroboration polymerization was applied in which a mixture of AD and AIBN (total 3,93 mmol) was dissolved in 2 ml of dry dichloromethane and purged with nitrogen. Thexylborane (0.77 g, 7.87 mmol) was added with stirring over a period of 2 h at room temperature. The viscosity of the solution increased gradually during the polymerization. The mixture was kept in dark for overnight and finally dissolved in THF and poured in ethanol/water (v/v = 1/3). After it had dried, colourless, gummy polymer was obtained.

Free Radical Polymerization

The appropriate solutions of St and above obtained macroinitiators were degassed in the usual manner. After heating at 70 ^{o}C for 3 h, polymers were recovered by precipitation into ten-fold excess methanol.

Analysis

^{1}H-NMR spectra were recorded on a Brucker-200 spectrometer in $CDCl_3$ solution with tetramethylsilane as internal standard. IR spectra were obtained on a Jasco FT-IR 5300 spectrometer. Gel permeation chromatograms were obtained by using a Knauer M-64 instrument and THF as eluent at a flow rate of 1 ml min^{-1}.

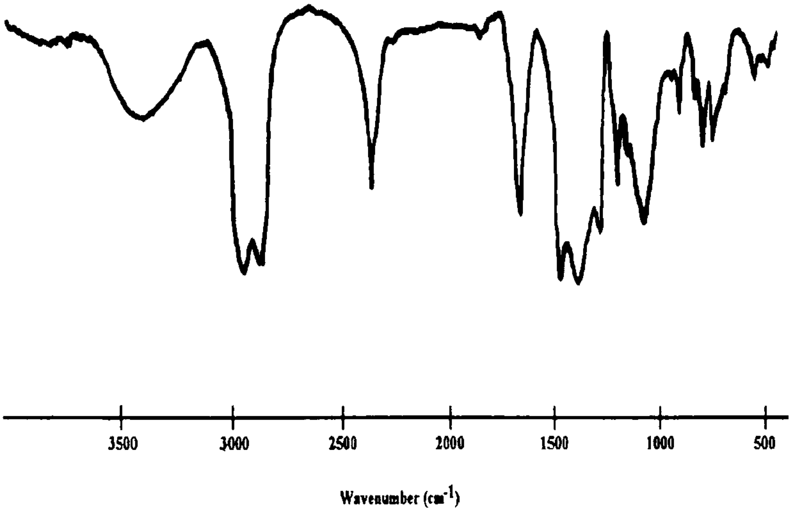


Figure 1: IR spectrum of macroazoinitiator obtained by hydroboration polymerization between thexyl borane and AIBN/AD (0,5/0,5 mol/mol)

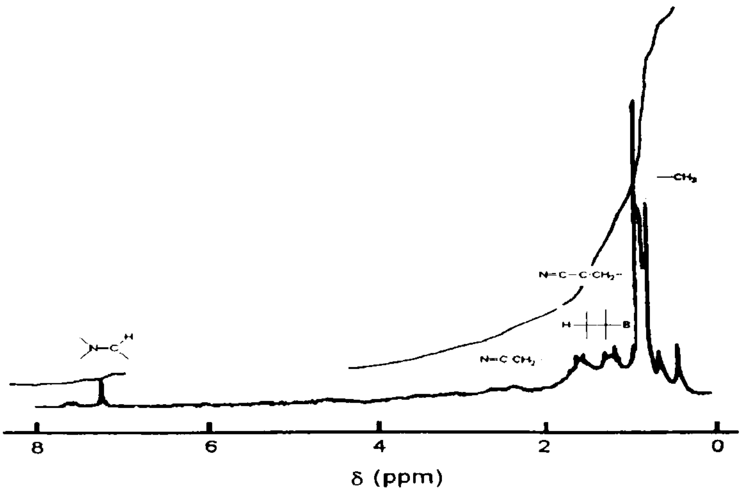


Figure 2: ^{1}H-NMR spectrum of macroazoinitiator obtained by hydroboration polymerization between thexyl borane and AIBN/AD (0,5/0,5 mol/mol)

Table 1

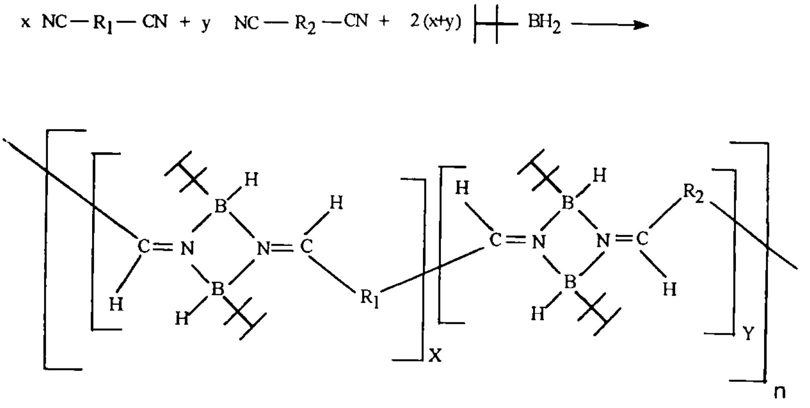
Bulk polymerization of styrene with macro-azoinitiators at 70 °C

Macro-Azo-initiator	AIBN mol ratio in the initiator	Conversion %	Mn x 10^4
MA-1	0.3	2.4	19.2
MA-2	0.5	3.8	19.0
MA-3	0.7	10.2	11.8
MA-4	1.0	15.8	3.0

Polymerization time = 3 h, [macro-azoinitiator] = 33.1 g/l.

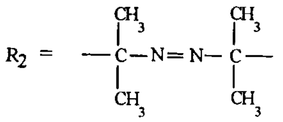
RESULTS AND DISCUSSION

Two molar equivalent of thexylborane was added to a AD and AIBN mixture in CH_2Cl_2 under nitrogen at room temperature to produce cyclodiborazane polymer according to the reaction (3).



(3)

$R_1 = —CH_2—CH_2—CH_2—CH_2—$



$$R_2 = —\underset{CH_3}{\overset{CH_3}{C}}—N=N—\underset{CH_3}{\overset{CH_3}{C}}—$$

The polymeric azoinitiator is adequately soluble in common solvents as benzene, dichloromethane and tetrahydrofuran. The cycloborazane structure of the macroazoinitiator was confirmed by spectral investigation. The infrared spectrum of the polymer (Figure 1) exhibits specific stretching bands at 2400 cm^{-1} (B-H) and 1640 cm^{-1} (C=N). No peaks attributable to nitrile groups (C≡N) were detected. In its ^{1}H-NMR spectrum (Figure 2), methyl protons of thexyl, AD and AIBN moities, and protons of imines were observed.

It was observed that there was no dependency of viscosity on the feed composition in thexyl borane/AIBN-AD system indicating similar reactivities of the dinitrile compounds. The obtained polymers with various amounts of azo units in the main chain were used in the polymerization of St. Typical results are shown in Table 1. It is seen that as the AIBN segment increased in main chain, the rate of polymerization increased. Notably, the molecular weights of the polymers decreased, since the azo concentration regulates the segment length of organo polymer. The IR spectrum of the resulting polymers exhibit the B-H band, in addition to characteristic polystyrene bands. Further investigations concerning properties of these polymers are now in progress.

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