



Synthesis and Characterization of Linear Poly (divinylbenzene-co-ethylvinylbenzene) Via A Cationic Solid Catalyst

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ABSTRACT

The polymerization of divinylbenzene (DVB) catalyzed by Maghnite-H⁺ is investigated. This paper shows that the cationic polymerization of DVB is initiated by Maghnite-H⁺ at 28°C in bulk and gives the linear poly (divinylbenzene-co-ethylvinylbenzene) which is proved with ¹H and ¹³C NMR spectra. The effect of the amount of Maghnite-H⁺ on the molecular weight and the intrinsic viscosities is studied. The results indicate that the molecular weight and the intrinsic viscosities increased with the decrease in the proportion of catalyst. According to our results, a mechanism of this polymerization was proposed.

Key words: catalysts; Maghnite-H⁺; Cationic polymerization; Divinylbenzene; poly (divinylbenzene-co-ethylvinylbenzene).

INTRODUCTION

The commonly used commercial divinylbenzene (technical grade) contains *meta*- and *para*- isomers of divinylbenzene (DVB) and ethylvinylbenzene (EVB). It is usually composed of 50 to 80 wt % DVB, and, depending on polymerization methods, either linear or crosslinked polymers or copolymers of DVB can be prepared ¹.

The most popular method for preparing linear polydivinylbenzene is by using anionic polymerization techniques. With this method Aso et al obtain, in 1968, *ortho*-divinylbenzene using organolithium and alkali metal-naphthalene catalysts in various ethers ². Further work on this method was

carried out by Bates et al ³. They were able to produce homogeneous gels of DVB-EVB using technical grade DVB (60% DVB, 40%EVB), and either *n*-butyl lithium or *sec*-butyl lithium. In 1978, Nitadori and Tsuruta polymerized *meta*-divinylbenzene, as well as *para*-divinylbenzene, using lithium diisopropylamide (LDA) or butyl lithium as initiators ⁴. However, a mixture of these same compounds (*meta*: *para*, 70:30) were synthesized by Hasegawa et al using BF₃-OEt₂ (oxoacids) as catalytic initiators, and 1, 2-dichloroethane as solvent ⁵.

Acid-treated clays, such as montmorillonite, kaolinite, are widely used in a number of industrial significant reactions because they constitute an available, inexpensive solid source of protons. They

have been employed as cracking catalysts until the 1960s⁶, and are still used in industrial processes, such as alkylation of phenols⁷ and dimerization⁸ and polymerization of vinylic and heterocyclic monomers⁹⁻¹⁵. With their both Brønsted and Lewis acid sites, montmorillonites exchange cations having a high charge density with protons, producing highly active catalysts for acid-catalyzed reactions of polymerization⁷⁻¹⁰.

The main goal of this paper is to synthesize and characterize linear poly (divinylbenzene-*co*-ethylvinylbenzene) obtained from commercial divinylbenzene via Maghnite-H⁺, a new nontoxic cationic catalyst¹⁰. In this work, the characterization of the synthesized product was carried out by means of ¹H and ¹³C NMR. The effect of the amount of the Maghnite-H⁺ on both the molecular weight and the intrinsic viscosities of the product as well as the mechanism of initiation of this polymerization are discussed.

EXPERIMENTAL

Materials

The monomer [technical grade: 65% *meta*- and *para*-isomers of DVB, 33% EVB and 2% of stabilizing (tert-butyl-4-pyrocatechol) Fluka], was purified by fractional distillation under reduced pressure. Methanol was initially dried over magnesium sulfate, and then distilled. Dichloromethane, (Aldrich Chemical) was used as received.

Preparation of Maghnite-H⁺

The preparation of the Maghnite-H⁺ was carried out using a method similar to that described by Belbachir and al.¹⁰. The raw-Maghnite (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder and dried by baking at 105°C for 2 h. It was subsequently weighed and placed in an erlenmeyer flask together with 500 mL of distilled water. The suspension solution was first stirred using a magnetic stirrer and then combined, at room temperature, with 0.25M sulfuric acid, until saturation, which is achieved after 2 days. The product was washed with distilled water and finally dried at 105°C for 24 h.

Polymerization procedures

DVB-EVB copolymers were obtained by using 7.69 mmol (1 g) of DVB and various amounts

of Maghnite-H⁺ (10, 20, 30 and 50 % wt). The mixtures were stirred with a magnetic stirrer under dry nitrogen. After 48 h, the product was dissolved in 10 ml of dichloromethane. The catalysts were removed from the mixtures of the products by simple filtration. Subsequently, the filtrates were precipitated in 100 ml of methanol. The precipitates were then filtered and dried in vacuum. The monomer conversion was determined gravimetrically by weighing the precipitated linear poly (DVB-*co*-EVB) chains.

Characterization

¹H and ¹³C NMR spectra were recorded under ambient temperature on an AM 300 FT Bruker spectrometer using tetramethylsilane as internal standard and deuterated chloroform as solvent.

Gel permeation chromatography (GPC) measurements of the polymer were carried out using a WISP 712, Waters Associates chromatograph, THF was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weight.

Intrinsic viscosity measurements were performed on SEMATECH Viscologic TI 1 apparatus at 25°C using THF as solvent.

RESULTS AND DISCUSSION

Characterization of copolymer

During the past, linear poly divinylbenzene by oxoacids initiating the cationic polymerization of DVB has been obtained⁵. In this paper, we try to use Maghnite-H⁺ to initiate the polymerization of commercial DVB, and obtain a copolymer between EVB and DVB.

Catalyst

This study is concerned with cationic polymerization and examines the catalytic activity of a proton-exchanged montmorillonite clay called "Maghnite-H⁺" via DVB polymerization. The structure and the composition of the catalyst were reported in previous work¹⁰. The elementary analysis of Maghnite-H⁺, obtained using XRF spectroscopy and monomer conversions, show that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite-H⁺. Acid treatment of "raw-Maghnite" reduces the octahedral

content (Al_2O_3) which causes an increase in the proportion of silica ^{7, 10, 16, 17}. It has been found that the best value for monomer conversion was obtained with raw-Maghnite treated by 0.25M sulfuric acid solution, in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure ¹⁰.

¹H and ¹³C NMR measurements

¹H and ¹³C NMR spectra of polymer were recorded in CDCl_3 using a Bruker AM 300 MHz apparatus at 25°C. These characterizations gave the following informations:

- (1) The ¹H NMR spectrum (see figure 1) allowed confirmation of the structure of the copolymer obtained in this study. The signals between 6,9 and 7,4 ppm (h) are attributed to the aromatic protons; the signals observed between 5,25(f) and 5,8 ppm (g) are attributed to the vinylic hydrogens (conjugation); the signals at 2,1 (c) and 2,4 (d) and 1,6 (b) ppm are assigned to methine, methylene and methyl protons of the polymer repeating unit respectively; the signals at 2,65 (e) and 1,25 ppm (a) are attributed to the CH_2 and CH_3 of the pendant ethyl groups from the EVB repeat unit (The

letters used in the text are indicated on figures 1).

- (2) The peaks of the ¹³C-NMR spectra are assigned as follows: the 128 ppm peak is attributed to phenyl C; the 115 ppm and 138 ppm are from $\text{CH}=\text{CH}$, the 28 ppm peak is attributed to CH_3 . The resonances at 18 ppm and 30 ppm are assigned to the CH_3 and CH_2 of the pendant ethyl groups from the EVB repeat unit and the 47 ppm and 57 ppm peaks are tentatively assigned to the CH_2 and CH in the sequence of EVB units.

Table 1: Mn, I, and intrinsic viscosity of PDVB

Maghnite-H ⁺ /DVB weight ratio (%)	Mn ^a	I ^b	Intrinsic viscosity ^c [ml/g]
10	1369	1.75	3.59
20	1324	2.13	3.12
30	1215	2.00	2.68
50	1178	2.09	1.97

^a determined by GPC with polystyrene standard; ^b I – polydispersity index (M_w/M_n); ^c in THF at 25°C.

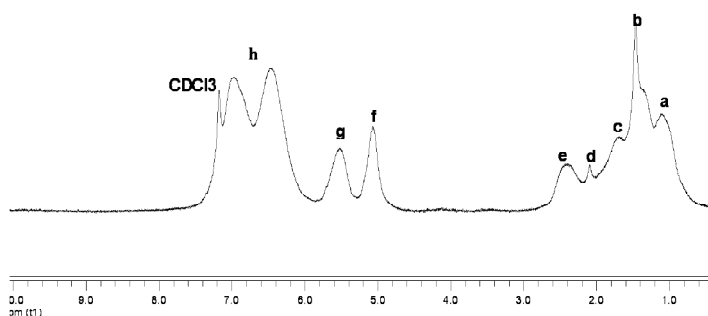
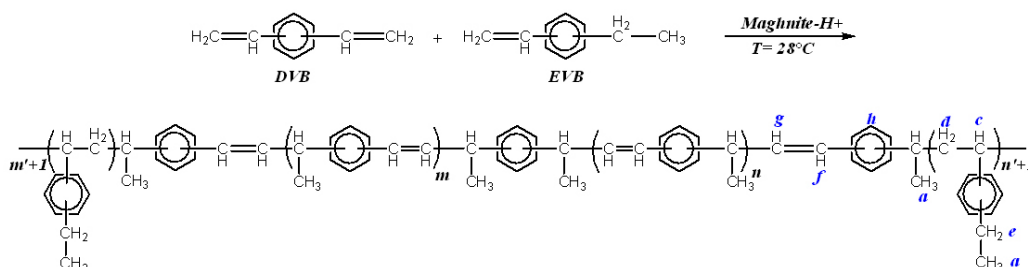


Fig.1: ¹H NMR spectrum of poly (divinylbenzene-co- ethylvinylbenzene) in CDCl_3



Scheme 1: Polymerization of DVB

According to this analysis, the resulting poly (DVB-*co*-EVB) (PDVB) seems to be the only detectable product and no ambiguity remains on its structure.

GPC and intrinsic viscosity Analysis

Table 1 shows that the molecular weight and the intrinsic viscosity of PDVB increase when the proportion of Maghnite-H⁺ decrease, thus clearly showing the effect of Maghnite-H⁺ as a catalyst. This phenomenon is probably the result of number of 'initiating active sites' responsible of inducing polymerization, a number that is prorata to the catalyst amount used in the reaction ¹⁶.

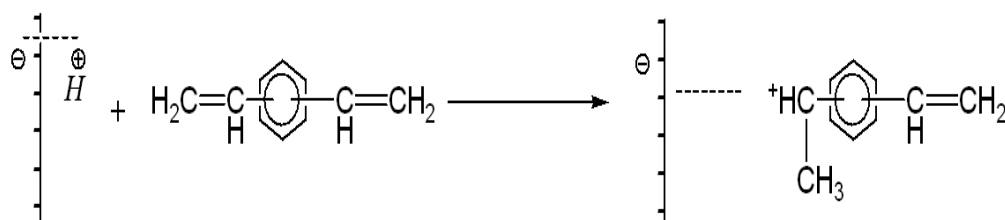
Mechanism

It has been reported that the cationic polymerization of DVB can be initiated by oxoacids in solution ⁵. Using this procedure, commercial DVB was examined in the presence of Maghnite-H⁺ powder in

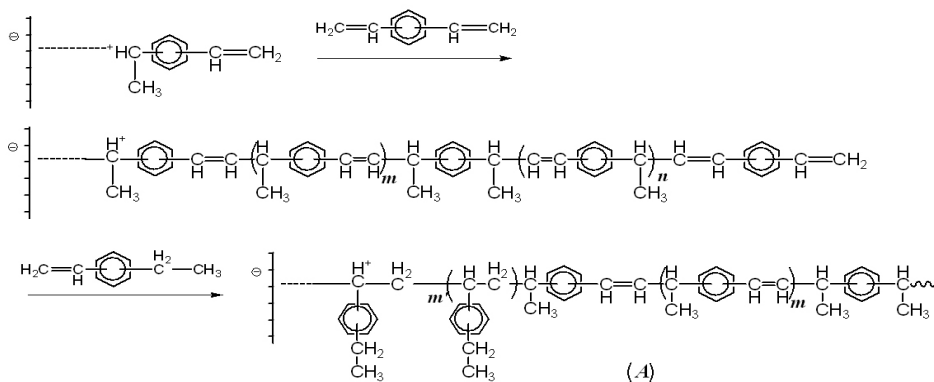
bulk at 28°C.

The reaction between the components of commercial DVB leads to several products via cationic catalyst because of the presence of *meta*- and *para*-isomers. It was found that the *para*-isomer polymerized more readily than the *meta*-isomer ¹. The overall order of reactivity was: *para*-DVB > *meta*-DVB > *meta*-EVB > *para*-EVB ¹⁹. Due to the relatively *higher* reactivity of *para*- and *meta*-DVB ³, the proportion of DVB to EVB groups in the polymer was greater than in the monomer mixtures.

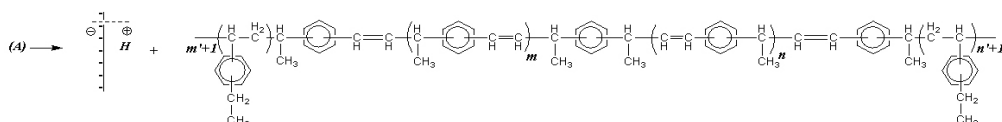
According to these relative reactivities of monomers ¹⁹ and the mechanism proposed by Hasegawa and Higashimura ⁵, we propose the following mechanism, which leads to the corresponding linear poly (DVB-*co*-EVB) as shown in Scheme 1.



Scheme 2: Initiation



Scheme 3: Propagation



Scheme 4: Termination

The polymerization of DVB is considered to be initiated between the initiator and a first molecule of DVB to form the active species (Scheme 2), the Maghnite-H⁺ acting as counterion. Propagation is ensured by successive adjunction of DVB and is followed by successive adjunction of molecules of EVB (Scheme 3). Termination is probably caused by spontaneous transfer of EVB to the linear polymer growing chains (Scheme 4).

via cationic catalyst. The linear polymerization was found to be initiated by Maghnite-H⁺ powder. It has been shown that -the polymerization rate increased with the amount of Maghnite-H⁺, and the cationic catalyst role of Maghnite-H⁺ for commercial DVB is clearly shown. Finally, the mechanism of polymerization was defined; the structure of the polymer explained and confirmed with ¹H and ¹³C NMR spectra.

CONCLUSION

This paper provides a method for synthesizing linear copolymer of poly (divinylbenzene -co-ethylvinylbenzene) from commercial divinylbenzene

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