



Synthesis of block copolymers consists on vinylidene chloride and α -Methylstyrene by cationic polymerization using an acid exchanged motmorillonite clay as heterogeneous catalyst (Algerian MMT)



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ABSTRACT

The aim of this study was to develop the efficient and versatile method for the synthesis of block copolymers consists by cationic polymerization vinylidene chloride (VDC) and alpha-methylstyrene (alpha-MS) in the presence of a natural Algerian montmorillonite clay modified by 0.05–0.35 M H_2SO_4 (Algerian MMT- H^+). It was found that H_2SO_4 concentration allows controlling the chemical composition, the porous structure of the acid-activated clays and their catalytic performance. The maximal yield of polymer is observed in the presence of Algerian MMT modified by 0.25 M H_2SO_4 . Effects of VDC/MS molar ration, catalyst concentration, reaction time, reaction temperature and polarity medium on yield and molecular weight of polymer were revealed in the presence of the most active sample.

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1. Introduction

Vinylidene chloride (VDC) copolymers have a number of excellent characteristics which have placed them in a position of prominence in the plastic packaging industry. These polymers are used, often in connection with other structural polymers, as a barrier to prevent the entry of oxygen into food containers (to avoid food spoilage) and to limit the loss of flavor and aroma constituents (flavor scalping) during long periods of storage (warehouse, supermarket shelves, etc.). Although these polymers display outstanding characteristics for use in food packaging, they suffer from sensitivity to thermal treatments during processing. Vinylidene chloride (VDC) copolymers have several outstanding properties, such as high crystallinity, resistance to non basic solvents and most importantly extremely low permeability to a wide variety of gases. VDC can be polymerized with a wide variety of monomers using either free radical or ionic initiation [1–13].

The objective in most cases has been to prepare a material with

specific properties rather than to study the copolymerization of VDC. VDC was one of the four monomers included in the significant study by Lewis, Mayo and Hulse [14]. (The others were styrene, acrylonitrile, and methyl methacrylate) [15]. Both the homopolymers and copolymers containing VDC as the major component are known as Saran. The polymers used commercially are copolymers of VDC with various other unsaturated monomers. Wiley [16] discovered the ability of Saran copolymers to supercool and cold draw into highly oriented films and fibers. The most valuable property of these polymers, low permeability, was also observed in this fruitful period. The major application utilizing this and other properties were identified. These included fibers, biaxially oriented films, Molded pipe, And lacquer coatings. Haldon [17] investigated the dehydrochlorination reaction of VDC/Styrene copolymers. This was again found to be a radical process accompanied by chain scission and cross-linking in competition. The copolymers were more easily dehydrochlorinated than the homopolymer, and eliminated HCl at rates that could only be interpreted in terms of styrene group activation, indicating that initiation occurred at VDC units adjacent to styrene units, but the exact nature of the Styrene activation was not known. The kinetics of the elimination reaction were consistent with retardation by some of its products. In VDC

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-rich copolymers the normal HCl elimination may also be present. In the synthesis of most plastics polymers, many researchers used metal catalysts to activate the reaction [18]. The cationic polymerization of VDC seems unlikely in view of its structure, Lewis acid catalysis explains the difficulties encountered in trying to fabricate Saran resins [19]. Other attempts to induce cationic copolymerization of vinylidene chloride have been unsuccessful [20–22]. We chose the VDC to prepare new polymer [poly (α -MS -b-VDC)] because there is, to date, no information on the polymerization of VDC with clay catalyst (Maghnite-H⁺) as a cationic process [23]. In continuation of our studies on environmentally benign methods using solid supports, we report for the first time the synthesis of poly (α -MS -b-VDC) via cationic polymerization by an acid-exchanged Montmorillonite called Maghnite-H (Maghnite-H⁺) [24–28]. In recent years, our group has explored new modified natural clay catalysts or initiators for polymerization of vinylic and hetero-cyclic monomers [29–43]. In this article we report the kinetics study of the polymerization of VDC with α -MS catalyzed by a proton-exchanged montmorillonite clay, called Maghnite-H⁺.

2. Experimental section

2.1. Materials

Vinylidene chloride (99%) and α -Methylstyrene (99%) were purchased from Aldrich (Paris, France) and were purified by fractional distillation under reduced pressure. Methanol was dried over magnesium sulfate. 1,4-Dioxane, Chloroform, THF and 1,2-Dichlorobenzene, (Aldrich Chemical) were used as received. Raw-Maghnite: Algerian Montmorillonite clay, was procured from "BENTAL" (Algerian Society of Bentonite). Montmorillonite clay, or 'raw-maghnite' was obtained from ENOF Maghnia (Western of Algeria). The protonated forms of montmorillonite (Maghnite-H⁺) were prepared by shaking the clay in a solution of sulfuric acid until saturation was achieved (normally after two days at room temperature). The cation-exchanged clay was then recovered by filtration, and again suspended in deionized water. This process was repeated until no sulfate ions were indicated present in the filtrate using BaCl₂. The Maghnite-H⁺ was then isolated by filtration, dried at 105 °C and then finely ground. The cation exchange capacity (CEC) of the clay was found to be 84 mEq (100 g)⁻¹ of dried clay. The concentrations 0.05 M, 0.10 M, 0.15 M, 0.20 M, 0.25 M, 0.30 M and 0.35 M of sulfuric acid treatment solutions were used to prepare "Maghnite-H⁺ 0.05 M", "Maghnite-H⁺ 0.10 M", "Maghnite-H⁺ 0.15 M", "Maghnite-H⁺ 0.20 M", "Maghnite-H⁺ 0.25 M", "Maghnite-H⁺ 0.30 M" and "Maghnite-H⁺ 0.35 M" respectively [23].

2.2. Characterization of Maghnite-H⁺

The BET surface area and pore volume of sample were determined by Nitrogen sorption at 77 K using an ASAP 2020 V3.04 E from Micromeritics.

X-ray fluorescence (XRF): the chemical compositions of raw and acid-activated Maghnite were determined by XRF using a PW 2400 Philips Analytical wavelength-dispersive sequential XRF spectrometer with SuperQ PANalytical software.

X-ray diffraction (XRD): the XRD spectrum was performed on oriented samples with a Bruker AXS D8 Advance diffractometer equipped with LynxEye linear detector, with Co K α 1 radiation ($\lambda = 1.54056 \text{ \AA}$) and a scanning interval of $2\theta = 0^\circ\text{--}70^\circ$ and a scanning speed of $0.02^\circ/\text{s}$, at room temperature.

FTIR: the FTIR spectrum was recorded on an Alpha FTIR Bruker spectrometer (400–4000 cm⁻¹).

2.3. Polymer characterization

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¹H NMR and ¹³C NMR measurements were carried out on a 300 MHz Avance Bruker spectrometer equipped with a probe BB05 mm, in CDCl₃ solution under ambient temperature using Tetramethylsilane (TMS) as internal standard in these cases.

Gel-permeation chromatography was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series, and packed with Ultrastaygel 10³, 10⁴, 10⁵, 10⁶ Å. THF was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic T11, version 3-1 Sematec). Intrinsic viscosity, $[\eta]$ (mL/g), was measured at 25 °C in THF. Viscosity-average molecular weight, M_v , was calculated according to the following equation [44]:

$$[\eta] = 10,1 \times 10^{-3} \times M_v^{0,71}$$

Differential scanning calorimetry (DSC) studies were conducted with a SETARAM-DSC92 in a nitrogen atmosphere at a heating rate of 10 °C/min.

2.4. Polymerization procedure

The copolymerization of α -MS with VDC were carried out in stirred flasks at different (α -MS/VDC) molar ratios, between 20/80 and 40/60. The catalyst was dried in a muffle at 120 °C overnight and then transferred to a vacuum desiccator containing P₂O₅. After cooling to room temperature under vacuum, the catalyst (15% by weight) was added to the α -MS. The mixtures were kept in a thermostat at 0 °C and stirred with a magnetic stirrer under dry nitrogen. After a definite period of time when the mixture becomes viscous, the second monomer of VDC is added subsequently for 24 h. The resulting polymer was extracted with 1,4-dioxane, precipitated in methanol.

3. Results and discussion

3.1. Preparation of the Maghnite-H⁺

The preparation of the "Maghnite-H⁺ 0.25 M" was carried out by using a method similar to that described by Belbachir and co-workers. Indeed, the raw-Maghnite (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105 °C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with 500 ml of distilled water. The maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M of sulfuric acid solution, until saturation was achieved over two days at room temperature, the mineral was washed with distilled water until it became sulfate free, and then dried at 105 °C [23–28].

3.2. Characterization of catalyst

Natural montmorillonite clay has been used. Maghnite-H⁺ was obtained by treating the raw maghnite with H₂SO₄ concentrations of 0.05, 0.15, 0.25, 0.35, 0.5 M and 1 M. After the activation process and filtration, the samples were washed until pH close to 7 and dried at 105 °C overnight and characterized by XRF and XRD.

The best value of copolymer yield was obtained with Maghnite-H⁺ 0.25 M, in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure [23].

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