Preparation of vinyl chloride – vinyl ether copolymers via partial etherification from PVC

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Abstract. The chemical modifications of poly (vinyl chloride) with aliphatic and aromatic alcohols compounds have been investigated at room temperature and atmospheric pressure, catalysed by a new green basic catalyst, the Maghnite- K^+ . The presence of ether groups in the products is proven by infra red spectroscopy (IR) as well as by nuclear magnetic resonance spectroscopy (¹H NMR), and characterized by intrinsic viscosity as well as by gel permeation chromatography (GPC).

Keywords: polymer membranes, Maghnite-K, PVC, grafting copolymers, Algerian clay, basic catalyst

1. Introduction

The purpose of this work was to highlight the chemical interaction of poly (vinyl chloride) with diverse alcohols and trying to introduce them onto polymer chain.

PVC is one of the most important commercial polymers due to its low production costs and its excellent stability to acids and bases [1]. However, there is some shortcoming such as limited thermal and mechanical stability or sensitivity to ultraviolet radiation [2].

By chemical modifications reactions of PVC with appropriate compounds, new polymers with improved physical properties can be obtained [3, 4].

The nucleophilic substitution of chlorine atoms with thiophenolate [1], amine [5] and thiol [6] has been intensively studied in recent years.

On the other hand, it has recently been shown [6, 7] that PVC can also be used as an interesting starting membrane material for gas separation when the polymer is chemically modified.

In the present communication, we show that reaction of PVC with alcohols catalysed by Maghnite-K⁺ in THF solution gives a new white copolymer (VC-Ether) product which is soluble in DMF, DMSO, partially soluble in toluene and chloroform and insoluble in pentane and water.

2. Experimental part

2.1. Materials

- 1. Commercial bulk polymerized PVC was obtained from ENIP (Skikda Algeria, type 4000M Kwert = 65–66), its average molecular weights determined by Gel Permeation Chromatography were $M_w = 149\ 000\ \text{g/mole}$ and $M_n = 71\ 700\ \text{g/mole}$. It was used as the base polymer.
- 2. Tetrahydrofuran, ethanol and pentane were supplied from Prolabo (Paris, France) and used as good solvent and nonsolvents respectively.
- 3. Ethanol (Prolabo, France), ethylene glycol (Merck) and phenol (Fluka) were used as reagents.

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4. The preparation of Maghnite-K was carried out with the method described by Belbachir and coworkers [8–11], using 100 g of the raw Algerian clay (Maghnia; West Algeria) and 20 g of potassium hydroxide (KOH, Fisher Scientific). It was crushed for 20 min with a Prolabo ceramic balls grinder, then dried through baking at 105°C for 2 h and cooled to room temperature.

2.2. Modifications of PVC

PVC (3 g; 48 mmole) was dissolved in 30 ml of THF (solution 1).

48 mmole from each alcohol (ethanol 2.2 g, ethylene glycol 3 g and phenol 4.5 g) was mixed each one with 3 g of Maghnite-K and agitated for 15 minutes at room temperature and added to the solution 1.

After 4 hours the reactions were stopped, filtered and precipitated in cold ethanol. The modified polymers were purified using THF/Pentane (for sample with ethanol: copolymer 1) and THF/ Ethanol (for sample with ethylene glycol: copolymer 2, and phenol: copolymer 3).

The yield of the grafted PVC was optimized after 4 hours, and it was been between 50 and 83%.

2.3. Test methods

¹H NMR spectra were recorded at room temperature, on a 300 MHz Bruker Avance spectrometer, using deuterated DMSO or chloroform. as solvents. FT-IR measurements were performed on thin cast films of polymers using ATI MATTSON FT-IR spectrometer.

GPC measurements of the grafted PVC samples 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 weights. The flow rate of tetrahydrofuran was 10 ml/min.

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

3. Results and discussion

Reaction of PVC with various alcohols in a THF solution gives primarily the corresponding copolymers in high transformation yield (Figure 1). The

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Figure 1. Grafting of PVC with various alcohols using Maghnite-K



Figure 2. ¹H NMR spectra of alcohols grafting on PVC. a) PVC-g-ethanol (CDCl₃), b) PVC-g-ethylene glycol (CDCl₃) and c) PVC-g-phenol (DMSOd6)

resulting products are soluble in many organic solvents such as ethyl acetate, DMF, DMSO and THF. PVC itself is not soluble in ethyl acetate.

3.1. Characterizations of modified PVC

The modification reactions were performed as indicated in experimental part section.

Samples were withdrawn, purified and analysed by ¹H NMR spectroscopy.

In Figure 2 the corresponding spectra of the modified PVCs are shown. With the appearance of alcohols proton peaks [7, 12].

- 1. In copolymer 1 (Figure 2a) two signals at 1.24 ppm and 3.73 ppm corresponding to CH₃ and CH₂ of ethanol respectively arise.
- 2. In copolymer 2 (Figure 2b) a signal at 3.74 ppm appear corresponding to CH₂ of ethylene glycol.
- 3. In copolymer 3 (Figure 2c) aromatic's signal (6.7–7.2 ppm) are appeared.

The variation of the chemical structure through the grafting of various alcohols onto the PVC was confirmed by FT-IR as shown in Figure 3.

The most significant change in each spectra of the grafted PVC was the appearance of the red-shifted ($1042-1047 \text{ cm}^{-1}$) absorption band due to the C–O stretching vibration of ethers.



Figure 3. FT-IR spectra of alcohols grafting on PVC. a) PVC-g-ethanol and b) PVC-g-ethylene glycol

Also, the major characteristic peaks for PVC appeared at 720, 760, 800 cm^{-1} representing C–Cl stretching bands.

It is important to note that, GPC analysis of the PVC and various copolymers shows a sharp decrease in the molecular weight in relation to that of the starting PVC in sample with phenol, and outstanding increase in sample with ethanol, a light increase in sample with ethylene glycol, as shown in Table 1.

Also comparison of the intrinsic viscosities (Table 1) of PVC and copolymers 1, 2 and 3 shows a same variations during modification with ethanol, ethylene glycol and phenol. At the moment it is not possible to suggest a mechanism for this process which appears to take place under very mild conditions. Further work is necessary to shed light on this.

4. Conclusions

This study reveals that:

PVC can be chemically modified by various alcohols using Maghnite- K^+ as catalyst without appreciable dehydrochlorination.

The PVC modified with alcohols is not explosive under ambient conditions.

The conversion rate of PVC to copolymer (VC-Ether) product is high (~63%).

It has been shown that ethanol; ethylene glycol and phenol are appropriate agents to introduce ether groups onto the PVC.

The presence of the ether groups in PVC changes markedly the chemical and physical properties of the systems.

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Table 1. M_n , M_w , I, intrinsic viscosity and color of copolymer 1, 2 and 3

Samples	M_n^a	$\mathbf{M_w}^{\mathbf{a}}$	I ^b	Intrinsic viscosity ^c [ml/g]	Color
PVC	71 700	149 100	2.00	8.12	white
Copolymer 1	76 400	159 600	2.09	8.65	white
Copolymer 2	89 500	172 300	1.90	14.74	white
Copolymer 3	25 800	43 200	1.57	nd	yellow

nd: not determined

adtermined by GPC with polystyrene standard; bI - polydispersity index (M_w/M_n) ; cin THF at 25°C

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