

# Polyvinylidene fluoride heterogeneous alkaline reaction mechanism in propan-2-ol

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The reaction between polyvinylidene fluoride (PVDF) nanofibers and sodium hydroxide in the presence of propan-2-ol (IPA) as phase transfer catalyst (PTC) was studied. In this work, a new reaction mechanism for the formation of the conjugate structure. Sodium isopropylalcoholate catalyzes the  $C_{sp^2}-F$  bond cleavage in a transfer hydrogenation step and results in the formation of  $C_{sp^2}-H$  bond, a mechanism supported by the presence of acetone. These findings are of particular importance to PVDF alkaline reaction, it indicates that the use of IPA as PTC alter the reaction mechanism.

**Keywords:** Polyvinylidene fluoride; Nanofibers; Catalytic transfer hydrogenation; Surface modification

## Introduction

The reaction of PVDF and alkaline solutions is recognized as a key surface functionalization method and hence has been studied repeatedly over the past three decades for improving various inherent characteristics such as electrical conductivity, adhesiveness, or wetting properties[1–4].

From previously reported studies, there is a common consensus on the mechanism of PVDF defluorination by an alkaline solution, or at least on the initiate elimination  $E_2$  step of the mechanism[1–4]. Ross et al. further elaborated on a mechanism based on surface characterization techniques by reacting PVDF with NaOH using tetrabutylammonium bromide as the PTC[5]. The aim of this work is to study the mechanism of PVDF reaction with NaOH in propan-2-ol, focusing on group theory and symmetry tools in analyzing the vibrational modes of the dehydrofluorinated PVDF for a better understanding.

## Methodology

The aim of this work is to study the mechanism of PVDF reaction with NaOH in propan-2-ol, focusing on group theory and symmetry tools in analyzing the vibrational modes of the dehydrofluorinated PVDF for a better understanding.

Table 1. Parameters for the dehydrofluorination of PVDF nanofibers mats.

PVDF nanofibers (density of  $3.5 \text{ g/m}^2$ ) were obtained from the Laboratory of Nanofibers Materials Development and Testing, Institute of Nanomaterials, Technical University of Liberec.

The dehydrofluorination reaction was performed by soaking various  $5 \times 5 \text{ cm}^2$  PVDF nanofiber mats in 20 ml of different concentrations of NaOH solutions (0.1–1 M) in 1 ml of 99.8% IPA for 15 min. The nanofiber mats were then placed into covered Petri dishes and heated at either 60 or 80 °C in an oven. The reaction parameters of temperature, contact time and NaOH concentration were varied to observe their effects on the reaction.

Quantification of acetone in PVDF and NaOH/IPA reaction medium was carried out by gas chromatography GC coupled with a mass spectrometer.

## Results and discussion

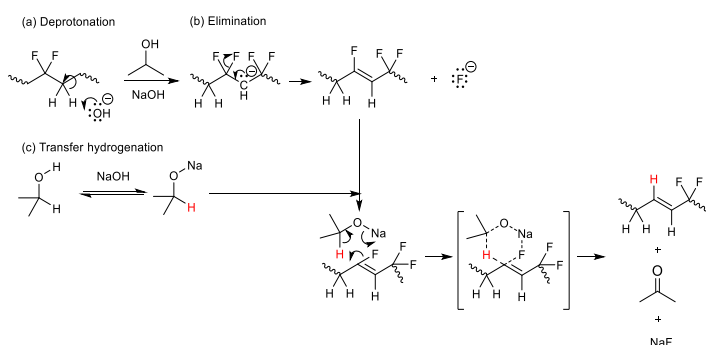
The reaction of PVDF nanofibers with NaOH in IPA was performed using a variety of reaction parameters.

FTIR signals at  $840 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$  from the post reacted PVDF nanofiber spectra suggests that the reaction substrate has an all *trans* or  $\beta$  conformation. FTIR spectra of the treated PVDF nanofibers displayed

functional groups signals, where two distinct FTIR spectra were observed based on the reaction variables. The first spectra displayed no new bands (silent spectra) being formed from the measurements of samples modified at 60 °C regardless of contact time or concentration of NaOH. Similarly, no new bands appeared from reaction parameters at 80 °C and the lowest concentrations and contact times of 0.1–0.5 M NaOH and 1–2 h, respectively. In contrast, the spectra from all other samples treated at 80 °C (at harsher conditions) displayed new bands (active spectra), showing the appearance of a new weak band at around 1570 cm<sup>-1</sup> assigned to two overlapping bands, the first is C=C st and the second is OH deformation, and also a broad OH band at around 3350 cm<sup>-1</sup>. The silence of the double bond signal within FTIR spectra implies that the rule of mutual exclusion is in effect, whereby all IR active vibrational modes are Raman inactive and vice versa. Hence the structure of the product displaying silent FTIR spectra is the hydrated conjugated structure CH=CH.

The formation of hydrated conjugate structure prior to hydroxylation dictates the proposal of a new mechanism, whereby a hydrogenation step takes place after the elimination. Given the reaction components, the hydrogenation may be justified by a formation of a base-catalyzed transfer hydrogenation mechanism (Scheme 1c). The intermediate structure then decomposes in a hydrodefluorination step to produce the vinylene segment as a key product, and acetone plus sodium fluoride as side products (Scheme 1c).

The results of the GC analysis showed the presence of acetone ranging between 2.7 and 12.4 µg/L. Primarily, the presence of acetone when using IPA is considered to be conclusive evidence of the catalyzed transfer hydrogenation mechanism proposed.



Scheme 1. Proposed mechanism for PVDF dehydrofluorination. (a) deprotonation, (b) elimination, (c) transfer hydrogenation.

## Conclusion

This study revealed that using propan-2-ol as a PTC in PVDF alkaline reaction with NaOH alters the dehydrofluorination reaction mechanism. In conclusion, a new transfer hydrogenation mechanism is proposed for the heterogeneous reaction of PVDF with NaOH in IPA, it explains the second fluorine departure and the hydration of the unit cell CF=CH, whereby IPA was shown to be the hydrogen source in addition to its role as a PTC.

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