

# Hydroperoxidation of EPDM Rubber Using Singlet Oxygen: Synthesis and Grafting Studies

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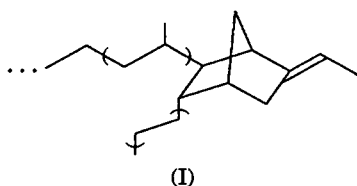
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## SYNOPSIS

Chemically generated singlet oxygen hydroperoxidizes the ethylidene double bond in terpolymers of ethylene, propylene, and ethylidene norbornene (EPDM rubber). The EPDM-hydroperoxide was reduced exclusively to 2-(1-hydroxyethyl)-norbornene-EPDM rubber using either triphenylphosphine or sodium sulfite. Thermal decomposition of EPDM-hydroperoxide in the presence of either methyl methacrylate or 2- or 4-vinyl pyridine free radically grafted these monomers to the rubber. In the absence of graftable monomer, however, thermal decomposition of EPDM-hydroperoxide generated an intractable polyether.

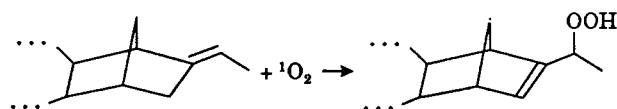
## INTRODUCTION

The presence of a reactive and isolated pendant double bond in terpolymers of ethylene, propylene, and ethylidene norbornene (EPDM rubber) (I) suggests that it is an attractive candidate for polymer modification. Previous workers have photohydroperoxidized

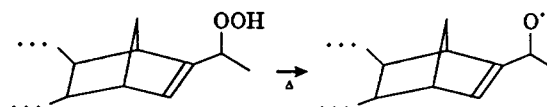


and reduced the ethylidene portion of EPDM rubbers.<sup>1,2</sup> Moreover, photohydroperoxidized EPDM rubber has recently been utilized as a component in IPNs.<sup>2</sup> Our studies are unique in that monomers were grafted to the peroxidation reaction site of the EPDM rubber once was thermally decomposed:

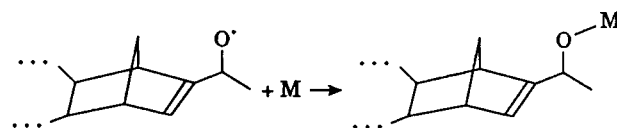
### 1. PEROXIDE FORMATION



### 2. RADICAL FORMATION



### 3. MONOMER ATTACHMENT

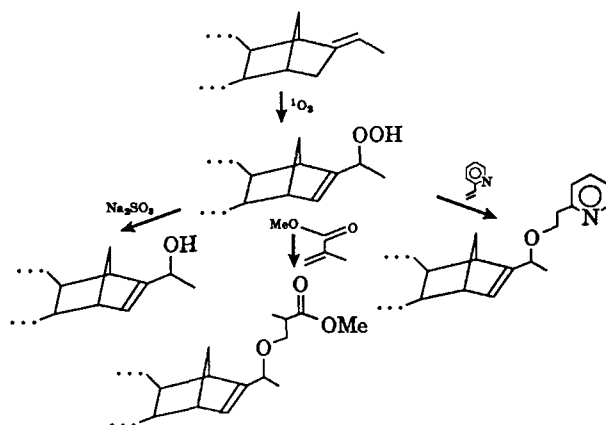


Scheme I

Hydroperoxidations were modeled after the work of McKeown and Walters<sup>3</sup> using chemically generated singlet oxygen for a substrate insoluble in methyl alcohol.<sup>3</sup> Singlet oxygen is generated in a lower aqueous phase using hydrogen peroxide and bromine and interfaces with an organic layer containing the polymer. The reaction of EPDM rubber with singlet oxygen would be localized to the pendant double bond generating an allylic hydroperoxide.

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Free radical grafting of monomers to the allylic hydroperoxide site was performed by thermally decomposing the EPDM-peroxide in a solution containing either methyl methacrylate (MMA) or 2- or 4-vinyl pyridine (2- or 4-VP), respectively:



Scheme II

## EXPERIMENTAL

EPDM rubber containing 4% ethlidene norbornene was obtained from Copolymer Rubber and Chemical Corp. It was purified by precipitation in spectral grade methanol and dried. Methyl methacrylate and 2- and 4-vinyl pyridine were obtained from the Aldrich Chemical Co.; the inhibitor in all cases was removed prior to grafting. Bromine, 30 wt % hydrogen peroxide, and reagent grade chlorobenzene were used as received.

Infrared spectra were recorded neat as a film on potassium chloride plates using a Nicolet 5-DX spectrometer. Proton magnetic spectra (H-NMR) were recorded at 300 MHz using a Varian VXR-300. Samples were run in *d*5-chlorobenzene using *d*-chloroform as the internal lock and TMS as the reference standard.

### Preparation of EPDM-Hydroperoxide

A glass immersion tube containing a magnetic stirrer bar is charged with 0.5 g EPDM rubber dissolved in 50 mL chlorobenzene and 3.5 mL 30 wt % hydrogen peroxide containing 0.7 g potassium hydroxide and the charge is cooled to  $-10^{\circ}\text{C}$ . A solution of 2.0 mL bromine containing 8.0 mL chloroform is added in 0.4 mL increments over the course of approximately 3 h. The lower layer is removed and the organic layer dried over calcium chloride at  $0-5^{\circ}\text{C}$ . IR (film):  $3437.5\text{ cm}^{-1}$  (OOH)

### Reduction of EPDM-Hydroperoxide Using Sodium Sulfite

Approximately 50 mL of EPDM-peroxide is added to a 100 mL reaction flask containing a magnetic stirrer and a slurry of 1.0 g sodium sulfite containing 3 mL anhydrous methanol at  $5^{\circ}\text{C}$ . The material is stirred for 4 h at  $5^{\circ}\text{C}$  and an additional 2 h at  $30^{\circ}\text{C}$ . H-NMR (*d*5-chlorobenzene): 3.72 ppm (s, OH) and 4.45 ppm (m, CHOH); IR (film):  $3189.2\text{ cm}^{-1}$  (OH).

### Reduction of EPDM-Hydroperoxide Using Triphenylphosphine

The reduction of EPDM-hydroperoxide was performed using the method of Duystee and Mevis. Spectra were identical to the aforementioned reduction procedure utilizing sodium sulfite.

### Preparation of EPDM-graft-Poly(methyl Methacrylate)

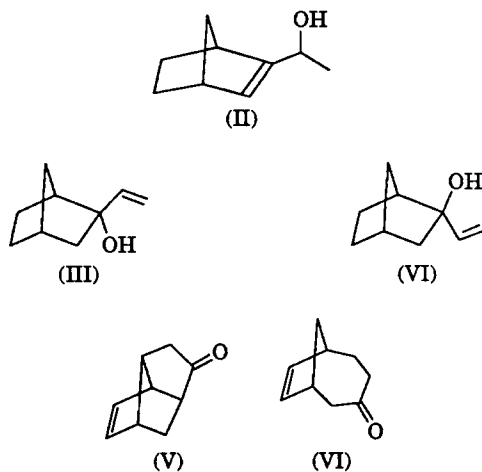
A solution of 25 mL 5% EPDM-hydroperoxide in chlorobenzene is cooled to  $0^{\circ}\text{C}$  and 2 mL inhibitor-free methyl methacrylate added. The solution is stirred for 1 h at this initial temperature and 4 h at  $45^{\circ}\text{C}$ . The polymer is precipitated in 100 mL acetone, redissolved in warm *n*-heptane, and precipitated in acetone, this procedure repeated three times to ensure removal of oligomeric MMA. IR (film):  $1735.1\text{ cm}^{-1}$  (CO).

### Preparation of EPDM-graft-Poly(2- or 4-Vinyl Pyridine)

The previous grafting procedure is utilized for either 2- or 4-pyridine grafting but employing 6 mL of uninhibited monomer and maintaining the grafting at  $45^{\circ}\text{C}$  for 6 h. The grafted polymer is precipitated in acetone and then redissolved in *n*-heptane, this process performed three times. Trace amounts of poly(2- or 4-vinyl pyridine) were removed by dissolving the grafted polymer in *n*-heptane and precipitating in a 2 : 1 v/v acetone-DMF solution. IR (film): (graft-2-VP)  $1622.6\text{ cm}^{-1}$  (heteroaromatic CN); (graft-4-VP)  $1626.2\text{ cm}^{-1}$  (heteroaromatic CN).

## RESULTS AND DISCUSSION

The exclusive reduction product, 2-(1-hydroxyethyl)-norbornene EPDM rubber (II), suggests that only one hydroperoxidation product was formed.



The conspicuous absence of a vinyl absorption at  $925\text{ cm}^{-1}$  is supportive of this conclusion. Singlet oxygen hydroperoxidation of EPDM rubber was initially performed by Duynstee and Mevis<sup>1</sup> in benzene. These authors inferred that three peroxidation products would be obtained on the basis of an earlier investigation by Adams and Trecker.<sup>4</sup> Adams and Trecker, however, actually reported five products when ethylidene norbornene is photohydroperoxidized in methanol (II–VI). Our investigation detected a single peroxidation product limited exclusively to the ethylidene portion of the termonomer. It is unclear, however, whether this is a consequence of solvent, conformational, or steric restrictions imposed upon the reactive site of the polymer or the other factors. Specifically, this peroxidation occurs almost exclusively at the solvent interface since the lifetime of singlet oxygen is very short in solution.<sup>5</sup> At this interface greater polymer segmental aggregation occurs since one of the solvents is a “non-solvent” for the rubber, thereby severely restricting both reactive site orientations and their availability.<sup>6</sup>

Since we were unable to accurately assay peroxide content in the EPDM rubber, we were prevented from determining the half-life of the grafted peroxide. FTIR indicated that a sizable portion of the

pendant ethylidene moiety was unreacted, implying that trace amounts of reagent hydrogen peroxide would dramatically inflate this assay. For this reason methods utilizing either potassium iodide and sodium thiosulfate for bulk peroxide determination or triphenylphosphine for trace analysis were rejected.<sup>7</sup>

Monomers free radically grafted to the rubber were identified using infrared spectroscopy of films. The key absorbing moiety for EPDM-*graft*-poly(methyl methacrylate) was the ester carbonyl stretch at  $1735.1\text{ cm}^{-1}$ ; EPDM-*graft*-poly(2- or 4-vinyl pyridine) were fingerprinted by their heteroaromatic CN stretch at  $1622.6$  and  $1626.2\text{ cm}^{-1}$ , respectively. Infrared spectra of mixtures of oligomeric poly(methyl methacrylate) and poly(2- or 4-vinyl pyridine) and EPDM rubber had key infrared fingerprint absorbances at least  $10\text{ cm}^{-1}$  from grafted samples. Thermally decomposing EPDM-hydroperoxide in the absence of any graftable monomer at  $55^\circ\text{C}$  for 2 h produced an intractable material. A broad polyether absorbance was detected at  $1198.4\text{ cm}^{-1}$  with the norbornene unsaturation remaining intact.

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