

# Synthesis and Characterization of Poly(vinyl acetate peroxide)

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## SYNOPSIS

Poly(vinyl acetate peroxide) (PVACP) was prepared from vinyl acetate by free-radical-initiated oxidative polymerization. The polyperoxide was isolated and characterized by different spectroscopic methods. The extreme instability of PVACP was demonstrated by FTIR spectroscopy. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR studies show the irregularities in the polyperoxide chain due to the cleavage reactions of the propagating peroxide radical. Thermal degradation studies using differential scanning calorimetry revealed that PVACP degrades at a lower temperature and the heat of degradation is in the same range as reported for other vinyl polyperoxides. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In view of some significant explorations on their physico-chemical properties, the vinyl polyperoxides are witnessing a current renaissance which has stimulated a revival of interest in this narrow but important class of polymers.<sup>1,2</sup> Recent reports point to the potential of polymeric peroxides as specialized thermal<sup>3,4</sup> and photoinitiators<sup>5</sup> and emphasize the need to synthesize such new materials. Since the first report of its kind in 1925 by Staudinger and Schwalbach,<sup>6</sup> only a small number of polyperoxides have been studied. Of these, poly(styrene peroxide) (PSP), first reported by Bovey and Kolthoff,<sup>7</sup> has received considerable attention. Polyperoxides have been used as initiators in preference to the conventional simple peroxides, in a search to obtain novel polymers such as block polymers. Recently, poly(styrene peroxide) and poly( $\alpha$ -methylstyrene peroxide) have been shown to possess unique features as photo- and thermal initiators, respectively.<sup>3,5</sup> In view of their use in initiator applications, the importance lies in making polyperoxides having special degradation characteristics.

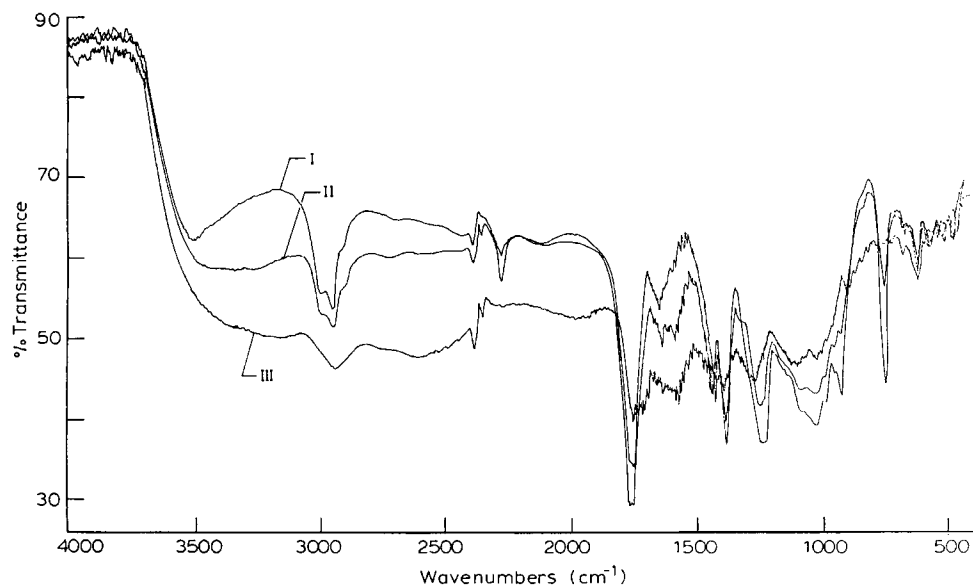
In this preliminary communication, we report the synthesis and spectral characterization of poly(vinyl acetate peroxide). The thermal degradation of polyperoxide was studied and found to have an exothermic heat of degradation approximately equal to that of poly(styrene peroxide). The gaseous degradation products make poly(vinyl acetate peroxide) a good candidate for initiator applications.

## EXPERIMENTAL

The commercially obtained vinyl acetate was distilled under reduced pressure prior to use. The polyperoxide was prepared by passing a copious flow of oxygen through the monomer containing 0.01 *M* AIBN as the initiator, at 50°C for 72 h. The resulting reaction mixture was freed from the monomer by applying a vacuum. The yellow-colored gummy solid obtained was dissolved in benzene and precipitated into petroleum ether.

The isolated polyperoxide was characterized by IR spectra recorded on a Bio-Rad FTS7 FTIR spectrometer, and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker AC-F 200 MHz NMR machine. The differential scanning calorimeter (DSC) characterization was performed on a DuPont 990 system under a nitrogen atmosphere at a heating rate of 20°C/min.

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**Figure 1** FTIR spectra of PVACP at different intervals of time: (I) 0 min; (II) 15 min; (III) 30 min.

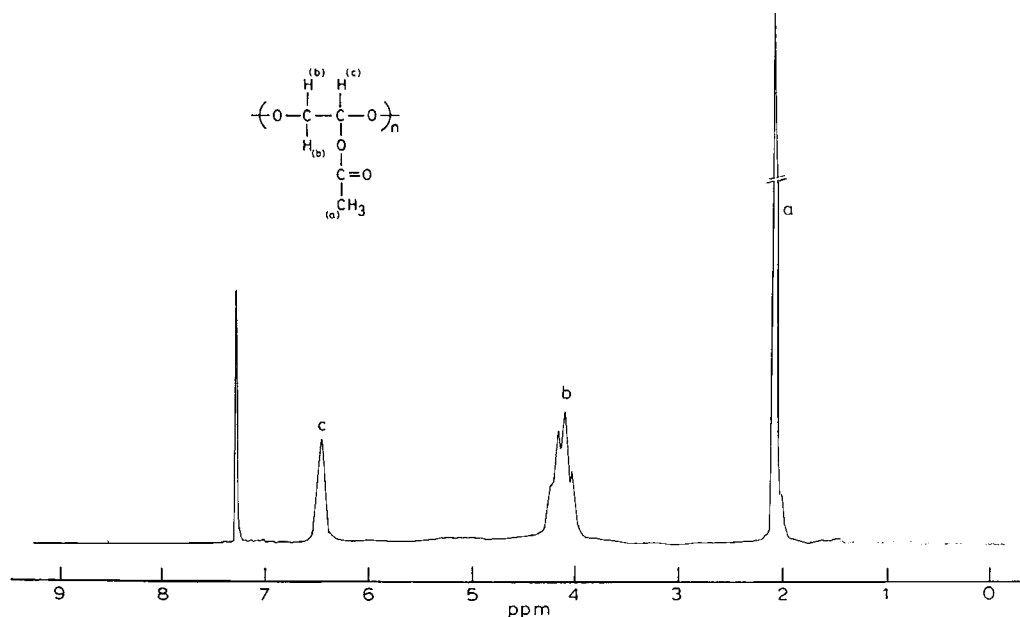
## RESULTS AND DISCUSSION

### FTIR Spectra

The extreme instability of poly(vinyl acetate peroxide) (PVACP) is shown by the FTIR spectra depicted in Figure 1. Spectrum (I) was obtained immediately after the polyperoxide was isolated; spectrum (II), 15 min after keeping the sample in the

IR instrument; and spectrum (III), after another 15 min. It is seen that the peroxide stretching band at  $1018\text{ cm}^{-1}$  completely disappeared during this time; concomitantly, the hydroxyl band at  $3555\text{ cm}^{-1}$  widens.

Unlike poly(styrene peroxide), in PVACP, the pendent group is an acetoxy group which is attached to the backbone carbon atom through that carbon atom's second C—O bond. This formally relates



**Figure 2**  $^1\text{H-NMR}$  spectrum of PVACP in  $\text{CDCl}_3$ .

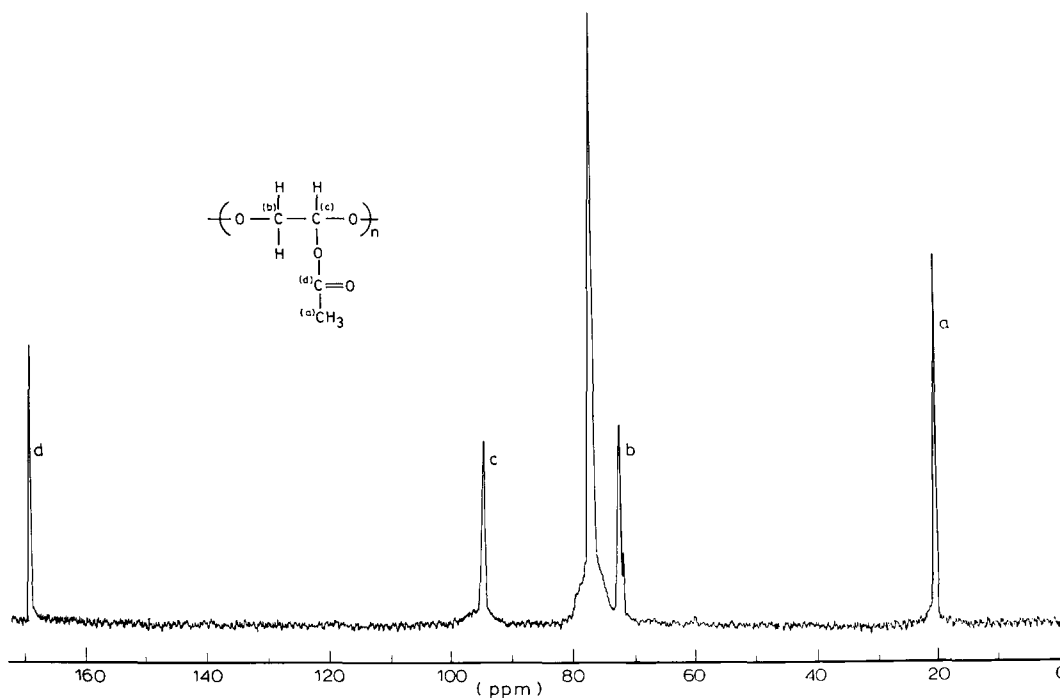


Figure 3  $^{13}\text{C}$ -NMR spectrum of PVACP in  $\text{CHCl}_3$ .

this site to a typically unstable "gem" diol.<sup>8</sup> This makes PVACP more unstable than other vinyl polyperoxides.

#### $^1\text{H}$ -NMR Spectra

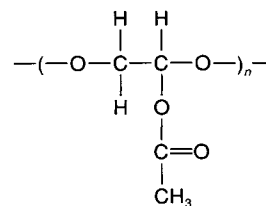
The 200 MHz  $^1\text{H}$ -NMR spectra of PVACP is depicted in Figure 2. The signals at  $\delta = 2.07$ , 4.1, and 6.45 ppm are assigned to the methyl, methylene, and methine protons, respectively. The methyl resonance signal is not shifted considerably, whereas the methine signal is shifted more downfield due to the two oxygen atoms directly attached to it. The methylene region shows complexity, which could be due to the excess methylene groups present in the polyperoxide chain as defects. This happens because, during the oxidation of vinyl acetate, the peroxy radical undergoes more cleavage reactions than does addition to another vinyl acetate molecule.<sup>9</sup> This kind of excess methylene groups has been shown to be present in the case of poly( $\alpha$ -methylstyrene peroxide).<sup>10</sup>

#### $^{13}\text{C}$ -NMR Spectra

The 50.12 MHz broadband  $^{13}\text{C}$ -NMR spectra of PVACP is presented in Figure 3. The resonance signals at  $\delta = 20.63$ , 72.3, 94.5, and 169.28 ppm are

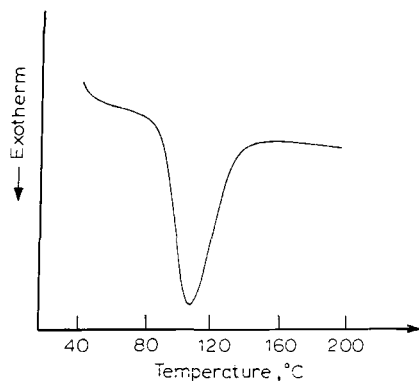
assigned to the methyl, methylene, methine, and carbonyl carbons, respectively. Here, also, a considerable downfield shift of the methine carbon is observed which is due to the two electronegative oxygen atoms directly attached to it. The methylene carbon signal also appears complicated due to the stereosensitivity of this backbone carbon as well as to the excess methylene groups present in the polyperoxide chain.

Based on the spectral observation, the general structure of PVACP can be written as



#### Thermal Degradation

PVACP degrades exothermally into formaldehyde, acetic acid, carbon monoxide, and an unidentified reddish black noncrystalline substance. The degradation was studied by DSC. Figure 4 is a typical thermogram showing the exothermal degradation of the polyperoxide. The exothermic degradation starts



**Figure 4** DSC thermogram for the degradation of PVACP heating rate = 20°C/min.

at about 65°C, which is very low compared to poly(styrene peroxide), which starts degrading at about 110°C under similar conditions.<sup>11</sup> The value of  $\Delta H_d$  has been calculated to be 249.8 cal/g, which is similar to that observed for other polyperoxides.

## CONCLUSIONS

The spectral characterization of poly(vinyl acetate peroxide) (PVACP) was carried out. Due to the fac-

ile cleavage reactions of the peroxide radicals, the chain irregularities in PVACP is found to be greater compared to other vinyl polyperoxides.

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