

# Determination of oxygen permeability of polymers using *in-situ* photo-generated heptacene<sup>☆</sup>

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## Abstract

Heptacene generated *in-situ* in a polymer matrix using a photochemical route undergoes oxidation with diffused oxygen leading to the formation of endoperoxides. We have found the high reactivity of heptacene, a linear poly(acene), toward molecular oxygen can be used to determine oxygen permeability of polymer films. The rate of disappearance of heptacene, due to oxidation, was found to be directly related to the oxygen permeability of the polymer. A simple spectroscopic method to estimate oxygen permeability of polymer films by monitoring the visible/near infra-red absorption of heptacene is described.

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**Keywords:** Heptacene; Photodecarbonylation; Oxygen permeability; Polymer

## 1. Introduction

The oxygen permeability ( $P_m$ ) of biocompatible and other polymers used in the packaging industry, as surface protective coatings, and in drug delivery membrane systems is an important physical parameter [1–3]. Permeability of a polymer film depends on several factors including density, crystallinity, orientation and cross-linking characteristics of the polymer as well as on the conditions of measurement [4]. Determining the  $P_m$  of a polymer film usually requires measurement of a change in gas pressure across the film [5,6]. The pressure difference is caused by the gas transferring through the membrane from a high-pressure side to a low-pressure side and measured in a specific apparatus. Although the principle is simple, these measurements are tedious and require a long time and expensive instrumentation.

Polarographic methods and membrane covered electrode techniques are used to measure the  $P_m$  [7,8]. Optical spectroscopy techniques, such as fluorescence, phosphorescence, and triplet-triplet absorption quenching of organic compounds have also been used for this purpose with varying degree of suc-

cess [3,9–16]. However, these spectroscopic methods require the generation of the excited states of the sensing molecule and depend upon the measurement of the dynamics and behavior of those excited states. Fluorescence methods are also found to be sensitive to the presence of even small amount of impurities in the polymer.

In this paper, we demonstrate the use of a UV–visible spectroscopic technique to estimate the  $P_m$  of polymer films in a simple, fast, and reliable manner. Recently, we reported the synthesis of a highly reactive poly(acene), heptacene, using photodecarbonylation of its  $\alpha$ -diketone precursor (**2**) (Scheme 1) [17].

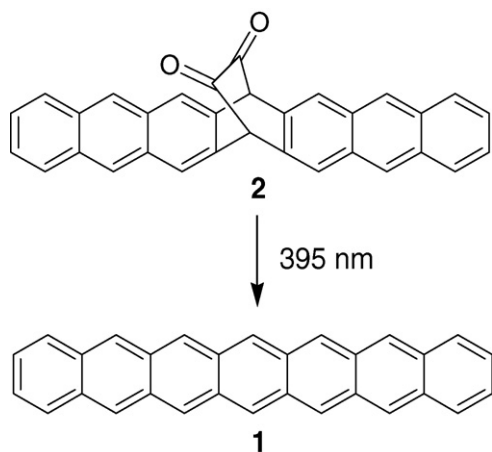
Heptacene (**1**) was generated in a poly(methyl methacrylate) matrix and the photodecarbonylation achieved with a ultraviolet light-emitting diode (UV-LED) light source ( $\lambda_{\max}$  395 nm) that almost selectively addresses the  $n$ - $\pi^*$  absorption band of the dione **2**. The photodecarbonylation is a clean process exclusively leading to the formation of **1**, which shows absorption bands in the visible and near infra-red region (600–825 nm). However, **1** is extremely sensitive to oxidation and is easily converted to oxidized products (endoperoxides) by molecular oxygen when the latter diffuses into the polymer matrix as visibly demonstrated by the gradual disappearance of its absorption [17].

We report that quenching of the absorption of **1** due to its oxidation in polymer matrices follows a pseudo first order kinetics and is dependent on the  $P_m$  of the polymer. The lower the  $P_m$  of

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Scheme 1. Photochemical synthesis of heptacene (1).

the polymer, the lower was the rate of quenching of **1**, and *vice versa*. This has enabled us to develop a technique that utilizes **1** as a marker to estimate the  $P_m$  of polymer films. The technique is based on a simple concept—once **1** is generated in a thin film of a polymer, disappearance of its absorption in the visible region can be monitored as a function of the oxygen permeability of the polymer. Since this method is based on the measurement of the change in the absorption of **1** embedded in the polymer matrix, it requires a simple measurement setup and avoids fallacies and measurement difficulties associated with excited state chemistries.

## 2. Experimental

### 2.1. Materials and instruments

Five commercially available polymers—low-density polyethylene (LDPE), polystyrene (PS), poly(ethyl methacrylate) (PEMA), poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVC) were chosen for the study. These polymers have different  $P_m$  values. Linear LDPE (1,4-*cis*: 20–45%, 1,4-*trans*: 45–65%, vinyl: 13–30%; density = 0.918 g mL<sup>-1</sup> at 25 °C), PEMA [ $M_w = 340000$ ,  $M_w/M_n \sim 2.7$ ], PMMA [ $M_w = 120000$ ], and PVC [ $M_w = 43000$ ,  $M_w/M_n \sim 1.95$ ] were purchased from Sigma–Aldrich and PS [ $M_w = 100000$ ,  $M_w/M_n \sim 1.06$ ] was purchased from Polysciences Inc. All polymers were used as received without further purification.

Absorption spectra of the films were recorded on Cary 50 UV–vis spectrophotometer. Matrix assisted laser desorption ionization (MALDI) spectra were obtained using Bruker Daltonic Omnistar<sup>®</sup> instrument (N<sub>2</sub> laser, 337 nm). A Bruker spectrometer (working frequency 300.0 MHz for <sup>1</sup>H) was used to record NMR spectra. Photolysis of **2** was carried out using an ultraviolet light-emitting diode (UV-LED) light source ( $\lambda_{max}$  395 nm) from UV Process Supply, Inc. All measurements were carried out at room temperature (22 ± 2 °C) unless otherwise specified. The synthesis of **2** is described elsewhere [17].

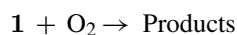
### 2.2. Sample preparation

A saturated solution of photoprecursor (**2**) in dichloromethane was mixed with a solution of the target polymers (except LDPE) in dichloromethane. Thin films were cast by carefully spreading a few drops of polymer solutions of **2** of identical concentration on quartz discs. The films were dried overnight at room temperature until all solvent had evaporated and the thickness (0.50 ± 0.02 mm) measured using a digital caliper. When similarly prepared films were put in the oven at 65–70 °C for 6 h, they showed no significant loss in weight, indicating that the amount of the solvent in the films before oven drying was negligible. The weight losses were 5%, 1%, 1.5%, and 2% for PS, PEMA, PMMA, and PVC, respectively. Films of LDPE embedded with **2** were cast thermally because of the poor solubility of LDPE in low-boiling organic solvents.

### 2.3. Determination of rate constant ( $k_d$ ) of disappearance of **1**

The prepared polymer films were irradiated using a UV-LED array (395 ± 25 nm) for 20 min to generate **1**. The relative amount of **1** generated was estimated from the intensity of its absorption spectra. The films were then left in the air under limited ambient light and the spectra of films of each polymer recorded at regular intervals until the absorption of **1** had completely disappeared. Decomposition of **1** as a function of time was recorded by monitoring the absorption intensity at 760 nm.

The oxidation of **1** by the diffused molecular oxygen into the polymer matrix can be represented as follows:



The rate law of the above reaction is written as:  $d[\mathbf{1}]/dt = -k'[\mathbf{1}][\text{O}_2]$ , where  $k'$  is the second order rate constant. In any particular polymer film, the concentration of diffused oxygen will depend on the oxygen permeability of the film. Oxygen diffusion depends on the oxygen permeability of the polymer and can be considered constant with time. Thus,  $k'[\text{O}_2]$  can be considered to remain constant for a particular polymer and the rate law becomes pseudo first order:  $d[\mathbf{1}]/dt = k_d[\mathbf{1}]$ , where  $k_d$  is the pseudo or effective first-order rate constant and equals to  $k'[\text{O}_2]$ . Solution of this rate law will be  $[\mathbf{1}] = [\mathbf{1}]_0 e^{-k_d t}$ . Without going into the details of Fick's and Henry's law of diffusion, we estimated  $k_d$  from the mono-exponential decay of **1** in polymer.

## 3. Results and discussion

In order to demonstrate the applicability of the concept, we chose five commercially available polymers—LDPE, PS, PEMA, PMMA, and PVC, showing different  $P_m$  values ranging from  $0.034 \times 10^{-13}$  to  $2.2 \times 10^{-13}$  cm<sup>2</sup> s<sup>-1</sup> Pa<sup>-1</sup> [4]. Films of PS, PEMA, PMMA, PVC, and LDPE of uniform thickness (0.50 ± 0.02 mm) containing **2** were formed. The prepared polymer films were irradiated to generate **1**. The relative amount of **1** generated could be estimated from the intensity of its absorption spectra.

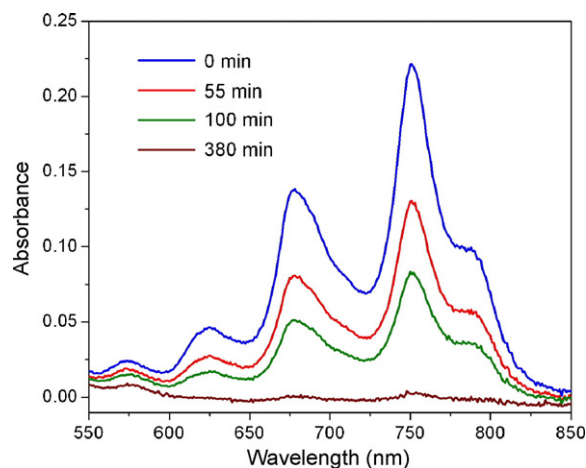


Fig. 1. The absorption spectra of a PMMA film containing **1** recorded at different times.

When the films were left in air under limited ambient light, the depletion of **1** as a function of time was recorded by monitoring the absorption intensity at 760 nm. The gradual disappearance of the absorption of **1** recorded at different times in the case of the PMMA film is shown in Fig. 1. The rates of decrease in the intensity at 760 nm were observed to be different for each polymer film. For example, the absorbance of **1** was found to completely disappear in about 115, 145, 380, and 435 min in the case of PS, PEMA, PMMA, and PVC, respectively. Interestingly, the order in which **1** underwent oxidation in these polymers correlates well with the order of their  $P_m$  and the depletion of **1** is directly related with the amount of oxygen that diffuses into the films. The decrease in the absorption of **1** followed mono-exponential decay in each case (Fig. 2). This can be explained by a pseudo-first order reaction rate law.

The rate of decomposition of **1** ( $k_d$ ) and its half-life ( $t_{1/2}$ ) in PS, PEMA, PMMA, and PVC films were calculated from the exponential fitting function (Table 1). The  $k_d$  value increases and half-life of **1** in the polymer films decreases with the decreasing  $P_m$  values of the polymers. A linear behavior was observed

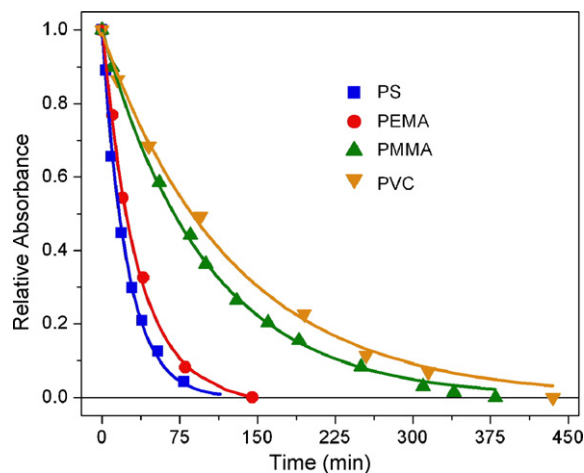


Fig. 2. Decomposition profiles of **1** in films of different polymers as monitored at 760 nm: (a) blue: polystyrene, (b) red: poly(ethyl methacrylate), (c) green: poly(methyl methacrylate), and (d) orange: poly(vinyl chloride).

Table 1

Rate constant of disappearance ( $k_d$ ) and half-life ( $t_{1/2}$ ) of **1** in different polymer films with varying oxygen permeability ( $P_m$ )

Polymer	Film thickness (mm)	$P_m^a$ ( $10^{-13} \times \text{cm}^2 \text{s}^{-1} \text{Pa}^{-1}$ )	$k_d$ ( $\text{s}^{-1}$ )	$t_{1/2}$ (min)
LDPE	0.52	2.2	–	<10
PS	0.51	1.9	$7.25 \times 10^{-4}$	16
PEMA	0.48	0.889	$4.27 \times 10^{-4}$	27
PMMA	0.48	0.116	$1.60 \times 10^{-4}$	73
PVC	0.50	0.034	$1.03 \times 10^{-4}$	112

<sup>a</sup> The  $P_m$  data were taken from [4].

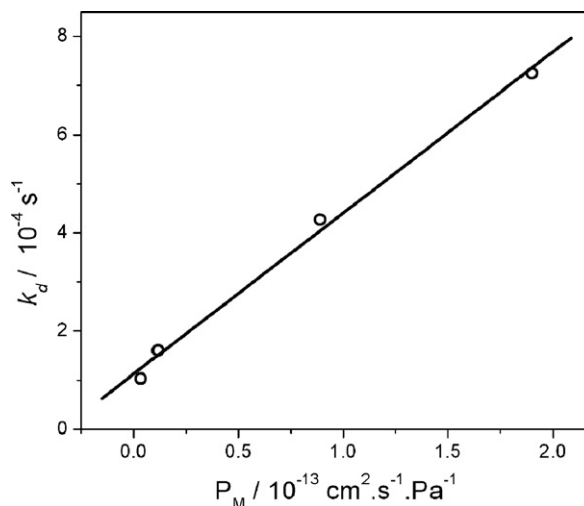
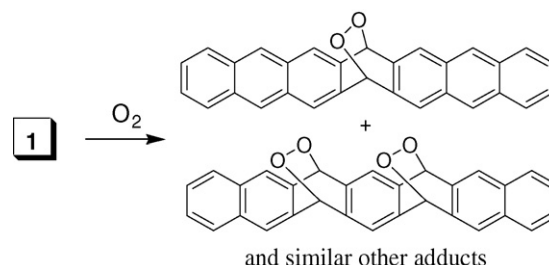


Fig. 3. Plot of the rates of disappearance ( $k_d$ ) of **1** vs. oxygen permeability ( $P_m$ ).

between  $k_d$  and  $P_m$  (Fig. 3). This linear relationship allows one to estimate the  $P_m$  of a polymer in the range of  $0.034 \times 10^{-13}$  to  $2.2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \text{ Pa}^{-1}$ , if its  $k_d$  can be experimentally evaluated using this technique.

A reasonable concentration of **1** could not be produced in LDPE film because of its higher  $P_m$  value preventing accurate monitoring of the reaction of **1** with oxygen in this polymer. In the case of PS, an equilibrium condition involving formation and disappearance of **1**, when produced over a longer time with a lower flux of photons, was observed. Thus, the technique may be most useful for polymers that show medium to low oxygen permeability. A limitation of the technique is that the polymer to be evaluated needs to be transparent >390 nm to facilitate formation of **1** in the film and to be compatible with UV–vis spectroscopic measurements in the visible region.



Scheme 2. Formation of endoperoxides of heptacene and similar other adducts.

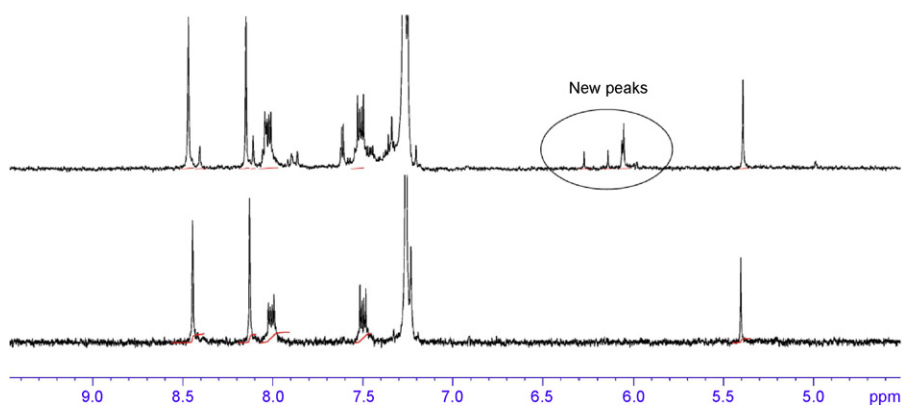


Fig. 4.  $^1\text{H}$  NMR spectra of **2** recorded before irradiation (bottom.) and after 15 min of irradiation (top) in  $\text{CDCl}_3$  purged with oxygen. (The peaks appeared in the 6.0–6.3 ppm region in the top spectrum are due to the protons at the C-atoms that are attached with the oxygen bridge in endoperoxides.)

Diels-Alder (DA) addition of molecular oxygen to **1**, preferably at the central ring, is responsible for its rapid disappearance [17]. Poly(acene)s are known to be highly reactive towards DA addition [18]. Pentacene, for example, undergoes oxidation at the central ring to form an endoperoxide [19]. Both concerted and stepwise processes have been postulated for formation of endoperoxides from acenes [20,21], and the reactivity is the highest at the central ring but gradually decreases as one moves outward. For example, the energy barrier ( $E_a$ ) of DA addition of acetylene to the central ring of pentacene is  $24 \text{ kcal mol}^{-1}$ , whereas the barrier is  $32.7 \text{ kcal mol}^{-1}$  for the edge ring of pentacene [18]. Nevertheless, endoperoxides were also formed due to oxidation at the peripheral rings in the case of **1** (Scheme 2).

Formation of oxygen adducts of **1** was verified by  $^1\text{H}$  NMR and MALDI-MS experiments. The protons of the bridged C-atoms of **2** appear at 5.4 ppm. When a  $\text{CDCl}_3$  solution of **2** purged with oxygen is irradiated, formation of **1** is instantly followed by its oxidation. The  $^1\text{H}$  NMR of such an irradiated solution showed three additional peaks between 6.0 and 6.3 ppm (Fig. 4) indicating endoperoxides of **1** as shown in Scheme 2. The peaks can be assigned to the protons at the C-atoms attached at the oxygen bridge. The reason for many proton peaks in the 6.0–6.3 ppm region comes from formation of bridges at different positions. The formation of endoperoxides containing two bridges is also possible. The MALDI-MS analysis of the same solution also suggested the formation of oxygen adducts of **1**, containing one as well as two molecules of oxygen.

Whether the oxidation of **1** is caused solely by molecular oxygen diffusing into the polymer or some other species is also contributing to its disappearance deserves consideration. Similar experiments carried out in the dark confirm that the disappearance of **1** was not light induced. There is a possibility that a small amount of moisture may permeate into the polymer films. However, it is highly unlikely that this will have any effect because permeation of moisture into the polymer film in comparison to that of oxygen can be considered negligible. Even if this is the case, moisture is likely to have no chemical effect on **1**. The calculated energy barrier for the reaction between **1** and water ( $43 \text{ kcal mol}^{-1}$ ) is much higher than that of the reaction between **1** and oxygen ( $<20 \text{ kcal mol}^{-1}$ ) and poly(acene)s do not generally react with water [22]. Thus, it can be safely said that the

depletion of **1** is due to its oxidation. This is substantiated by the fact that there exists a direct correlation between the rate of decomposition of **1** and  $P_m$  of polymer films.

#### 4. Conclusions

Rapid oxidation of **1** occurs when a polymer film containing **1** is exposed to air and this could be easily monitored by following gradual disappearance of its absorption in the visible region. The rates of disappearance of **1** in different polymer films were observed to follow pseudo first order kinetics. Interestingly, those rates measured in the films of PS ( $7.25 \times 10^{-4} \text{ s}^{-1}$ ), PEMA ( $4.27 \times 10^{-4} \text{ s}^{-1}$ ), PMMA ( $1.60 \times 10^{-4} \text{ s}^{-1}$ ), and PVC ( $1.03 \times 10^{-4} \text{ s}^{-1}$ ) were found to correlate well with their oxygen permeability values. This indicates that the high reactivity of **1** towards molecular oxygen can be used to determine the oxygen permeability of polymers.

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