# Synthesis of degradable network polymers containing peroxy units in the main chain or the cross-linking point

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## ARTICLE INFO

## ABSTRACT

We have synthesized degradable network polymers containing readily labile peroxy bonds as the repeating units in the main chain or as the cross-linking point in the side chain. Poly(2-hydroxyethyl sorbate-*alt*-$O_2$) was obtained by the radical copolymerization of 2-hydroxyethyl sorbate with oxygen, and then cross-linked using tolylene 2,4-diisocyanate as the cross-linking agent to obtain a new type of degradable gel. We also investigated the cross-linking of conventional polymers by the reaction of the diene moieties introduced into the polymer side chain with oxygen. The hydroxy group in the side chain of poly(vinyl alcohol) (PVA) was reacted with 1-isocyanate-1,3-pentadiene in order to introduce a diene moiety into the side chain of the PVA. The dienylated PVA was reacted with oxygen in the presence of a radical initiator, leading to the formation of a gel containing a labile peroxy linkage at the cross-linking point. These gels containing peroxy units in the main chain or at the cross-linking points degraded upon heating.

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## 1. Introduction

Degradable polymer gels have attracted significant interest due to their versatile functions and applications [1–15]. Vinyl polymers have successive carbon-to-carbon bonds in the main chain, which result in their advantageous thermal and biochemical stabilities during processing and long-term use in daily life. As a result, simultaneously, very few kinds of vinyl polymers are feasible for use as degradable materials. We previously revealed that polyperoxides are obtained by the conventional radical copolymerization process using 1,3-diene monomers, such as alkyl sorbates and oxygen, as the starting monomers [16–20]. The obtained polyperoxides include a labile O−O bond in their main chain, leading to degradation via a radical chain mechanism using stimuli such as heating, UV irradiation, or the addition of a base (Scheme 1).

The synthesis of environment-friendly and degradable polyperoxides from various kinds of diene monomers has been further developed in order to avoid the evolution of volatile and toxic compounds as the degradation products [21,22]. More recently, Kitamura and Matsumoto reported a facile method for the introduction of dienyl groups into conventional polymers using sorbic derivatives including epoxy and anhydride functional groups as the reagents for the dienylation of the precursor polymers with a high efficiency [23]. For example, a new degradable gel was prepared by the introduction of a dienyl group into the side chains or the

chain ends of conventional polymers such as poly(acrylic acid), poly(ethylene oxide), poly(2-hydroxyethyl methacrylate), and poly(vinyl alcohol) (PVA) and the subsequent radical copolymerization of the dienyl groups in the side chain with oxygen in the presence of a radical initiator. The obtained gels containing the polyperoxy units readily degraded upon heating. This method is useful for the preparation of polymer networks programmed for degradation after temporary use. The synthesis and fragmentation of poly(L-lactic acid) [24] and poly(macromonomer)s [25] modified with thermally degradable junctions consisting of a repeating polyperoxide structure were also demonstrated. These branched polymers readily degraded upon heating to yield linear polymer chains and induce a change in physical properties. Thus, the polyperoxides include a significant potential for a wide range of uses in various fields of polymer chemistry and material science such as adhesion, coating, environmental, and electrical application fields.

In this study, we used isocyanate compounds for the synthesis of degradable gels containing readily labile peroxy bonds as the repeating units in the main chain or as the cross-linking point in the side chain. The degradable network polymers were synthesized by the following methods; one is the cross-linking of poly(2-hydroxyethyl sorbate-*alt*-$O_2$) (PHES) using tolylene 2,4-diisocyanate (TDI) as the conventional cross-linking agent (Scheme 2), and the other is the introduction of dienyl groups into PVA using 1-isocyanate-1,3-pentadiene (IPD) as the dienylation agent and the subsequent cross-linking by the polymerization with oxygen in the presence of a radical initiator (Scheme 3). The thermal degradation of the obtained gels, which contain labile peroxy units in the main chain or at the cross-linking points, was investigated.

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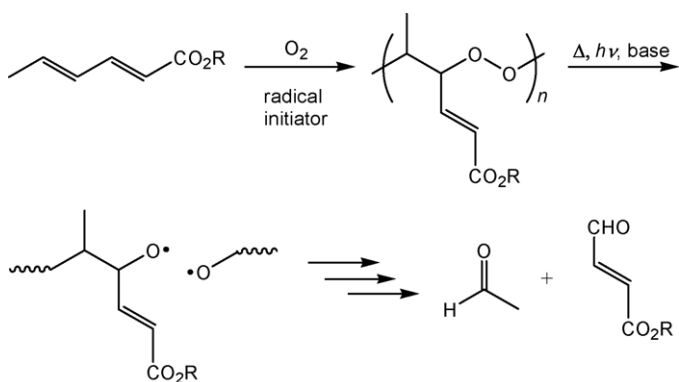
**Scheme 1.**
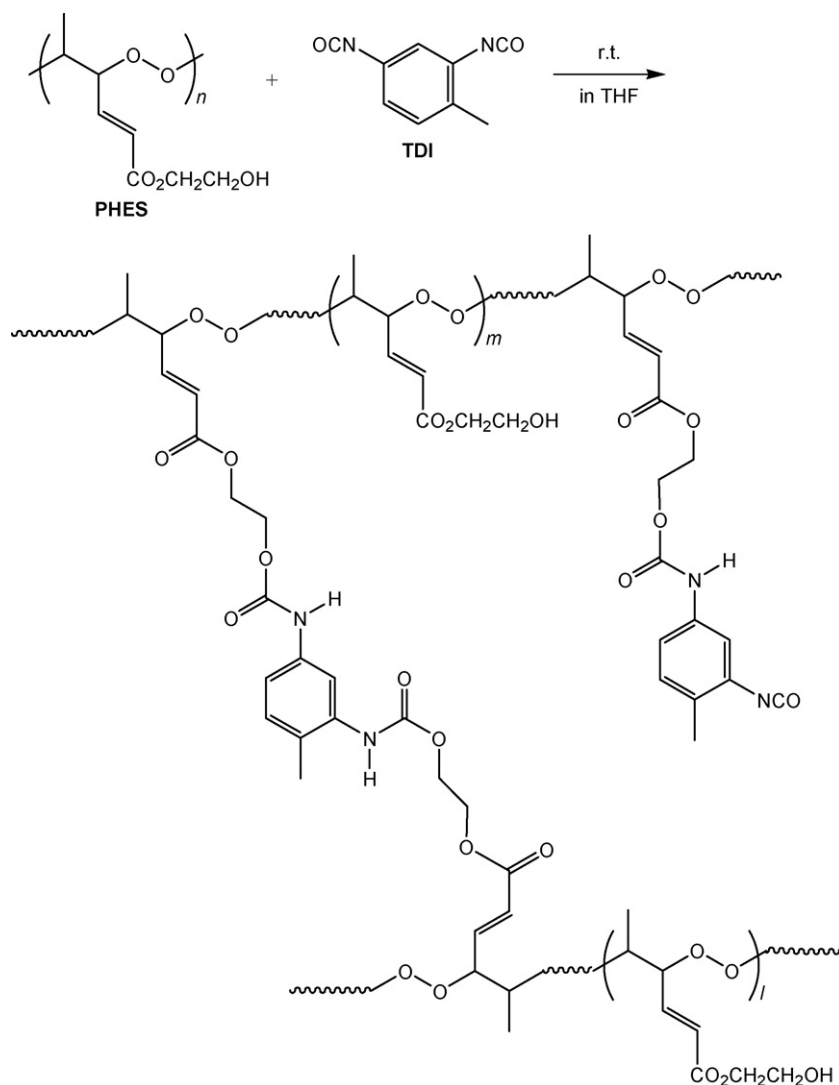
## 2. Experimental

### 2.1. General procedures

The NMR spectra were recorded using a JEOL JMN A-400 spectrometer. The FT-IR spectra were recorded using a JASCO FT/IR 430 spectrometer. The thermogravimetric and differential thermal analyses (TG and DTA) were carried out using a SEIKO TG/DTA 6200 at the heating rate of $10\,°C/min$ in a nitrogen stream. The number- and weight-average molecular weight ($M_n$ and $M_w$) were determined by gel permeation chromatography in tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes.

### 2.2. Materials

2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was purchased from Wako Pure Chemical Industries, Ltd., Japan, and used after recrystallization from methanol. Commercial tolylene 2,4-diisocyanate (TDI) (Tokyo Kasei Kogyo, Ltd., Japan), and poly(vinyl alcohol) (PVA, $M_n = 2.5 \times 10^4$, saponification degree 85%, Kishida Chemical Co., Ltd., Japan) were used without further purification. The solvents were used after distillation. All other commercial chemicals were used as received without further purification.

*Synthesis of 2-hydroxyethyl sorbate (HES).* Sorbic acid (5.6 g, 50 mmol), ethylene glycol (3.1 g, 50 mmol), and 4-(dimethylamino)pyridine (0.56 g, 4.6 mmol) were dissolved in 40 mL of 1,2-dichloroethane. To the solution, $N,N'$-dicyclohexylcarbodiimide (11 g, 53.4 mmol) in 5 mL of 1,2-dichloroethane was added dropwise over 15 min with stirring



**Scheme 2.**