Oxidative polymerization of *para*-substituted styrene derivatives: Synthesis, characterization and kinetics study

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ABSTRACT

Synthesis and characterization of four new polymeric peroxides of styrene monomers with substituents in the *para*-position are discussed. NMR spectroscopy and elemental analysis confirm the alternating copolymer structure with peroxy bonds in the backbone. The thermal degradation of the polyperoxides has been studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The measured highly exothermic heat of degradation of these polymers is nearly the same as that of poly(styrene peroxide). Electron-impact mass spectroscopy (EI-MS) supports alternating peroxide units in the polymer chain. Kinetics of oxidative polymerizations have been studied for various *para*-substituted styrene monomers in toluene in the presence of a free radical initiator 2,2′-azobisisobutyronitrile (AIBN) at 40–50 °C and 100 psi oxygen pressure. Interestingly, both electron-withdrawing and electron-donating substituent groups in the *para*-position increases rate of oxidative polymerization. Theoretical studies have been performed using density functional theory (DFT) to support the order of oxidation rates.

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1. Introduction

Radical polymerization of vinyl monomers in the presence of oxygen known as oxidative polymerization results in the formation of low molecular-weight products (such as alcohols, aldehydes, ketones, etc.) in addition to polyperoxide, an alternating copolymer of vinyl monomer and molecular oxygen [1,2]. Their technological importance as polymeric radical initiators for vinyl monomers [3,4], curators in coating and molding applications [5], autocombustible polymeric fuel [6], etc. has been established. Radical copolymerization of 1,3-diene monomers with molecular oxygen at an atmospheric pressure have been recently applied to prepare polyperoxides [7–9], and use of this type of polyperoxides as drug carrier [10] and dismantlable adhesion [11] has been reported. Since the first report [12] on vinyl polyperoxide by Staudinger in 1922, only a small number of polymers belonging to this category have been synthesized and characterized. Early work before the 1970s dealt with the mechanistic and kinetic aspects of the oxidative polymerization of vinyl monomers [13–17]. Later, the effect of oxygen pressure on the oxidative copolymerization of styrene with α-methylstyrene has been studied in detail [18]. The number of vinyl polyperoxides reported so far is only about 30 [2],

and only very few of them have been fully characterized. Of these polyperoxides, poly(styrene peroxide) (PSP) has received significant attention [19]. In view of their potential applications in various fields it is desirable to synthesize and characterize polyperoxides with diverse properties such as stability, solubility, etc. As an example, PSP is insoluble in hexanes and petroleum ether but substituted polyperoxides from styrene derivatives (such as, poly(4-*tert* butoxystyrene) is soluble in hexanes but polystyrene is not soluble [20]) might be soluble in these non-polar solvents and could be used as polymeric additives in petroleum fuel.

In the present study, we have synthesized and characterized various new *para*-substituted polystyrene peroxides. During our efforts to quantify the reactivities of various α-substituted styrene monomers towards oxidative polymerization, we have recently studied the kinetics of polymerization of styrene (St), α-methylstyrene (AMS), 4-chloro α-methylstyrene (CAMS), and α-phenylstyrene (APS) at 100 psi oxygen pressure and 40–50 °C in anhydrous toluene [21]. In order to add *para*-substituted styrenes to the oxidative polymerization reactivity list, we have now studied the kinetics of their reactions with molecular oxygen at 100 psi and 40–50 °C in toluene, which yield the corresponding polyperoxides (Scheme 1). The benefit of this reactivity scale in synthesis design is obvious. Interestingly, the rate of oxidative polymerization is minimum for styrene, but increases with increasing or decreasing the Hammett substituent constant at *para*-position of the phenyl group.

Scheme 1. Oxidative polymerization of *para*-substituted styrene derivatives.
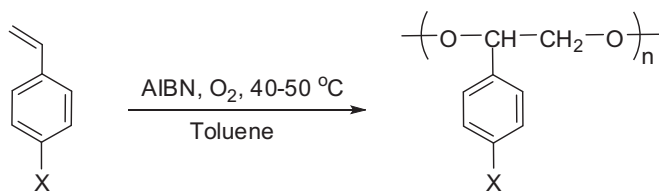
Substitution	Monomer	Polymer
X = H;	St	PSP
X = F;	FS	PFSP
X = Cl;	CS	PCSP
X = Br;	BS	PBSP
X = Me;	MS	PMSP
X = C(CH$_3$)$_3$;	*t*BS	P*t*BSP
X = MeO;	MeOS	PMeOSP
X = O-C(CH$_3$)$_3$;	*t*BuOS	P*t*BuOSP

2. Experimental section

2.1. Materials

Styrene (St, 99+%), 4-flurostyrene (FS, 98%), 4-chlorostyrene (CS, 97%), 4-bromostyrene (BS, 98%), 4-methylstyrene (MS, 96%), 4-methoxystyrene (MeOS, 97%), 4-*tert* butoxystyrene (*t*BuOS, 99%) and 4-*tert* butylstyrene (*t*BS, 98%) were purchased from Sigma and purified by passing through a basic alumina column prior to polymerization to remove the antioxidant and/or inhibitor. The 2,2′-azobisisobutyronitrile (AIBN, Sigma, 98%) was recrystallized twice using methanol. Anhydrous toluene (Sigma, 99+%) and CDCl$_3$ (Cambridge Isotope, 99% D) were used as received. The oxygen used was of high purity (BOC, 99.99+%). The solvents, petroleum ether (boiling range, 60−80 °C), tetrahydrofuran (THF), methanol, chloroform were purified by standard procedures.

2.2. Polymerization

The kinetics of oxidative polymerizations were studied at 100 psi oxygen pressure using 2 mol L^{-1} monomer solution in anhydrous toluene in the presence of AIBN (0.02 mol L^{-1}) as radical source in a 100 mL Parr reactor (Parr Instrument Co., USA) equipped with a digital pressure transducer, temperature controller, and mechanical stirrer. The polymerization reactions were carried out at constant oxygen pressure (100 psi) and mechanical stirring (220 rpm) for four different temperatures (40, 44, 47 and 50 °C). The oxygen consumption was measured as a function of time using a digital pressure transducer. The polymeric peroxides, poly(styrene peroxide) (PSP), poly(4-flurostyrene peroxide) (PFSP), poly(4-chlorostyrene peroxide) (PCSP), poly(4-bromostyrene peroxide) (PBSP), poly(4-methylstyrene peroxide (PMSP), and poly(4-methoxystyrene peroxide) (PMeOSP) were precipitated in petroleum ether. They were isolated and purified by repeated precipitation from chloroform solution followed by the removal of the solvent by vacuum drying at room temperature. The poly(4-*tert* butylstyrene peroxide) (P*t*BSP) and poly(4-*tert* butoxystyrene peroxide) (P*t*BuOSP) were precipitated from methanol. They were further purified by repeated precipitation from chloroform solution followed by the removal of the residual solvent by vacuum drying at room temperature (∼25 °C). Caution!!! Since polyperoxides degrade highly exothermically, they should be handled carefully and should be stored in the dark and in a refrigerator to minimize degradation.

2.3. Instrumentation

^{1}H NMR spectroscopic measurements were carried out on a Bruker Avance^{III} 500 spectrometer operating at 500 MHz in CDCl$_3$ solvent. The FT-IR spectrum was recorded on KBr pellets using a Perkin−Elmer RXI spectrometer. Number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) using Waters 515 HPLC pump, Waters 2414 refractive index detector and two columns (Styragel HT4 and Styragel HT3). The eluent was THF at 30 °C and the flow rate was 0.3 mL/min. Narrow molecular weight polystyrene standards were used to create the calibration curve. The elemental analysis was performed on a Perkin−Elmer Series-II, CHNO/S Analyzer-2400. The thermal studies was carried out using a Mettler Toledo DSC1 STARe differential scanning calorimeter (DSC) at different heating rates (5, 10, 15, and 20 °C min^{-1}) with sample sizes of ∼3−6 mg in N$_2$ atmosphere. The thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min^{-1} with a sample weight of ∼4−8 mg in N$_2$ atmosphere. Electron-impact mass spectrometry (EI-MS) spectra in the positive mode were obtained at 70 eV in a Shimadzu QP5050A gas chromatograph-mass spectrometer with a direct inlet.

2.4. Computational studies

The density functional theory (DFT) has been employed as an established and predictive means to understand the effect of *para* substitution on the kinetics of oxidative polymerization of styrenic monomers. Geometry optimizations and vibrational frequency analyses were carried out at the level of DFT based methods as implemented in the electronic structure program Gaussian 03 [22]. We have used the Becke's three parameter hybrid exchange functional [23] combined with the Lee-Yang-Parr non-local correlation function [24] abbreviated as B3LYP. The split-valence basis set with diffuse functions, namely 6-311++G for St, FS, CS and BS series, and 6-311++G(2d, 2p) for St, MS, *t*BS, MeOS and *t*BuOS series have been employed for all atoms. As oxygen is there at the *para*-position for the MeOS and *t*BuOS, we have used higher basis set for the second set of monomers. Vibrational frequencies were calculated for optimized molecular structures to verify that no negative frequencies were present for minimum energy structures and one negative frequency for the transition state (TS) structures.

3. Results and discussion

3.1. Synthesis and characterization of polyperoxides

Scheme 1 depicts the synthetic route of various *para*-styrene polyperoxides in toluene at different temperatures (40, 44, 47 and 50 °C) maintaining the pressure constant (100 psi). The M_n and polydispersity index (PDI) of various polyperoxides were determined from GPC measurements and listed in Table 1 with M_n ranging from 4340−5800 g/mol (see Fig. S1 for GPC refractive index traces of PFSP, PBSP, PMSP and PMeOSP in the Supporting Information). Earlier studies revealed that this category of polymers undergo facile degradation during polymerization process, generating chain transfer agents such as aldehydes, which react with propagating macro-peroxy radicals resulting in low molecular weights [25]. All the polyperoxides show relatively high PDI due to the chain transfer and chain termination reactions of macro-peroxy radicals. Elemental analysis was carried out for PFSP, PCSP, PMeOSP, and P*t*BuOSP (Table S1 in the Supporting Information). It can clearly be seen that the experimental values obtained from elemental