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# Copolyperoxides of 2-(acetoacetoxy)ethyl methacrylate with methyl methacrylate and styrene; Synthesis, characterization, thermal analysis, and reactivity ratios

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## ABSTRACT

Copolyperoxides of 2-(acetoacetoxy)ethyl methacrylate (AEMA) with styrene (St) and methyl methacrylate (MMA) of different compositions have been synthesized in the presence of 2,2′-azobisisobutyronitrile as a free radical initiator under 100 psi oxygen pressure at 50 °C. The rates of oxidative copolymerization reactions are determined from the oxygen consumption ($\Delta p$) against time plot. Highly exothermic thermal degradations of these copolyperoxides are studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and degradation products have been characterised by electron-impact mass spectroscopy (EI-MS). The NMR spectroscopy and EI-MS analysis confirm the alternating peroxy bonds in the main chain. The monomer reactivity ratios are computed by the Fineman–Ross and Kelen–Tüdös methods, using compositions obtained from $^1$H and $^{13}$C NMR analysis. These copolymers can potentially be used as polymeric initiators for the radical polymerization of vinyl monomers, autocombustible fuel. Also, the $\beta$-carbonyl moieties along the side chain of the copolyperoxides can be utilized to prepare degradable polyperoxide–metal complexes.

## 1. Introduction

Polymerization of vinyl monomers in the presence of oxygen is known as oxidative polymerization, which produces alternating copolymers (vinyl polyperoxides) of vinyl monomer and molecular oxygen [1]. Vinyl polyperoxides are an important class of polymer due to their interesting physico-chemical properties such as highly exothermic degradation, in contrast to common polymers which usually degrade endothermically [2]. Most recently, radical alternating copolymerization of 1,3-diene monomers with an atmospheric oxygen pressure has been carried out to prepare polymeric peroxides [3]. Solid-state copolymerizations of dibenzofulvene [4], 7,7,8,8-tetrakis (ethoxycarbonyl) quinodimethane and related monomers [5] with oxygen have been carried out to afford alternating copolymers consisting repeating peroxy units in the polymer main chain. This class of polymers are rapidly gaining their importance as coatings [6], dismantlable adhesion [7], polymeric initiators for the radical polymerization of vinyl monomers [8], autocombustible fuel [2], etc. Although polyperoxides are known [9] since 1922's, very little work has been done to understand the role of oxygen during oxidative copolymerization of two monomers. The oxidation of two vinyl monomers could be considered as a special case of terpolymerization, where the monomers (M) do not to homopolymerize. The uniqueness of this system is that it approximates to a binary copolymerization system in terms of $-\mathrm{MO}_2^{\cdot}$ units. The rate of polymerization may then be explained in terms of the copolymerization equation and reactivity ratios [10,11].

The incorporation of metal binding sites into polymers leads to advanced materials due to the combination of physical, chemical, and structural properties provided by the two components. The complexation of metal ions with polymer chains containing ligand groups can be achieved either along the polymer main chain [12] or as side group functionalities [13]. The homo- and copolymer of 2-(acetoacetoxy)ethyl methacrylate (AEMA) are interesting materials, due to the presence of $\beta$-carbonyl moieties along the side chain, in which the $\beta$-dicarbonyl compounds have high affinity towards metal and metal ions [14]. In addition, homopolymers of AEMA were found to self-assemble into a hierarchical superstructure of double-stranded helical tubes [15], due to the establishment of hydrogen bridges between adjacent acetoacetoxy groups and compensation of dipole moments. The $\beta$-carbonyl moieties, act as strong bidentate ligands, in the PAEMA-based polymers can be coordinated to a wide range of metal ions with different geometries and oxidation states. These kinds of polymers have great potential

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use in the fields of polymer-based hybrid materials [16], biomineralization process [17], waste water treatment for metal recovery [18], etc. In our recent effort, an alternating copolymer of AEMA and molecular oxygen, poly[2-(acetoacetoxy)ethyl methacrylate] peroxide (PAEMAP), has been synthesised and characterized [19]. In the present work, we have studied the effect of oxygen on the oxidative copolymerization of AEMA with styrene (St) and methyl methacrylate (MMA). The monomer reactivity ratios have been calculated by the Fineman-Ross [20] and Kelen–Tüdös [21] methods, using compositions obtained from NMR analysis. Thermal properties of copolymers with various compositions have been investigated and the kinetics of degradation was also determined.

## 2. Experimental section

### 2.1. Materials

Styrene (St, 99+%), methyl methacrylate (MMA, 99%) and 2-(acetoacetoxy)ethyl methacrylate (AEMA, 95%) were purchased from Sigma and passed through a column of basic alumina prior to polymerization to remove the antioxidant and/or inhibitor. Anhydrous toluene (Sigma, 99+%), high purity oxygen (BOC, 99.99%) and $CDCl_3$ (Cambridge Isotope, 99% D) were used as received. The 2,2′-azobisisobutyronitrile (AIBN, Sigma, 98%) was recrystallized twice using methanol. The solvents, petroleum ether (boiling range 60–80 °C), chloroform were purified by standard procedures.

### 2.2. Instrumentation

The $^1H$ and $^{13}C$ NMR spectra of polymers were measured on a Bruker Avance$^{III}$ 500 spectrometer operating at 500 MHz in $CDCl_3$ solvent. The $^{13}C$ NMR spectra were recorded under inverse gated decoupling with 10 s delay time between the pulses with a line broadening of 1 Hz. 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 with effective molecular weight range 5000–600,000 g/mol and Styragel HT3 with effective molecular weight range 500–30,000 g/mol). The eluent was tetrahydrofuran (THF) and the flow rate was 0.3 mL/min at 30 °C. The calibration curve was created using narrow molecular weight polystyrene standards [$M_p$ (PDI): 990 (1.11), 2170 (1.04), 3180 (1.04), 4910 (1.03), 7350 (1.03), 10730 (1.02), 20020 (1.02), 29510 (1.02), 52500 (1.03) and 113300 (1.03)]. The FT-IR spectrum was recorded on KBr pellets using a Perkin–Elmer Spectrum 100 FT-IR Spectrometer. The thermal degradations were carried out using a Mettler Toledo DSC1 STARe differential scanning calorimeter (DSC) with sample sizes of ~3–7 mg in $N_2$ atmosphere at different heating rates (5, 10, 15, 20 and 25 °C $min^{-1}$). The thermogravimetric analysis (TGA) at a heating rate of 10 °C $min^{-1}$ was studied on a Mettler Toledo TGA/SDTA 851e instrument with a sample weight of ~4–6 mg in $N_2$ atmosphere. Electron-impact mass spectrometry (EI-MS) spectra of polymers in the positive mode were obtained at 70 eV in a Shimadzu QP5050A gas chromatograph-mass spectrometer with a direct inlet.

### 2.3. Synthesis of polymers

A typical oxidative copolymerization procedure was as follows (CPAS1 in Table 1): AEMA (10.28 g, 0.048 mol), St (1.25 g, 0.012 mol) AIBN (49.30 mg, 0.3 mmol) and dry toluene (3.6 mL) were charged in a Parr reactor (Parr Instrument Co., USA) equipped with a digital pressure transducer, temperature controller and mechanical stirrer. The polymerization reaction was carried out at 50 ± 1 °C for 62 h under an oxygen pressure of 100 psi with mechanical stirring (220 rpm). The feed ratio was varied to give copolymers of various compositions. For the reliable kinetic analysis, conversions were kept between 5 to 12%. During copolymerization reactions, $O_2$ consumption was measured as a function of time using a pressure transducer. Polymers were precipitated from the reaction mixture using petroleum ether as non-solvent and finally isolated by repeated precipitation from chloroform as a solvent and petroleum ether as a non-solvent, followed by the removal of the solvent by vacuum drying at room temperature. Details of the polymerization reaction are given in the Table 1. Copolyperoxides obtained are either sticky or dry solid materials depending on the ratio of AEMA to St. All polymers obtained from AEMA-MMA-$O_2$ system are gummy material. *Caution!!!* Since polyperoxides degrade highly exothermically, homo and copolyperoxides should be handled carefully and stored in the dark and in a refrigerator to minimize degradation.

**Table 1**
Experimental results for the oxidative copolymerization of AEMA with St and MMA initiated by AIBN at 50 °C.[a]

| | | | | Molar fraction of AEMA | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Copolyperoxide | | | |
| Polymer | Time (h) | $R_p \times 10^7$ (mol $L^{-1}s^{-1}$) | Conv[b] (%) | Feed (AEMA) | $^1H$ NMR | $^{13}C$ NMR | $M_n$[c] (g/mol) | PDI[c] |
| AEMA-St-$O_2$ System | | | | | | | | |
| PAEMAP | 95 | 1.52 | 9 | 1.000 | 1.000 | 1.000 | 3350 | 2.0 |
| CPAS1 | 62 | 4.27 | 8 | 0.800 | 0.308 | 0.302 | 4420 | 1.8 |
| CPAS2 | 52 | 6.47 | 10 | 0.600 | 0.147 | 0.141 | 4700 | 1.9 |
| CPAS3 | 35 | 8.07 | 8 | 0.500 | 0.109 | 0.095 | 3550 | 1.7 |
| CPAS4 | 26 | 10.2 | 7 | 0.400 | 0.069 | 0.073 | 3800 | 1.8 |
| CPAS5 | 21 | 12.2 | 12 | 0.200 | 0.033 | 0.023 | 4250 | 2.0 |
| PSP | 12 | 12.8 | 11 | 0.000 | 0.000 | 0.000 | 5300 | 1.7 |
| AEMA-MMA-$O_2$ System | | | | | | | | |
| CPAM1 | 85 | 1.51 | 8 | 0.800 | 0.722 | 0.748 | 2650 | 1.8 |
| CPAM2 | 95 | 1.51 | 9 | 0.600 | 0.537 | 0.603 | 3710 | 1.5 |
| CPAM3 | 89 | 1.46 | 8 | 0.500 | 0.475 | 0.489 | 2880 | 1.6 |
| CPAM4 | 85 | 1.38 | 6 | 0.400 | 0.392 | 0.416 | 3440 | 1.7 |
| CPAM5 | 83 | 1.34 | 5 | 0.200 | 0.231 | 0.239 | 3460 | 1.9 |
| PMMAP | 90 | 1.26 | 6 | 0.000 | 0.000 | 0.000 | 3390 | 1.7 |

[a] [AIBN] = 0.02 mol $L^{-1}$, 100 psi $O_2$ pressure.

[b] Monomer conversion as determined by gravimetric analysis on the basis of the amount of monomer feed.

[c] Determined by GPC measurements.