

# Facile synthesis of polyperoxides with intermolecular peroxy bonds as macroinitiators for free radical graft copolymerization

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**ABSTRACT:** A facile synthetic strategy to prepare a new type of on-chain polyperoxide bearing intermolecular peroxy bonds is reported. Polyketone from the copolymerization of ethylene and carbon monoxide was quantitatively transformed into amorphous and powdery polyperoxide using aqueous hydrogen peroxide at room temperature. This synthetic pathway allowed the highly selective and complete conversion of carbonyl groups into intermolecular peroxy groups that can initiate free radical graft copolymerization without generating fragmentary alkoxyl radical species. The thermal properties of polyperoxide were characterized by differential scanning calorimetry and thermogravimetric analysis, and the polyperoxide was further applied as a macroinitiator to prepare densely grafted copolymers, polyethylene-g-poly(4-methyl styrene) and polyethylene-g-poly(methyl methacrylate), via grafting from approach.

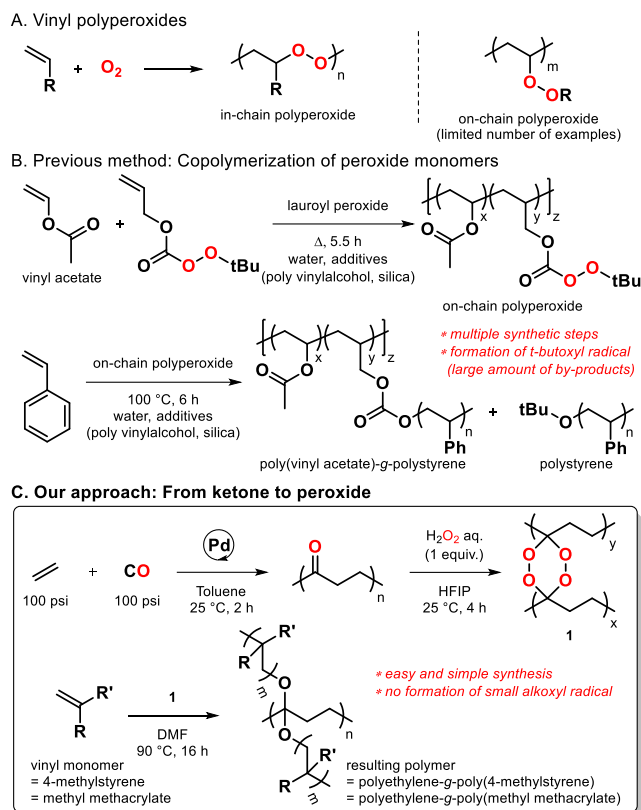
Since the first discovery of a small organic peroxide compound with a peroxy linkage ( $-O-O-$ ), benzoyl peroxide, reported by Brodie in 1858,<sup>1</sup> a broad range of organic peroxide compounds and their derivatives have been developed.<sup>2</sup> These peroxides are used in wide applications owing to their exceptional reactivity and oxidative potential, making them versatile agents such as cross-linking agents, free radical polymerization initiators, and oxidants in organic synthesis.<sup>3-5</sup> Polyperoxide is another class of organic peroxide compounds that have multiple peroxy linkages in the molecule. Although polyperoxide chemistry was pioneered by Staudinger in 1922, with the first example of polyperoxide, poly( $\alpha$ -phenylstyrene peroxide),<sup>6</sup> polyperoxides have not been studied extensively afterward. However, polyperoxides are gaining increasing interest due to their capability of storing several peroxy groups in the solid state, and opening new applications such as surfactant, drug delivery vessels, auto-combustible fuels, and macroinitiators for the preparation of block and branched polymers.<sup>7-11</sup>

Among different types of polyperoxides, many studies have been done on vinyl polyperoxides that are more stable to heat, shock, and friction than acid polyperoxides. Generally, vinyl polyperoxides with a repeating unit  $-[CH_2-CH(R)-OO]-$ , where R can be H, alkyl, aryl, CN, and  $C(O)OR'$  ( $R'$  = alkyl or aryl), have been synthesized via the alternating copolymerization of a vinyl monomer and oxygen (Scheme 1A).<sup>12</sup> As described in the formula above, the majority of vinyl polyperoxides reported to date have peroxy bonds in the polymer backbone that are called in-chain polyperoxide. Therefore, they have been explored as macroinitiators to prepare block copolymers of various vinyl monomers.<sup>13-16</sup> The radical polymerization of the first vinyl monomer initiated by the random cleavage of the peroxy bond forms an active first block with peroxy segments in the chain end. This key intermediate can be further used as a macroinitiator to build another block by polymerizing the next vinyl monomer. However, many polyperoxides are gummy liquids that make them difficult to handle and suffer from slow degradation at room temperature.<sup>17,18</sup> In addition, they generally are formed in low yields (10-25%), although a high oxygen

pressure is essentially required to synthesize them. Furthermore, their degradation products, such as alcohols, are readily generated during the synthesis and act as chain transfer reagents, leading to low molecular weights of polyperoxides in the range of 1000-5000 g/mol.<sup>18</sup>

On the other hand, on-chain polyperoxides with pendant peroxy bonds in the side chain can be useful to prepare graft copolymers, however, they are largely unstudied (Scheme 1A), with the exception of a few reports of polyperoxides used as a macroinitiator for radical graft copolymerization.<sup>19-24</sup> The only strategy established so far is to incorporate a peroxy bond in vinyl monomers (Scheme 1B). The radical copolymerization of typical vinyl monomers and separately prepared vinyl monomers containing a peroxy bond provides polyolefins with pendant peroxy groups. Such macroinitiators can be mixed with other vinyl monomers to obtain graft copolymers. For example, Oshibe and co-workers prepared poly(vinyl acetate)-g-polystyrene and poly(methyl methacrylate)-g-polystyrene via radical copolymerizations of either vinyl acetate or methyl methacrylate with their derivatives containing a peroxy group, followed by graft copolymerization with styrene (Scheme 1B).<sup>19</sup> However, this method requires multiple synthetic steps to prepare peroxide monomers that involve toxic phosgene gas, alkali metal hydroxides, and distillation of moisture-sensitive chloroformates. In addition to the desired graft copolymers, homopolymers of each vinyl monomer initiated by fragmentary alkoxyl radical species are largely generated as byproducts during the polymerization reactions.

Herein, we report a facile synthetic strategy to prepare a new type of on-chain polyperoxide with intermolecular peroxy groups (Scheme 1C). Starting with ethylene and carbon monoxide gases, the intermediate polyketone can be readily and quantitatively converted into polyperoxide under ambient reaction conditions. The characterization of obtained polyperoxide using various techniques reveals that every ketone group is transformed into a peroxide group allowing the storage of dense peroxide bonds safely.



**Scheme 1.** (A) Two types of vinyl polyperoxide, (B) Previous method to prepare on-chain polyperoxide as a macroinitiator for graft polymerization, and (C) Present work: Post-polymerization modification of polyketone to prepare on-chain polyperoxide as a macroinitiator for graft polymerization.

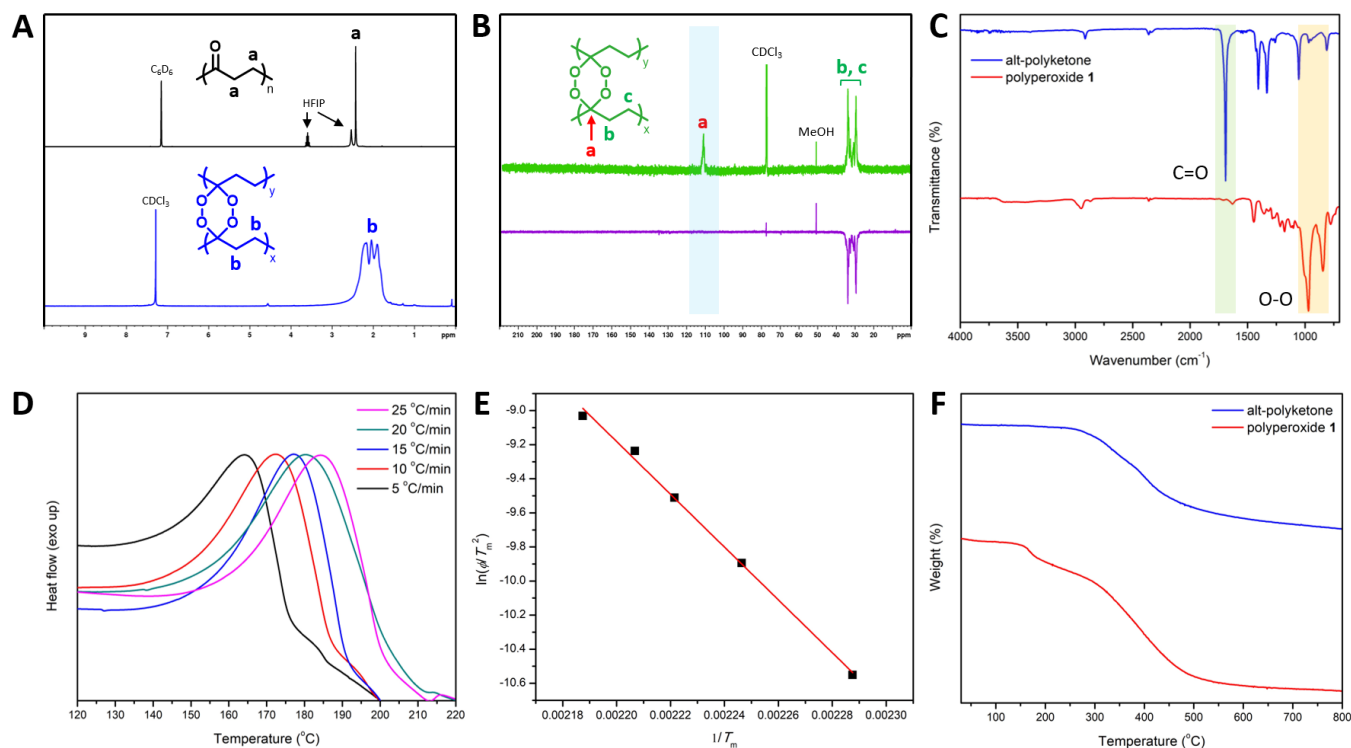
The thermal properties are compared to those of previously reported polyperoxides. The polyperoxide is further explored as a macroinitiator for the formation of graft copolymers with 4-methyl styrene and methyl methacrylate to obtain densely grafted copolymers, polyethylene-g-poly(4-methyl styrene) and polyethylene-g-poly(methyl methacrylate), respectively.

**Synthesis and characterization of polyperoxides from polyketones.** The on-chain polyperoxide with intermolecular peroxy bonds **1** was readily synthesized via post-polymerization modification of polyketone. The alternating polyketone was prepared by the copolymerization of ethylene ( $C_2H_4$ ) and carbon monoxide (CO) catalyzed by cationic the palladium methyl complex  $[(dppp)Pd(Me)(MeCN)][BAr_4^F]$  [dppp = 1,2-bis(diphenylphosphino)propane,  $Ar^F$  = 3,5-bis(trifluoromethyl)phenyl].<sup>25</sup> The high-pressure reactor was charged with 5 mM of palladium catalyst in toluene and a mixture of  $C_2H_4$  and CO at 100 psi, respectively. The copolymerization reaction at room temperature afforded polyketone as an off-white powder in 2 hours; the polymers were characterized by  $^1H$  and  $^{13}C[^1H]$  nuclear magnetic resonance (NMR) spectroscopy and attenuated total reflectance infrared (ATR-IR) spectroscopy to confirm their alternating microstructure. The  $^1H$  and  $^{13}C[^1H]$  NMR spectra of polyketone in a mixture of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and  $C_6D_6$  (1:4) at room temperature showed

characteristic sharp peaks of ethylene backbone protons at 2.44 ppm and carbonyl carbons at 212 ppm, respectively (Figures 1A and S2). The  $C=O$  stretching of polyketone in ATR-IR spectrum appeared at  $1691\text{ cm}^{-1}$ , consistent with that of previously reported polyketone (Figure 1C).<sup>25</sup>

Subsequently, the polyketone dissolved in HFIP was treated with an aqueous solution of hydrogen peroxide ( $H_2O_2$ , 30w%) at room temperature. Simply, the addition of  $H_2O_2$  equivalent to the number of a polyketone repeating unit transformed the polyketone into the polyperoxide **1** with intermolecular peroxy bonds completely in 4 hours (Table 1, entry 1). In comparison with the previously reported polyperoxides,<sup>24</sup> a much higher molecular weight of **1** was achieved via the present synthetic pathway. Given that the Baeyer-Villiger oxidation of ketones using peroxide compounds as oxidants is well-established to form small molecules of ester and lactones,<sup>26</sup> the reaction conditions were explored further in case the oxidation of polyketone could potentially occur in addition to the formation of polyperoxide.<sup>27</sup> The use of HFIP as a solvent was essential to generate the polyperoxide owing to the electrophilic activation of  $H_2O_2$  by HFIP.<sup>28</sup> There was no conversion of polyketone when the solvent was changed from HFIP to isopropanol (Table 1, entry 2). Although an equimolar amount of  $H_2O_2$  was sufficient to produce polyperoxide **1**, further transformation to polyesters was not observed even with excess  $H_2O_2$  (Table 1, entry 3). In addition, polyperoxide **1** was the sole product regardless of heating and adding a mild Lewis acid additive,  $LiClO_4$ , however, a slight decrease in molecular weight of **1** was observed (Table 1, entry 4). When  $FeCl_3$ , which is a stronger Lewis acid than  $LiClO_4$ , was added to the reaction, the polyperoxide was not formed probably due to the decomposition of  $H_2O_2$  (Table 1, entry 5). Therefore, the simple reaction of polyketone and  $H_2O_2$  can exclusively synthesize polyperoxide **1** without any other structural modifications. This high selectivity for polyperoxide formation can be explained by previous studies showing that the Baeyer-Villiger oxidation of dialkyl ketones with a less substituted alkyl group is unfavorable.<sup>26</sup> Interestingly, *meta*-chloroperoxybenzoic acid (mCPBA), one of the common organic peroxide compounds, formed neither polyperoxides nor polyesters (Table 1, entries 6 and 7).

The polyperoxide **1** was analyzed by various methodologies. The solubility of **1** in common organic solvents changed drastically compared to that of polyketone. The obtained polyperoxide was soluble in chloroform, dichloromethane, and *N,N*-dimethylformamide (DMF), solvents that do not dissolve polyketone. Therefore, NMR analysis could be done in  $CDCl_3$  rather than a mixture of HFIP and  $C_6D_6$ . The  $^1H$  NMR spectrum ( $CDCl_3$ , 25 °C) of **1** only showed broad peaks in the range of 1.70–2.47 ppm corresponding to methylene protons of the polyethylene backbone (Figure 1A). The quaternary carbon of the bisperoxide group was identified at 110 ppm in the  $^{13}C[^1H]$  NMR ( $CDCl_3$ , 25 °C) spectrum of **1** and further confirmed by the  $^{13}C$  distortionless enhancement by polarization transfer (DEPT)-135 spectrum ( $-CH_2-$  negative and  $-C-$  not observable) (Figure 1B).<sup>29</sup> In the ATR-IR spectrum of **1**, the disappearance of the strong  $C=O$  stretching of polyketone at  $1691\text{ cm}^{-1}$  was indicative of the complete transformation of ketone, and characteristic peaks of  $O-O$  appeared at 970 and  $844\text{ cm}^{-1}$ , suggesting the formation of peroxide (Figure 1C).<sup>30</sup>



**Figure 1.** (A)  $^1\text{H}$  NMR (25  $^\circ\text{C}$ ) spectra of *alt*-polyketone (top) in  $\text{C}_6\text{D}_6$  and polyperoxide **1** (bottom) in  $\text{CDCl}_3$ . (B)  $^{13}\text{C}$  [ $^1\text{H}$ ] NMR ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum (top) and DEPT-135 spectrum (bottom; CH and  $\text{CH}_3$  positive and  $\text{CH}_2$  negative) of polyperoxide **1**. (C) ATR-IR spectra of *alt*-polyketone (top) and polyperoxide **1** (bottom). (D) DSC thermograms of polyperoxide **1** at five different heating rates (5, 10, 15, 20, and 25  $^\circ\text{C}/\text{min}$ ). (E) Kissinger's plot of  $\ln(\phi/T_m^2)$  versus  $1/T_m$  for polyperoxide **1**. (F) TGA plots of *alt*-polyketone (top) and polyperoxide **1** (bottom).

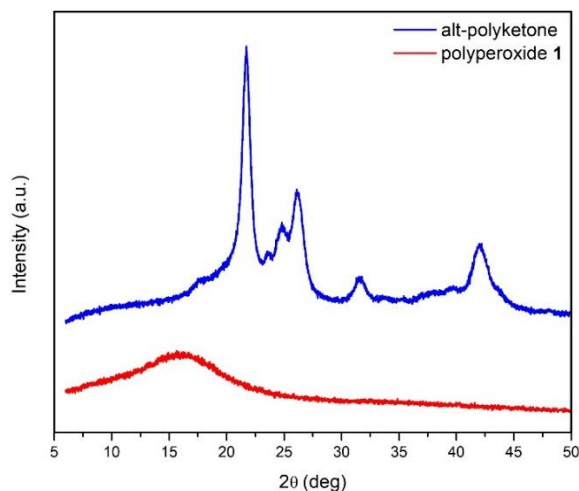
**Table 1. Synthesis of polyperoxide 1.<sup>a</sup>**

Peroxide (equiv.)	Solv. <sup>b</sup>	Temp. <sup>c</sup> ( $^\circ\text{C}$ )	Add. <sup>d</sup>	$M_n$ <sup>e</sup> (g/mol)	$\bar{D}$ <sup>e</sup>	
1	$\text{H}_2\text{O}_2$ (1)	HFIP	25	-	13,240	1.83
2 <sup>f</sup>	$\text{H}_2\text{O}_2$ (1)	iPrOH	25	-	-	-
3	$\text{H}_2\text{O}_2$ (10)	HFIP	25	-	14,580	1.77
4	$\text{H}_2\text{O}_2$ (10)	HFIP	60	$\text{LiClO}_4$	9,710	1.52
5 <sup>f</sup>	$\text{H}_2\text{O}_2$ (10)	HFIP	60	$\text{FeCl}_3$	-	-
6 <sup>f</sup>	mCPBA (10)	HFIP	25	-	-	-
7 <sup>f</sup>	mCPBA (10)	HFIP	60	-	-	-

<sup>a</sup> General reaction conditions: *alt*-polyketone = 200 mg (3.56 mmol of  $-\text{CH}_2\text{CH}_2\text{CO}-$  units), peroxide = 3.56 mmol (1 equivalent to  $-\text{CH}_2\text{CH}_2\text{CO}-$  units), HFIP = 1.5 mL, room temperature, 4 hours. <sup>b</sup> Solvent (1.5 mL). <sup>c</sup> Temperature. <sup>d</sup> Additive (0.1 equivalent to  $-\text{CH}_2\text{CH}_2\text{CO}-$  units). <sup>e</sup> Values were determined by SEC measurements in DMF. <sup>f</sup> No conversion of *alt*-polyketone was observed.

The thermal analysis of **1** by differential scanning calorimetry (DSC) under nitrogen at the heating rate of 10  $^\circ\text{C}/\text{min}$  revealed an absorption of heat between 60 and 93  $^\circ\text{C}$  and a broad exotherm between 136 and 187  $^\circ\text{C}$  due to the exothermic degradation of peroxy bonds (Figure 1D). The Kissinger method was employed to determine the activation energy ( $E_a$ ) for the thermally activated degradation of **1**.<sup>31</sup> A Kissinger plot of  $\ln(\phi/T_m^2)$  versus  $1/T_m$ , where  $\phi$  is the heating rate and  $T_m$  is the peak temperature in the DSC thermogram, was obtained by measuring  $T_m$  values at different heating rates (5, 10, 15, 20, and 25  $^\circ\text{C}/\text{min}$ , Figure 1E). The  $E_a$  of **1** was found to be  $31.08 \pm 0.41$  kcal/mol from the slope of the plot divided by the gas constant. The calculated  $E_a$  is comparable to the dissociation energy of the O–O bond, suggesting that the thermal degradation of **1** is initiated by the cleavage of O–O bonds.<sup>24</sup> The thermogravimetric analysis (TGA) curve showed a two-step weight loss that is attributed to the degradations of O–O bond and backbone of **1**, respectively (Figure 1F).

As observed in the DSC thermogram, the on-chain polyperoxide **1** is an amorphous solid, while many in-chain polyperoxides are generally gummy liquids or semisolids. Therefore, previously, long-side chains were incorporated to synthesize solid in-chain polyperoxides. For example, styrene monomers with long aliphatic hydrocarbon chains were prepared separately and then copolymerized with  $\text{O}_2$  to form crystalline domains.<sup>32</sup> However, powdery **1** can be easily synthesized without any other modification of the polymer or monomer. The amorphous nature of **1** due to the formation of intermolecular peroxy bonds from crystalline polyketones was evidenced by the powder X-ray diffraction (PXRD) pattern (Figure 2).



**Figure 2.** PXRD patterns of *alt*-polyketone (top, blue) and polyperoxide **1** (bottom, red).

**Graft copolymerization initiated by free radical macroinitiator **1**.** Since polyperoxide **1** has intermolecular peroxy bonds unlike any other on-chain polyperoxides, **1** can avoid generating fragmentary alkoxyl radical species that can initiate homopolymerization of vinyl monomers resulting in low grafting efficiency. The graft copolymerizations of 4-methyl styrene or methyl methacrylate onto **1** were carried out in DMF at 90 °C for 16 hours, and self-initiated thermal homopolymerizations of each vinyl monomer as control experiments were also investigated under the same reaction conditions. The graft copolymerizations using 25 equivalents of each vinyl monomer with **1** were first attempted and full conversions were achieved in both cases (Table 2, entries 2 and 6). When the monomer feed ratio was doubled to 50 equivalents, each graft copolymerization still attained complete conversions of vinyl monomers and showed increases in molecular weights of the resulting graft copolymers (Table 2, entries 3 and 7). By comparison, in the absence of **1**, self-initiated thermal homopolymerizations of 4-methyl styrene and methyl methacrylate were sluggish under the same reaction conditions and exhibited 7% and 14% conversions of monomers, respectively (Table 2, entries 4 and 8). Despite their very low conversions of monomers, the molecular weights of homopolymers were much higher than those of the corresponding graft copolymers obtained under the same reaction conditions. These polymerization results suggest that the rate of graft copolymerization was much faster than homopolymerization at 90 °C owing to the aid of peroxide bonds in **1**.

The graft copolymers with shorter side chains of poly(4-methyl styrene) or poly(methyl methacrylate) were prepared to ensure that grafting took place by the cleavage of O–O bonds in **1** (Table 2, entries 1 and 5). The graft copolymerizations with reduced amounts of each vinyl monomer showed full conversions of monomers and the resulting graft copolymers had significantly curtailed molecular weights. Therefore, the polyethylene backbone and grafted side chains became observable together by diffusion ordered spectroscopy (DOSY). The DOSY of both graft copolymers displayed resonance peaks corresponding to the polyethylene backbone at around 2.15 ppm diffused with other resonance peaks of side chains at the same rate, confirming the formation of graft copolymers (Figure 3A and S20–21).

**Table 2. Graft copolymerization of 4-methyl styrene (MSt) and methyl methacrylate (MMA) with polyperoxide **1**.<sup>a</sup>**

	Init. <sup>b</sup>	M. <sup>c</sup>	M./init.	Conv. <sup>d</sup> (%)	$M_n^e$ (g/mol)	$\bar{D}^e$
1	1	MSt	4	>99	27,520	1.73
2	1	MSt	25	>99	119,900	1.73
3	1	MSt	50	>99	182,100	1.77
4	-	MSt	50	7	259,500	1.84
5	1	MMA	4	>99	24,590	1.50
6	1	MMA	25	>99	56,590	1.58
7	1	MMA	50	>99	164,100	1.65
8	-	MMA	50	14	1026,000	1.63

<sup>a</sup> All graft copolymerizations were carried out in DMF at 90 °C for 16 hours. <sup>b</sup> Initiator. <sup>c</sup> Monomer. <sup>d</sup> Conversions were determined by the analysis of the crude material by <sup>1</sup>H NMR spectroscopy (400 MHz, CDCl<sub>3</sub>, 25 °C). <sup>e</sup> Values were determined by SEC measurements in THF.

Unlike the DSC analysis of **1** showing the characteristic exotherm due to the exothermic degradation of peroxy bonds, none of these graft copolymers exhibited such exotherm in their DSC thermograms, suggesting all O–O bonds were cleaved to initiate graft copolymerizations (Figure 3B). The lack of thermal transitions of poly(4-methyl styrene) or poly(methyl methacrylate) in the DSC thermograms due to the very short length of side chains also supports the formation of graft copolymers. Similarly, the characteristic absorption bands of peroxide bonds were not observed in the ATR-IR spectra of these graft copolymers suggesting **1** is a macroinitiator for radical graft copolymerization (Figure 3C).

In conclusion, a new type of on-chain polyperoxide with intermolecular O–O bonds was prepared via post-polymerization modification of polyketone using an aqueous solution of H<sub>2</sub>O<sub>2</sub> under ambient reaction conditions. This synthetic pathway allowed the facile and complete formation of solid on-chain polyperoxide without multiple synthetic steps to prepare peroxide monomers separately. The high selectivity for the formation of structurally pure polyperoxide as an exclusive product was maintained even under harsher reaction conditions. Since the polyperoxide has intermolecular peroxy bonds, only alkoxyl radicals on the polymer backbone can be generated upon dissociation of O–O bonds. Therefore, this polyperoxide is suitable as a macroinitiator for radical graft copolymerization with vinyl monomers, and the synthesis of polyethylene-*g*-poly(4-methyl styrene) and polyethylene-*g*-poly(methyl methacrylate) was achieved. Further endeavors will focus on expanding the substrate scope of  $\alpha$ -olefin to prepare a series of on-chain polyperoxide and developing strategies to control the number of peroxide bonds in polyperoxide.

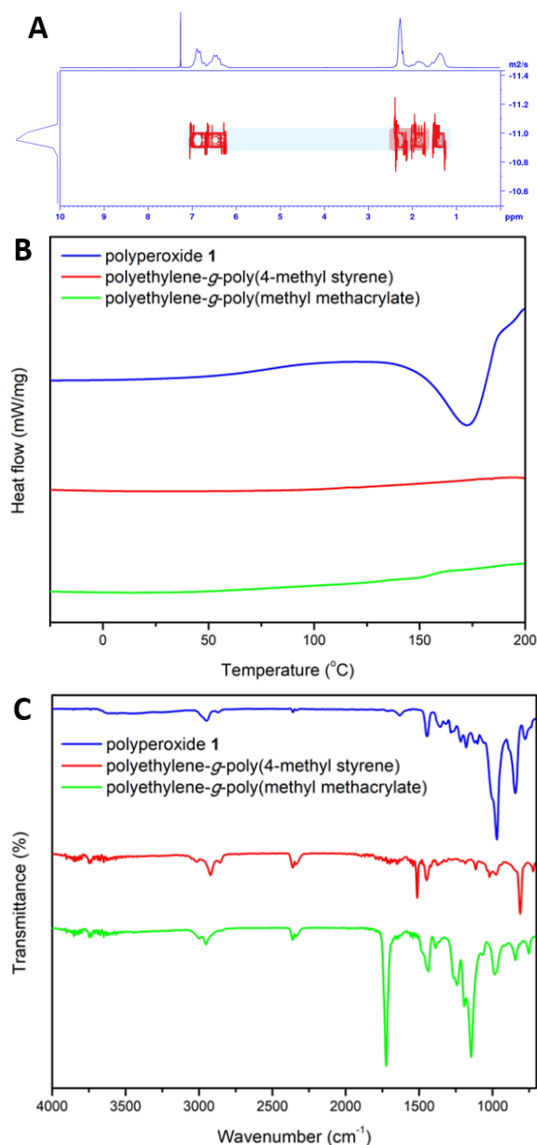
## ASSOCIATED CONTENT

### Supporting Information.

Experimental details and characterizations of polyperoxide and graft copolymers.

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.





**Figure 3.** (A) DOSY of polyethylene-*g*-poly(4-methyl styrene) (Table 2. Entry 1). (B) DSC thermograms of polyperoxide **1** and grafted copolymers with short side chains (Table 2, entries 1 and 5). (C) ATR-IR spectra of polyperoxide **1** and grafted copolymers with short side chains (Table 2, entries 1 and 5).

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### Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

### Notes

The authors declare no competing financial interests.

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