



Radical homopolymerization of tetrafluoroethylene initiated by perfluorodiacyl peroxide in supercritical carbon dioxide: Reaction mechanism and initiation kinetics

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ABSTRACT

Radical homopolymerizations of tetrafluoroethylene (TFE) in supercritical carbon dioxide (*sc*-CO₂) initiated by bis(perfluoro-2-*n*-propoxypropionyl) peroxide (BPPP) were conducted. Low molecular weight polytetrafluoroethylenes (PTFEs) which are widely used in diverse fields with stable end groups were successfully obtained. PTFEs were characterized by solid-state ¹⁹F NMR and FT-IR spectroscopy. From rational assignment of the characteristic signals, an overall reaction mechanism explaining the homopolymerization processes is proposed. The carboxyl radicals resulted from thermal decomposition of BPPP were completely decarboxylated to *n*-C₃F₇OCF(CF₃)· before reacting with TFE. Additionally, a small amount of *n*-C₃F₇OCF(CF₃)· rearranged into *n*-C₃F₇· with decreased rearrangement fraction from 0.11 to 0.04 when the reaction temperature was lowered from 35 to 5 °C. Initiation rate constants (*k_i*) were slightly increased with elevated pressure. The initiation activation energy derived from *k_i* is 90.3 kJ mol⁻¹, which is much lower than those of the other systems where nonfluorinated diacyl peroxides are used. Such mechanism and kinetics insights into the homopolymerizations of TFE in *sc*-CO₂ will be instructive for the syntheses of fluoropolymers with desired properties in future.

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1. Introduction

Supercritical carbon dioxide (*sc*-CO₂) has emerged as the most extensively studied environmentally benign medium for organic transformations and polymerizations. In the supercritical state (*T_c* = 31.1 °C, *p_c* = 73.8 bar) [1], CO₂ has unique properties such as liquid-like density and gas-like diffusivity, which are “tunable” with small variations in pressure and/or temperature. Previously, DeSimone and other researchers have shown that *sc*-CO₂ is a promising alternative medium for free radical, cationic,

and step-growth polymerizations [2–4]. Moreover, since it is inert to highly electrophilic radicals (no chain transfer to solvent), inexpensive, non-toxic, non-flammable, and environmentally benign [5], *sc*-CO₂ has drawn increasing concerns. For example, considerable attentions are being paid on the syntheses of fluoropolymers in *sc*-CO₂ [6–8], which give facile post-treatment of the resultant polymers in an economic and environmental friendly way [9,10].

For such applications, particularly, the utility of perfluorodiacyl peroxides as initiators is attractive and promising because it endows the polymers with stable perfluoroalkyl end groups, thus avoiding the troublesome time- and energy-consuming fluorination steps when compared with normal technical procedures for emulsion polymerization. Among varying perfluorodiacyl initiators,

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bis(perfluor-2-*n*-propoxypropionyl) peroxide [BPPP, ($n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COO}$)₂] has been successfully utilized for copolymerizations of TFE with hexafluoropropylene (HFP), perfluoropropyl vinyl ether (PPVE) or 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) [11,12]. Recently, we also found that BPPP is a proper initiator for TFE polymerization in preparing low molecular weight polytetrafluoroethylene (PTFE) with excellent thermal stability [13]. Low molecular weight PTFE, also called PTFE wax, not only keeps the functions of normal PTFE, but also enjoys high dispersibility, thus it can be used as additives in a wide variety of applications, including rocket propellant, aeronautic lubricating oils, high-speed printing inks, and nonstick coatings [14,15].

In view of the fundamental importance and technical implication, it is essential to study the mechanism and kinetics on the polymerization of TFE in *sc*-CO₂. Detailed information about initiation kinetics and reaction mechanism is mandatory for all-encompassing understandings of radical polymerizations. Meanwhile, the nature and reaction pathways of the radicals generated by initiator decomposition are of central interest. According to previous study [16], a general decomposition mechanism of BPPP can be described as O–O single bond cleavage to a carboxyl radical pair and subsequent decomposition. Afterwards, the resulting carboxyl radical may either directly react with monomer or decarboxylate to a perfluoroalkoxy radical. In the former case, less stable polymeric materials with perfluorinated ester end groups will be generated [17]. For low molecular weight polymers, such as polymeric additives for powder coatings and oligomers for waxes or synthetic oils, end groups may substantially affect material properties. The initiation reaction, namely the addition of initiator-derived radicals to monomer, finally incorporates these radicals into polymer chains as terminal groups. The characterization of polymer end groups is thus an efficient way to trace various reactions that primary radicals potentially undergo from formation to termination. Such reactions may not only influence initiator decompositions, but also impact on the properties of the resulting polymeric materials.

Carbon dioxide is an extraordinary inert solvent to highly active radicals. Meanwhile, its density (and therefore solvent properties) is tunable over a wide range through facile changes in pressure or temperature, which also can be used to control the initiation rate of perfluorodiacyl peroxides [18]. Thermal decomposition of the initiators in *sc*-CO₂ has been studied, and unique decomposition rate constants owing to the “zero-viscosity” and low dielectric constant of the medium [16,19] are derived. However, since TFE-CO₂ mixture can form a “pseudoazeotrope” [20], pressure effect on the decomposition kinetics of BPPP during TFE homopolymerization process in *sc*-CO₂ remains unclear.

Very recently, we have investigated the homopolymerization of TFE using BPPP in *sc*-CO₂ [13]. The low molecular weight PTFE products bearing thermally stable perfluoroalkyl end-groups were collected as dry, free-flowing powders, without contamination by solvent or surfactants. To gain more detailed information about such homopolymerizations, particularly, the initiation mechanism, we

conducted the present work. IR and ¹⁹F NMR techniques were used to determine the nature and relative concentration of the terminal moieties in PTFE, from which the decomposition sequences of BPPP initiator were identified. Additionally, the initiation rate constants as well as their temperature and pressure dependent properties were studied.

2. Experimental section

2.1. Materials

TFE (>99.999%) was supplied by Shandong Dongyue Polymer Material Co. Ltd. and used without further purification (Caution: TFE can decompose explosively under pressure and temperatures higher than –20 °C even in the absence of oxygen. In the presence of oxygen, at low temperatures, TFE can form dangerous shock-sensitive polymeric peroxides. Anyone contemplating handling TFE under high pressures should familiarize him(her)self with safe handling procedure). CO₂ (99.99%, oxygen content ≤ 10 ppm) was supplied from Zibo Baiyan Gases company. PFC-8, *n*-C₃F₇OCF(CF₃)CF₂OCF₂CF₃, a low-boiling perfluorinated solvent was kindly provided by Shandong Dongyue Shenzhou New Material Co. Ltd. and used as received. BPPP initiator, [*n*-C₃F₇OCF(CF₃)COO]₂ was synthesized according to the reported procedures in PFC-8 [21]. A PFC-8 solution of BPPP (~5%) was stored in a dry-ice bath in dark. An iodometry technique, ASTM Method E 298-91, was utilized to determine the initiator concentration in solution.

2.2. Homopolymerization of TFE in *sc*-CO₂

The experimental setup is shown in Fig. 1. Polymerization was conducted in a 100 mL high pressure reactor equipped with a magnetic stirring bar, a thermocouple and a rupture disk. The reactor was immersed in water bath with a thermocouple connected to a temperature controller. In a typical experiment, the reactor system was sealed and purged with CO₂ three times to remove oxygen. Then, the valves (V-3, V-4 and V-5) of the initiator tube were closed and the reactor was cooled down to 0 °C in ice-water. After being charged with TFE/CO₂ mixture (~50 wt.%) under stirring, the reactor was heated to fixed reaction temperature and further filled with CO₂ (using an air driven gas booster SC, Model GB-30) to achieve a pressure lower than the desired reaction pressure by 3–5 MPa, and then the valves (V-6 and V-7) to the reactor were closed.

After the initiator tube was evacuated with a vacuum pump, PFC-8/BPPP solution was filled. Then valves V-5 and V-7 was opened and the initiator solution was fed into the reactor under the pressure of CO₂. Then the initiator tube was purged with CO₂ until a desired reaction pressure was achieved ($t \leq 2$ min). 3–5 min later, the pressure was slowly decreased and got nearly balanced after 3 h.

At the end of the polymerization, the reactor was cooled down to below 0 °C. Then V-8 was opened to slowly release CO₂. After the reactor was opened, powdery product was

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