



# Mechanical and optical properties of the copolymers of perfluoro(2-methylene-4-methyl-1,3-dioxolane) and chlorotrifluoroethylene

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## ABSTRACT

Aiming at improving the flexibility of polymer films, the copolymers of perfluoro(2-methylene-4-methyl-1,3-dioxolane) (PFMMD) and chlorotrifluoroethylene (CTFE) with different compositions were prepared by radical polymerization using perfluorobenzoyl peroxide (PFBP) as the initiator, and their thermal, mechanical, and optical characteristics were investigated. These copolymers are amorphous, soluble in fluorinated solvents, with glass transition temperatures ( $T_g$ s) in the range of 100–135 °C, and thermally stable to near 400 °C. Stress-strain curves of polymer films were obtained and tensile strength as well as Young's modulus were calculated. Film flexibility and elongation are improved with increasing fraction of CTFE in the copolymers. The copolymer films have low refractive indices (1.33–1.40) and exhibit extraordinary optical transmittance within the visible and near-infrared regions. The copolymers are promising materials for applications including plastic optical fibers, waveguides, and anti-reflective coating.

## 1. Introduction

Fluoropolymers are a unique class of materials with many attractive attributes such as excellent thermal and chemical resistance, distinctive electrical, optical and surface properties, as well as unique gas separation properties [1–5]. These attributes have led to widespread application of fluoropolymers in the aerospace, automotive, electrical, specialty coating, and medical industries, and have attracted an increasing academic interest in the continuing study of fluoropolymers. Teflon® AF, Cytop®, and Hyflon® AD are perhaps the three most commercially successful amorphous fluoropolymers, and they have been extensively studied over the past few decades [1]. Nevertheless, the search and study of new amorphous fluoropolymers are still needed to broaden material choices and improve specific properties.

In the past ten years, our laboratory has synthesized a series of perfluorodioxolane monomers and investigated the thermal, optical and gas separation properties of their homopolymers and copolymers [6–10]. One of these monomers is perfluoro(2-methylene-4-methyl-1,3-dioxolane) (PFMMD), which was prepared through a direct fluorination route from its hydrocarbon precursor (Scheme 1). Homopolymerization of PFMMD yields an amorphous

polymer which is soluble in fluorinated solvents such as hexafluorobenzene (HFB) and perfluoro-2-butyltetrahydrofuran (Fluorinert® FC-75). Membranes prepared from poly(PFMMD) showed gas separation

properties for gas pairs He/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>/CO<sub>2</sub> superior to the commercial perfluoropolymers [11]. However, one problem associated with these polymer films is that they show brittleness and can crack upon bending. One way to improve the film flexibility is to copolymerize the bulky PFMMD with a smaller monomer to reduce the steric crowding along the polymer chain while at the same time making sure the amount of the smaller monomer is right so that the resultant copolymer can still be amorphous. The best comonomer choice would be tetrafluoroethylene (TFE). However, TFE is not easy to handle in academic environments and requires specially designed facility to do so due to its explosive nature. For example, Clemson University is capable of producing TFE in a 100 + g scale and handling TFE in kilogram scale safely with a specially built barricade facility [12]. On the other hand, chlorotrifluoroethylene (CTFE) can be an alternative since it is commercially available and safer to handle in academic laboratories. CTFE is the most widely used fluoroalkene after TFE and vinylidene fluoride (VDF) [13–16] and is readily copolymerized with various vinyl monomers to yield novel copolymers [17]. We have prepared copolymers of PFMMD and CTFE (Scheme 2) and they exhibited excellent gas separation properties [18], but we have never studied their mechanical properties. Thus, in this article, we report the mechanical properties of PFMMD and CTFE copolymers and the effect of CTFE on the copolymer mechanical characteristics. Meanwhile, we also shed some light on the optical properties of this fully halogenated material.

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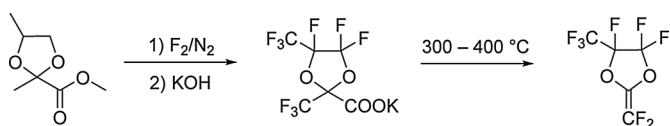
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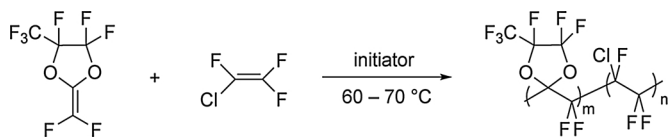
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**Scheme 1.** Synthetic route for monomer PFMMD involving a direct fluorination step.

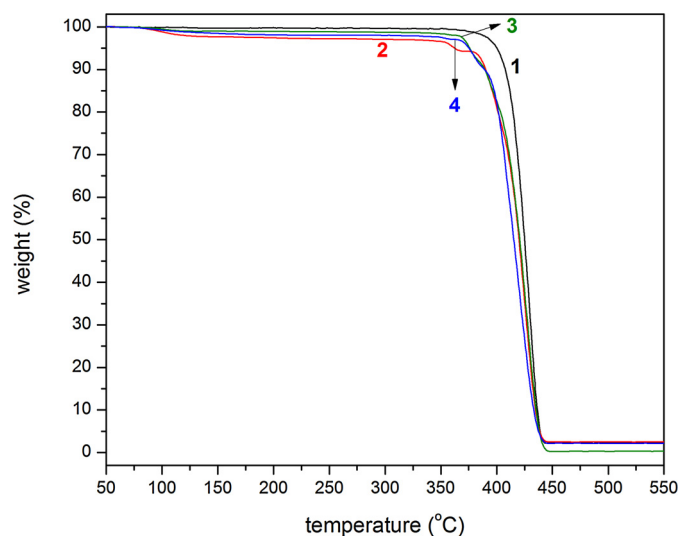


**Scheme 2.** Copolymerization scheme of PFMMD and CTFE.

## 2. Results and discussion

The copolymerization of PFMMD and CTFE was carried out in HFB using perfluorobenzoyl peroxide (PFBP) as the initiator at 60–70 °C. Perfluoro-1,3-dioxolane monomers exhibit higher reactivity compared to those of other fluoro vinyl monomers [19]. The reactivity ratio obtained is  $r(\text{PFMMD}) = 4.0$  and  $r(\text{CTFE}) = 0.8$  using the Kelen-Tudos method [20] based on the low-conversion polymerization data (see Supporting Information). A series of copolymers containing different amounts of CTFE up to 50 mol% was prepared (Table 1). The polymers obtained are all soluble in fluorinated solvents such as HFB or Fluorinert® FC-75, and the X-ray diffraction measurements show no crystalline peaks, indicating the amorphous characteristics of this material. The physical properties of the PFMMD homopolymer and its copolymers with CTFE are summarized in Table 1. Both poly(PFMMD) and poly(PFMMD-co-CTFE) have similarly high molecular weight ( $M_v \sim 1.0 \times 10^6$  g/mol), as determined by viscosity measurement based on the intrinsic viscosity ( $[\eta]$ ) of the polymer solution and the Mark-Houwink equation [21] (see Supporting Information). The average molecular weight of these polymers can not be determined by NMR analysis of end groups, since the molecular weight is so high that the end groups signal cannot be detected. Fig. S1 depicts the  $^{19}\text{F}$  NMR spectra of sample 1–4, where the group of peaks at around -80 ppm correspond to the  $-\text{CF}_3$  and  $-\text{CF}_2-$  on the dioxolane ring, and the overlapped peaks from -105 to -130 ppm are attributed to the  $-\text{CF}-$  on the dioxolane ring, as well as  $-\text{CF}_2-$  and/or  $-\text{CClF}-$  units on the polymer backbone.

Poly(PFMMD) and poly(PFMMD-co-CTFE) are thermally stable to near 400 °C under nitrogen, as shown by the thermogravimetric curves (Fig. 1). A loss of about 3–5% of mass for sample 2–4 was observed at about 100 °C, probably due to the presence of CTFE-containing residue oligomers that are trapped in the polymer matrix and hard to remove at room temperature. The presence of CTFE in copolymer chains slightly decreases the decomposition temperature of the copolymers, as indicated by the left-shifted onset points of curves at around 380 °C compared to that of the homopolymer, while still maintaining thermal stability to at least 350 °C. The glass transition temperature ( $T_g$ ) of



**Fig. 1.** The thermogravimetric curves of polymer samples 1–4 in Table 1 under nitrogen: (1) poly(PFMMD) (2) poly(PFMMD-co-CTFE) (23 mol% CTFE) (3) poly(PFMMD-co-CTFE) (30 mol% CTFE) (4) poly(PFMMD-co-CTFE) (50 mol% CTFE).

PFMMD homopolymer is measured to be around 135 °C, and of CTFE homopolymer is reported to be 45–75 °C [15]. Thus the  $T_g$ s of PFMMD and CTFE copolymers can be varied by changing the relative amount of monomers (Table 1). Fig. S2 is a typical DSC thermogram in the second heating scan, from where the  $T_g$  is determined. Fig. 2 depicts the relationship between  $T_g$  and polymer composition. Clearly, the  $T_g$  of copolymers decreases as the content of CTFE increases in the copolymer chain.

The films of the copolymers are flexible, chemically and thermally stable, and highly transparent. In order to investigate the effect of CTFE on mechanical properties of the copolymers, the tensile strengths of each film were evaluated by continuously measuring the force as the film is elongated at a constant rate of extension at room temperature with an elongation speed of 0.1 mm/min. The stress-strain curves of both PFMMD homopolymer film and copolymer films are depicted in Fig. 3, and the tensile strength and elongation of the copolymers are measured as shown in Table 1. The breaking elongation for samples 1–4 are 1.5, 2, 3 and 9%, respectively; as increasing the amount of CTFE in the copolymer, the tensile strength and elongation at break of the copolymer are correspondingly increased, and Young's moduli are decreased (Fig. 4). These results suggest the brittleness of poly(PFMMD) film can be reduced and film flexibility improved when CTFE is present in polymer chains, and the effect of CTFE on the mechanical properties of the copolymer films is not linear, but more profound at higher content of CTFE.

The optical properties of the copolymers were also assessed. It is reported that carbon halogen bonds have very low absorption [22,23], thus high transmittance is expected in the visible to near-infrared

**Table 1**

The physical properties of PFMMD homopolymer and PFMMD-CTFE copolymers.

sample	polymer composition		$T_g$ (°C)	intrinsic viscosity ( $[\eta]$ ) (dL/g)	$M_v^c$ ( $10^6$ )	tensile strength (MPa)	elongation at break (%)	Young's modulus	refractive index (532 nm)
	Cl wt% <sup>a</sup>	mol% CTFE <sup>b</sup>							
1	–	0	135	0.175	1.07	9.0	1.7	6.6	1.3325
2	3.81	23	125	0.167	1.03	9.9	2.1	4.7	1.3632
3	5.14	30	120	0.160	0.99	10.2	3.1	3.3	1.3752
4	9.59	50	99	0.153	0.96	12.8	8.7	1.5	1.4039

<sup>a</sup> by elemental analysis.

<sup>b</sup> calculated from Cl data; CTFE mol% > 50 are semicrystalline and not studied here.

<sup>c</sup> viscosity-average molecular weight estimated by using Mark-Houwink equation (Supporting Information).

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