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## CO<sub>2</sub> transport behavior in poly(fluoroalkyl acrylate) and poly(fluoroalkyl methacrylate): a comparative study of fluoropolymer structure–property relationships†

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This study examines the CO<sub>2</sub> transport behavior of poly(fluoroalkyl acrylate) (PFA) and poly(fluoroalkyl methacrylate) (PFMA) thin films. Using time-resolved attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and a quartz crystal microbalance (QCM), we quantified CO<sub>2</sub> diffusivity and solubility, linking these properties to the polymer side-chain architecture. The results demonstrate that PFMA exhibits lower CO<sub>2</sub> permeability than PFA at comparable side-chain lengths, owing to restricted chain mobility caused by the  $\alpha$ -methyl backbone of PFMA. Additionally, longer fluorinated side chains increase CO<sub>2</sub> diffusivity while simultaneously reducing solubility owing to weaker polar interactions with CO<sub>2</sub>. Overall, the CO<sub>2</sub> permeability of PFA surpasses that of the PFMA series because of its higher diffusivity. These findings highlight the intricate balance between diffusivity and solubility governed by the molecular structure.

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### Introduction

Excessive CO<sub>2</sub> emissions into the atmosphere are a primary driver of global climate change, necessitating urgent strategies to mitigate greenhouse gas emissions. Among these strategies, direct air capture (DAC) has emerged as a promising technology for capturing CO<sub>2</sub> directly from the atmosphere.<sup>1</sup> DAC offers significant advantages, including the ability to capture diffuse CO<sub>2</sub> emissions and retrofit capture units in decentralized locations.<sup>2</sup> Membrane-based separation technologies have gained attention as a cost-effective and energy-efficient alternative for CO<sub>2</sub> capture.<sup>3</sup> These technologies rely on selective materials that facilitate CO<sub>2</sub> transport while minimizing the passage of other gases. Polymers represent a significant class of materials for such applications owing to their tunable properties and ease of fabrication. However, the performance of membrane-based systems depends critically on the interplay between gas permeability and selectivity, which is governed by the chemical structure and physical properties of the polymer.

Fluorinated polymers represent a significant class of high-performance materials, valued for their unique combination of thermal stability, chemical inertness, low surface energy, and tunable optical properties. Polyfluoroalkyl acrylates represent a unique class of functional polymers that combine the advantageous properties of fluorinated side chains with the structural versatility of acrylate backbones. The strong electron-withdrawing nature and low polarizability of the C–F bond impart exceptional thermal stability, chemical resistance, and notably low surface energy to these materials, making them ideal candidates for non-wetting coatings, anti-fouling surfaces, and advanced membranes.<sup>4,5</sup> Recent advances in controlled radical polymerization techniques, such as ATRP and RAFT, have enabled precise manipulation of molecular weight, architecture, and composition, allowing for the tailored design of polyfluoroalkyl acrylates with tunable surface and bulk properties.<sup>6,7</sup> Moreover, the self-assembly behavior driven by the incompatibility between fluoroalkyl side chains and hydrocarbon segments leads to microphase-separated structures that further enhance their performance in demanding environments.<sup>8,9</sup> Fluorinated polymers have emerged as a cornerstone material class for CO<sub>2</sub>-selective applications, particularly in supercritical CO<sub>2</sub> (scCO<sub>2</sub>) applications, thus revolutionizing various industrial processes in recent decades.<sup>10–12</sup> They are well known for their affinity for scCO<sub>2</sub> and exhibit higher solubility than non-fluorinated polymers.<sup>10,13</sup> Their low surface energy and chemical resistance make them ideal for use in aggressive scCO<sub>2</sub> environments, such as in separation, coating, and extraction

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processes. In particular, poly(fluoroalkyl acrylate) (PFA) and poly(fluoroalkyl methacrylate) (PFMA) have attracted attention because of their tunable side-chain architectures and robust performance in aggressive  $\text{scCO}_2$  environments.<sup>14</sup> The low cohesive energy density of fluorinated polymers, resulting from weak van der Waals interactions between polymer chains, facilitates easier  $\text{CO}_2$  penetration and diffusion. Additionally, Lewis acid–base and quadrupole-induced dipole interactions between  $\text{CO}_2$  and fluorinated segments enhance  $\text{CO}_2$  solubility. However, increasing regulatory restrictions on per- and poly-fluoroalkyl substances (PFAS)—driven by the extreme persistence and toxicity of bioaccumulative long-chain variants (*e.g.*, C8 compounds like PFOA/PFOS)—demand material innovation aligned with “essential use” principles.<sup>15,16</sup> Our molecular design prioritizes side-chain stability and mineralization pathways to mitigate environmental impact while retaining critical  $\text{CO}_2$  affinity and chemical resistance—advancing fluoropolymers that balance functionality with regulatory and sustainability mandates.

Our previous studies investigated the structural and transport behaviors of PFA and PFMA in  $\text{CO}_2$ -rich environments, particularly the influence of the fluoroalkyl side-chain length on aggregation and crystallite formation.<sup>4,17</sup> In  $\text{scCO}_2$  applications, PFA and PFMA demonstrated exceptional stability and performance. Their ability to swell in the presence of  $\text{CO}_2$  while maintaining their structural integrity, is critical for their use under such conditions. We also analyzed the structure of a PFA-C8 polymer brush subjected to  $\text{scCO}_2$  using grazing incidence wide-angle X-ray diffraction (GI-WAXD) and neutron reflectivity (NR) measurement.<sup>18</sup> Fluoroalkyl acrylates with  $\text{CF}_2$  chains longer than 8 carbons exhibit crystallinity owing to the ordered packing of sidechains.<sup>4</sup> Furthermore,  $\text{scCO}_2$  plasticizes semicrystalline fluoropolymer brushes by disrupting crystallites at pressures  $> 4.1$  MPa, enabling structural reorganization akin to high-temperature annealing. Understanding these phenomena is essential for optimizing PFA and PFMA in  $\text{scCO}_2$ -related processes. However, broadening the use of PFA and PFMA beyond specialized  $\text{scCO}_2$  applications requires exploring their behaviors at atmospheric pressure. The structural insights gained from high-pressure studies—such as the effect of the fluoroalkyl side-chain length on crystallinity and swelling—can help us understand how these polymers perform under milder conditions. This knowledge is critical for applications such as  $\text{CO}_2$  capture, where efficient gas separation occurs at atmospheric pressure, and for designing packaging materials and environmental sensors with tailored gas-permeation properties. Furthermore, studying permeability under atmospheric conditions provides valuable insights into the fundamental interactions between  $\text{CO}_2$  and fluorinated polymers, thus guiding the development of novel materials with enhanced  $\text{CO}_2$ -philic properties for both low- and high-pressure applications.

Building on our prior work, this study systematically evaluates the  $\text{CO}_2$  transport behavior in PFA and PFMA, focusing on the interplay among the polymer structure,  $\text{CO}_2$  solubility, diffusivity, and permeability. We examined the structural characterization of PFA and PFMA with varying fluoroalkyl

side-chain lengths and  $\text{CO}_2$  transport properties, including permeability, solubility, and diffusivity in PFA and PFMA under atmospheric conditions. This study provides a comprehensive understanding of the factors influencing  $\text{CO}_2$  transport in fluorinated polymers, with implications for their application in membrane-based separation systems. By correlating the structural properties with the gas transport performance, we sought to establish design principles for next-generation materials for  $\text{CO}_2$  capture and separation.

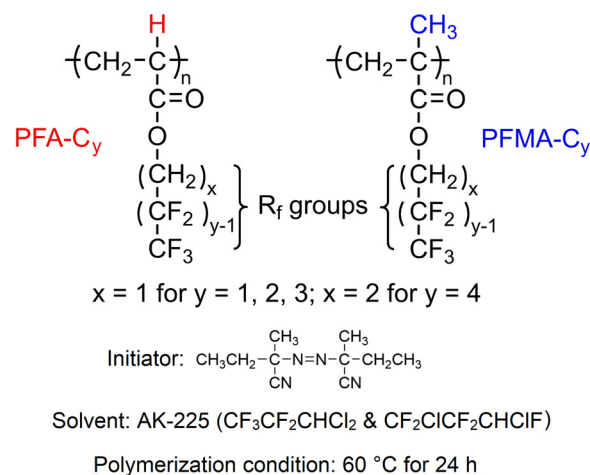
## Experimental section

### Materials

2,2,2-Trifluoroethyl methacrylate (TFEMA, FMA-C<sub>1</sub>), 2,2,3,3,3-pentafluoropropyl methacrylate (PFPMMA, FMA-C<sub>2</sub>), 2-(perfluorobutyl) ethyl methacrylate (PFBEMA, FMA-C<sub>4</sub>), 2,2,2-trifluoroethyl acrylate (TFEA, FA-C<sub>1</sub>), and 2,2,3,3,3-pentafluoropropyl acrylate (PFPA, FA-C<sub>2</sub>) were provided by AGC Inc. (Japan) and used as received. Monomers were labeled according to the length of carbon–fluorine ( $R_f$ ) side-chain for clarity. 2,2'-Azobis(2-methylbutyronitrile) (AMBN) was obtained from TCI (Tokyo, Japan) and recrystallized from methanol before use. AK-225 (a mixture of 3,3-dichloro-1,1,1,2,2-pentafluoropropane and 1,3-dichloro-1,1,2,2,3-pentafluoropropane) was provided by AGC Inc. and used without further purification. HPLC-grade methanol was obtained from Fujifilm Wako Chemical Corporation (Osaka, Japan). A two-component PDMS kit (Sylgard184) was purchased from Dow Corning (USA). Poly(methyl methacrylate) was obtained from TCI (Tokyo, Japan).

### Polymer synthesis

The synthesis procedure was identical for all the monomers as shown in Scheme 1. Herein, we describe the synthesis of poly(2,2,2-trifluoroethyl methacrylate) (PFMA-C<sub>1</sub>) as a representative example. In a typical synthesis, FMA-C<sub>1</sub> (10 g, 58.8 mmol) was dissolved in AK-225 (20 g) in a 50-mL round-bottom flask equipped with a magnetic stir bar. AMBN (0.02 g, 0.104 mmol)



**Scheme 1** Chemical structure of poly(fluoroalkyl acrylates) (PFA-C<sub>y</sub>) and poly(fluoroalkyl methacrylates) (PFMA-C<sub>y</sub>), where  $x$  and  $y - 1$  are the numbers of methylene and fluoromethylene repeating units, respectively.



was then added to the solution. The flask was sealed with a rubber septum, and the mixture was purged with nitrogen for 20 min to remove dissolved oxygen. The flask was then immersed in an oil bath preheated to 60 °C, and the polymerization was allowed to proceed for 24 h with constant stirring. After the reaction, the polymer solution was cooled to room temperature and precipitated in 300 mL of cold methanol. The precipitate was collected *via* filtration, washed thoroughly with methanol, and vacuum-dried at room temperature for 24 h to yield PFMA-C<sub>1</sub> as a white powder (yield of 85%). Identical conditions were applied to synthesize PFMA-C<sub>2</sub>, PFMA-C<sub>4</sub>, PFA-C<sub>2</sub>, and PFA-C<sub>4</sub> using their respective monomers with yields varying between 78 and 90%.

### Characterization of PFA and PFMA thin films

The synthesized polymers were characterized by gel permeation chromatography (GPC) using a Tosoh HLC-8320 GPC system with a evaporative light scattering detector (ELSD). The separation was performed using an Agilent PLgel 5 μm Mixed-C column (300 × 7.5 mm) at 40 °C. The mobile phase was a mixture of HFE-7300 (1,1,1,2,2,3,4,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)pentane) and HFIP (1,1,1,3,3,3-hexafluoroisopropanol) (9:1, v/v) at a flow rate of 1.0 mL min<sup>-1</sup>. The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and polydispersity index ( $\bar{D}$ ) were determined using PMMA calibration standards. The chemical structure of the synthesized PFMA and PFA was confirmed using <sup>1</sup>H-NMR spectroscopy. Samples were dissolved in a 50/50 vol% mixture of deuterated trifluoroacetic acid and CDCl<sub>3</sub> (5 mg mL<sup>-1</sup>). <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer (room temperature). The samples were referenced to tetramethylsilane (TMS) internal standard. Thermal properties of the polymers were analyzed using differential scanning calorimetry (DSC) on a Thermo Plus EVO2 DSC vesta equipped with an automated liquid–nitrogen cooling system (Rigaku Corp., Japan) under an N<sub>2</sub> atmosphere, with a heating/cooling rate of 20 °C min<sup>-1</sup> in the range of –80 °C to 150 °C.

The wide-angle X-ray scattering (WAXS) measurements were conducted at the SPring-8 synchrotron radiation facility using beamline BL38B1 with an incident wavelength of 1 Å. A PILATUS3X 2 M detector (Dectris Ltd) with 1475 × 1679 pixels of 172 × 172 μm<sup>2</sup> was placed 260 mm away from the sample. The samples were mounted between two Kapton films (20 μm each) and exposed to an X-ray beam for 10 s. CeO<sub>2</sub> was used as the standard for calibration of the detector geometry and image integration using the azimuthal integration tool pyFAI.<sup>19</sup> The scattered intensities were azimuthally averaged and recorded as a function of the scattering vector  $q$ , where  $q = 4\pi\lambda^{-1}\sin\theta$ , and  $\theta$  represents half the scattering angle. The  $q$  value was in the 2–36 nm<sup>-1</sup> range.

The polymers were analyzed using a Bruker Vertex70 FTIR spectrometer equipped with horizontally attenuated total reflectance accessories (PIKE). Thin films of the polymers were prepared by casting their solutions onto attenuated total reflection (ATR) crystals (45° Ge, length of 8 cm, and thickness of 4 mm). Spectra were recorded in the range of 4000–600 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. CO<sub>2</sub> (or N<sub>2</sub>) was introduced into the flow cell at a rate of 200 sccm (standard cubic centimeters per

minute) using a mass-flow controller (KOFLOC, 3660). For time-resolved data acquisition, 1000 spectra were collected in an interval of 78 ms with a resolution of 2 cm<sup>-1</sup>, accumulating 16 scans for each spectrum.

To determine the CO<sub>2</sub> diffusivity in the polymer using ATR–FTIR spectroscopy, the concentration was correlated with the experimental absorbance using the Beer–Lambert law. Barbari *et al.* integrated the equation for the evanescent field strength using the Beer–Lambert law to establish an ATR Fickian diffusion model based on certain assumptions.<sup>20,21</sup> A comprehensive derivation of the equation was conducted in previous studies.<sup>20</sup> The simplified equation for diffusion is as follows:

$$\ln\left(1 - \frac{A_t}{A_\infty}\right) = \ln\left(\frac{4}{\pi}\right) - \frac{D\pi^2}{4L^2}t \quad (1)$$

where  $L$  denotes the membrane thickness, and  $A_t/A_\infty$  represents the normalized absorbance.  $D$  is the only adjustable parameter and can be determined using a linear least-squares regression by plotting  $\ln(1 - A_t/A_\infty)$  against  $t$ .

The CO<sub>2</sub> sorption capacity was examined at room temperature using a quartz crystal microbalance (QCM922A, Seiko EG&G). CO<sub>2</sub> (or N<sub>2</sub>) was introduced into the flow cell at a flow rate of 50 sccm using a mass-flow controller (KOFLOC, BR-2C). The QCM crystals (QA-A9M-AU(M)(SEP), Seiko EG&G) were cleaned through UV/ozone treatment (ASM401OZ, ASUMI GIKEN) for 10 min. Thin films of the polymers were spin-coated (MS-B100 Spin-Coater, Mikasa) onto QCM crystals from their solutions (1 wt% in AK-225). The frequency changes were monitored in response to exposure to certain atmospheres (sorption and desorption). The Sauerbrey equation (eqn (2)) was used to relate the frequency change ( $\Delta F$ ) to the added mass ( $\Delta m$ ) on the crystal, either the deposited polymer ( $m_p$ ) or the gas sorption ( $m_g$ ).<sup>22</sup> The CO<sub>2</sub> sorption capacity is defined as  $m_g/m_p$  (mg g<sup>-1</sup>).

$$-\Delta F = \frac{2F_0^2}{A\sqrt{\mu_q\rho_q}}\Delta m \quad (2)$$

where  $F_0$  is the fundamental resonant frequency,  $A$  is the active area (0.196 cm<sup>2</sup>),  $\mu_q$  is the shear modulus of AT-cut quartz crystal ( $2.95 \times 10^{11}$  g cm<sup>-1</sup> s<sup>-2</sup>), and  $\rho_q$  is the density of quartz (2.65 g cm<sup>-3</sup>),  $\Delta F$  is the frequency change, and  $\Delta m$  is mass change.

The permeability ( $P$ ) of CO<sub>2</sub> was determined at 25 °C at a feed pressure of 150 cmHg and atmospheric permeate pressure using the constant-pressure/variable-volume method.<sup>23</sup> The samples were coated onto microporous polyacrylonitrile (PAN) support membranes (UF 010104, SolSep BV) and sealed inside a stainless steel filter holder (Millipore XX4404700). The permeation flow was measured using a mass flow meter (Agilent ADM Flow Meter, G6691A).  $P$  was calculated using the following equation:

$$P = \frac{l}{\Delta p} \frac{273p_{\text{atm}}}{TA76} \left(\frac{dV}{dt}\right) \quad (3)$$

where  $dV/dt$  is the permeate-side flow rate (cm<sup>3</sup> s<sup>-1</sup>),  $T$  is the operating temperature (K), and  $A$  is the effective area of the



membrane ( $\text{cm}^2$ ). All key transport measurements, including permeability, diffusivity, and sorption experiments, were performed in triplicate for each polymer sample. The reported values in figures and tables represent the mean of these measurements, and the associated uncertainty is reported as the standard deviation.

## Results and discussion

### Characterization of PFA and PFMA thin films

Poly(fluoroalkyl acrylates) (PFA- $C_y$ ) and poly(fluoroalkyl methacrylates) (PFMA- $C_y$ ) with varying  $R_f$  lengths were synthesized *via* radical polymerization.  $R_f$  was chosen to be short to yield an amorphous polymer. Polymers with  $C_2$  chains were soluble in THF, whereas longer  $C_4$  chains were dissolved in hydrochlorofluorocarbon solvents (AK-225). As shown in Fig. 1, the  $^1\text{H}$  NMR spectra of PFA and PFMA showed similar proton signals corresponding to methylene groups in the backbone ( $H_a$ ) as well as the sidechain ( $H_c$ ), which appeared at 2.4 ppm and 4.5 ppm, respectively. PFMA also showed proton signals corresponding to the methyl groups ( $H_b$ ) at 0.8–1.2 ppm. All the integral results were consistent with the stoichiometric ratio of the molecular structure. The GPC results (Table 1) indicated that all the samples exhibited  $M_n$  in the range of 20–100 kDa and  $D < 2.0$ . This high degree of polymerization suggests that structural integrity is necessary for membrane applications.

The glass transition temperatures ( $T_g$ ) of the polymer samples were obtained from the DSC traces, as shown in Fig. 2. Our findings indicate that both side-chain length and the presence of an  $\alpha$ -methyl group on the backbone played crucial roles in determining  $T_g$ , with notable differences between fluorinated polymers and their non-fluorinated counterparts. The side-chain length emerged as a primary factor influencing  $T_g$  in these systems. In both the PFA and PFMA series, shorter side chains resulted in higher  $T_g$  values, which can be attributed to the stronger intermolecular interactions between the polymer backbones.<sup>24–26</sup> This trend was also observed in non-fluorinated

Table 1 Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights and glass transition temperatures ( $T_g$ ) of various PFA and PFMA polymers

	$M_n$ (kDa)	$M_w$ (kDa)	PDI	$T_g$ (K)
PFA- $C_2$	75.3	147.0	1.95	258
PFA- $C_4$	94.4	166.7	1.76	249
PFMA- $C_2$	21.0	28.3	1.35	332
PFMA- $C_4$	45.2	58.9	1.30	294

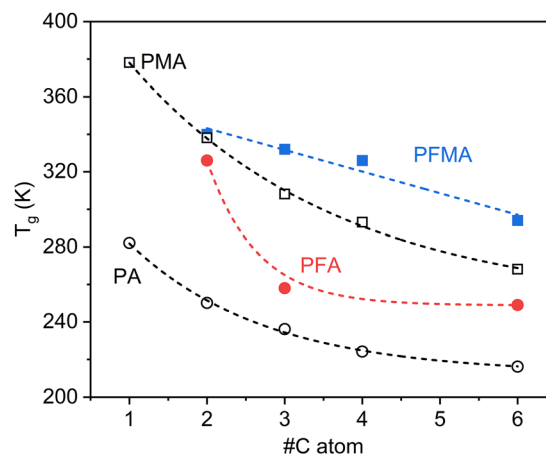


Fig. 2 Glass transition temperature ( $T_g$ ) of PFA and PFMA as well as nonfluorine counterparts PA and PMA.

analogs.<sup>27</sup> Notably, longer side chains lowered  $T_g$  by increasing the free volume and acting as internal plasticizers, reducing the energy required for segmental motion. Additionally, the presence of a methyl group on the backbone, which distinguishes methacrylates from acrylates, consistently led to higher  $T_g$  values.

A comparison of the fluorinated (meth)acrylates with their non-fluorinated analogs revealed consistently higher  $T_g$  values in the fluorinated versions. This can be attributed to a combination of factors. The high electronegativity of fluorine atoms creates strong C-F dipoles, leading to enhanced intermolecular dipole-dipole interactions between chains. Furthermore, the larger atomic radius of fluorine compared to hydrogen results in increased steric hindrance and segmental stiffness, which restricts chain mobility. Together, these effects elevate the energy barrier for segmental motion, resulting in a higher  $T_g$  compared to their non-fluorinated analogs. This effect was more pronounced for PFA with shorter side chains, suggesting a complex interplay between fluorination effects and side chain dynamics.

These structure–property relationships have significant implications for the  $\text{CO}_2$  transport behavior. Polymers with  $T_g$  values near or below the intended operating temperature are likely to exhibit enhanced  $\text{CO}_2$  permeability owing to the increased chain mobility in the rubbery state. Tuning the  $T_g$  of fluorinated (meth)acrylates *via* careful control of the side chain length, backbone substitution, and degree of fluorination could optimize the  $\text{CO}_2$  transport properties.

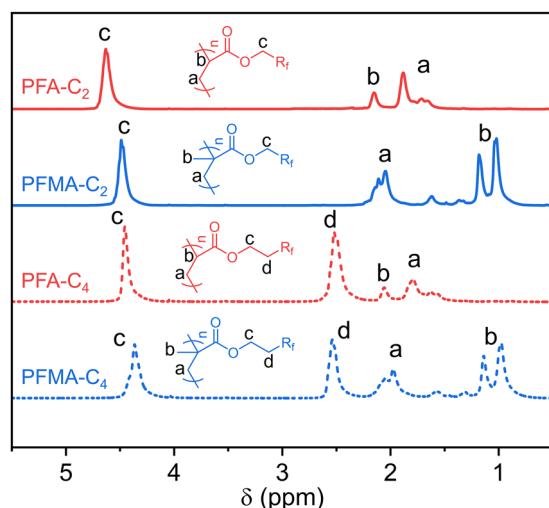


Fig. 1  $^1\text{H}$  NMR spectra of PFA and PFMA.



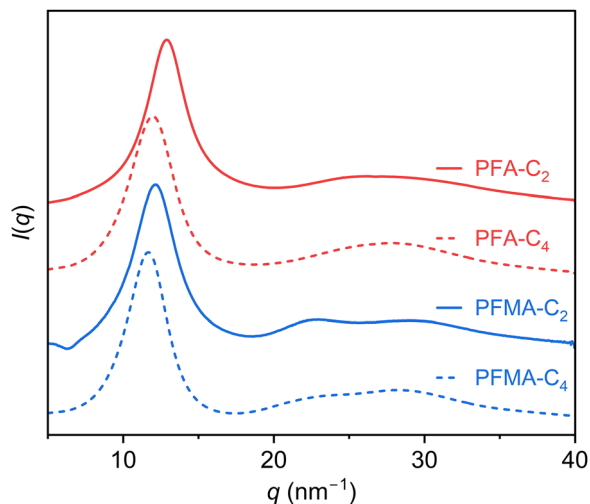


Fig. 3 WAXS 1d profiles of PFA and PFMA.

All samples exhibited broad, diffuse peaks in their WAXS profiles (Fig. 3), with no sharp crystalline peaks, confirming their amorphous nature. This finding is consistent with previous studies and is advantageous for applications requiring gas permeability, as amorphous polymers typically possess a higher free volume than semi-crystalline polymers, facilitating molecular diffusion.<sup>4</sup>

For PFMA, three characteristic peaks were observed at approximately  $1.2 \text{ \AA}^{-1}$  ( $q_I$ ),  $2.2 \text{ \AA}^{-1}$  ( $q_{II}$ ), and  $2.8 \text{ \AA}^{-1}$  ( $q_{III}$ ). The detailed  $d$ -spacing ( $d$ ) values were calculated from  $q_{\text{peak}}$  using the Bragg equation ( $d = 2\pi/q$ ) and summarized in Table 2. The  $q_I$  peak with  $d_I \approx 5 \text{ \AA}$  arose from the packing of fluoroalkyl sidechains.<sup>28</sup> The  $q_{II}$  peak corresponded to an intramolecular methyl–methyl correlation, while the third broad maximum  $q_{III}$  peak corresponded to the average repeat-unit correlation, averaged from the C–C distances along the backbone chains, which has the shortest correlation distance.<sup>29</sup> This profile resembled that of the nonfluorine counterpart PMMA, but with noticeable variations in peak positions. The  $q_I$  peak of PMMA at  $0.94 \text{ \AA}^{-1}$  arose from the intermolecular backbone–backbone, backbone–ester, and backbone–methyl correlations.<sup>29,30</sup> The  $q_{II}$  and  $q_{III}$  peaks were almost identical to those of PFMA, which corresponded to the average repeat-unit correlation in the (meth)acrylate backbone.

In contrast, PFAs exhibited only two prominent broad peaks at  $q_I = 1.2 \text{ \AA}^{-1}$  and  $q_{III} = 2.8 \text{ \AA}^{-1}$ . Similar to PFMA, the  $q_I$  peak of PFA arose from the packing of fluoroalkyl side chains. However,

Table 2 Peak positions ( $q$ ) and  $d$ -spacing ( $d$ ) values of PFA and PFMA from the WAXS 1d profiles

	$q_I$ ( $\text{\AA}^{-1}$ )	$d_1$ ( $\text{\AA}$ )	$q_{II}$ ( $\text{\AA}^{-1}$ )	$d_2$ ( $\text{\AA}$ )	$q_{III}$ ( $\text{\AA}^{-1}$ )	$d_3$ ( $\text{\AA}$ )
PFA-C <sub>2</sub>	1.29	4.88	—	—	2.77	2.27
PFA-C <sub>4</sub>	1.20	5.26	—	—	2.80	2.24
PFMA-C <sub>2</sub>	1.21	5.19	2.23	2.81	2.91	2.16
PFMA-C <sub>4</sub>	1.17	5.38	2.24	2.81	2.81	2.24

$d$ -Spacing ( $d$ ) is calculated from Bragg equation.

PFA showed a slightly reduced  $d_1$  spacing than PFMA. This is likely due to the presence of the  $\alpha$ -methyl group in PFMA, which caused steric hindrance and disrupted close packing of the fluorinated side chains. The absence of a  $q_{II}$  peak in PFA indicates the lack of an  $\alpha$ -methyl group, eliminating methyl–methyl correlations observed in PFA.

A subtle increase in  $d_1$  was observed for both PFA and PFMA with increasing side-chain length (C<sub>4</sub>). This indicates that a longer side chain introduced greater flexibility and potentially higher free volume, which is consistent with the trends observed in  $T_g$ . The WAXS data provide insights into the molecular packing and structural organization of these fluorinated polymers, which are crucial for understanding their properties, including their interactions with CO<sub>2</sub> and their potential performance in various applications.<sup>30</sup>

In addition, ATR-FTIR characterization of PFA and PFMA revealed key differences as well as similarities in their chemical structures (Fig. 4). The spectra indicated no presence of unreacted monomers, as evidenced by the absence of significant C=C stretching peaks around  $1640 \text{ cm}^{-1}$ . This aligns with the GPC results, confirming the high degree of polymerization in both PFA and PFMA. Both polymers exhibited characteristic absorption bands corresponding to their fluorinated side chains and ester functional groups. All the (meth)acrylate samples exhibited a characteristic carbonyl stretching vibration band at  $1730\text{--}1760 \text{ cm}^{-1}$  corresponding to the ester functional groups in their backbones. The subtle variation in wavenumber resulted from the  $\alpha$ -substituents and  $R_f$  groups, probably because of the differences in the chemical environment around the carbonyl group. Furthermore, the presence of spacer methylene groups and the  $\alpha$ -methyl group that could alter the electron density and steric interactions may have contributed to the observed shifts. The strong absorption bands at  $\nu_s$  (CF<sub>2</sub>)  $\sim 1130 \text{ cm}^{-1}$  and  $\nu_{as}$  (CF<sub>2</sub>)  $\sim 1200 \text{ cm}^{-1}$  attributed to the C–F stretching vibrations of fluoroalkyl side chains, were prominent in both PFA and PFMA.<sup>31</sup> A notable difference emerged when comparing the C<sub>4</sub> and C<sub>2</sub> variants: the C<sub>4</sub> samples exhibited peaks at higher wavenumbers compared with the C<sub>2</sub> samples

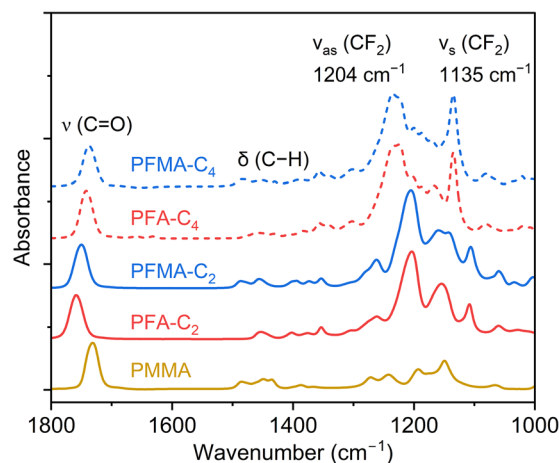


Fig. 4 ATR-FTIR spectra of PFA and PFMA.



(1135  $\text{cm}^{-1}$  vs. 1126  $\text{cm}^{-1}$ ). This shift could be related to side chain aggregation because the increased length favors stable packing.<sup>32</sup> Comparable peak profiles suggest that the fluorinated groups dominate the spectra in this region. However, a notable difference between the two polymers was observed in the absorption bands around 2950  $\text{cm}^{-1}$ , with PFMA exhibiting more pronounced bands. These bands were attributed to the methyl group associated with the methacrylate structure, which distinguishes PFMA from PFA.

The  $\text{CO}_2$  sorption by the polymer at equilibrium was demonstrated by ATR-FTIR spectra (Fig. 5). The  $\text{CO}_2$  that diffused into the polymer exhibited a distinct asymmetric stretching vibration ( $\nu_3$ ) band compared to gaseous  $\text{CO}_2$ . This result aligns with previous literature on  $\text{CO}_2$  dissolved in various solvents and polymers. The  $\nu_3$  band for all fluoro(meth)acrylates appeared at an identical wavenumber of 2342  $\text{cm}^{-1}$ , which is different from that of PMMA at 2338  $\text{cm}^{-1}$ . This discrepancy could be attributed to the different interaction sites of  $\text{CO}_2$  with the fluorine and nonfluorine counterparts. For PMMA,  $\text{CO}_2$  mainly interacts with the carbonyl groups.<sup>33</sup> In contrast, with the incorporation of  $R_f$  groups in PFMA,  $\text{CO}_2$  might have interacted with the side chain *via* weak Lewis base ( $R_f$ )–Lewis acid ( $\text{CO}_2$ ) interactions or *via* its quadrupole moment interacting with the induced dipoles of the  $R_f$ . The identical  $\nu_3$  band position at 2342  $\text{cm}^{-1}$  across all fluoromethacrylates (regardless of chain length) suggests that the  $R_f$  groups dominated the  $\text{CO}_2$  interactions, creating a consistent sorption environment distinct from that of PMMA.

In addition, time-resolved ATR-FTIR was used to analyze  $\text{CO}_2$  diffusion in both polymers. The concentration of  $\text{CO}_2$  was correlated to the experimental absorbance using the Beer-Lambert law. The absorbance ( $A_t$ ) of the  $\nu_3$  band was tracked as a function of time during sorption and desorption. The experimental data were fitted using Fickian diffusion, a model that describes diffusion driven by concentration gradients. The diffusion coefficient ( $D$ ) was derived from linear regression of  $\ln(1 - A_t/A_\infty)$  vs. time ( $t$ ) plot as shown in Fig. 6a. These plots reveal that  $\text{CO}_2$  diffused faster in PFA than in PFMA at

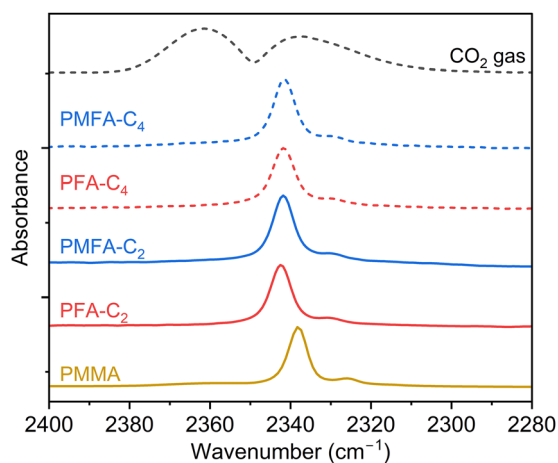


Fig. 5 ATR-FTIR spectra of  $\text{CO}_2$  in PFA and PFMA.

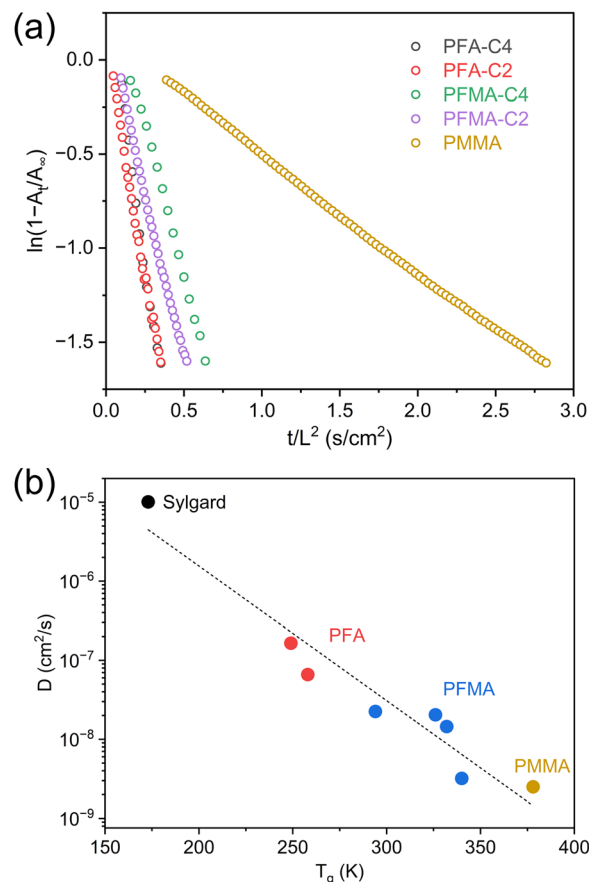


Fig. 6 (a) Plot of  $\ln(1 - A_t/A_\infty)$  for the  $\text{CO}_2$  asymmetric stretching band ( $\nu_3$ ) as a function of time. (b) Relationship between diffusivity ( $D$ ) and  $T_g$  for various polymers.

comparable side chain lengths. The faster diffusion in PFA is likely due to the absence of the  $\alpha$ -methyl group, which may reduce steric hindrance and enhance side chain mobility, thereby increasing free volume and facilitating  $\text{CO}_2$  transport. In addition, longer chain length induced higher  $D$  values for each polymer series.

The  $D$  values were plotted as a function of  $T_g$  for various polymer samples in Fig. 6b. This scatter plot, which is accompanied by a downward-sloping trend line, reveals an inverse relationship between  $D$  and  $T_g$ . Sylgard, with an exceptionally low  $T_g$  (170 K), exhibited a high  $D$  value ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), indicating significant chain mobility and free volume. In contrast, PMMA, which has a high  $T_g$  (380 K), exhibited a significantly lower  $D$  value ( $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ), indicating its rigid structure with a minimal free volume. Compared with PFMA, PFA chains were more mobile and thus increased the free volume, facilitating faster gas diffusion, as reflected by the higher  $D$  values. As discussed earlier, the  $T_g$  values of the samples were significantly influenced by the fluoroalkyl ( $R_f$ ) side-chain length. In both series, longer  $R_f$  chains induced higher  $D$  values. A side chain with faster dynamics increased the free volume, thus decreasing  $T_g$  and inducing faster  $\text{CO}_2$  diffusion.

The strong affinity of both polymers for  $\text{CO}_2$ , inferred from the pronounced C–F stretching bands, suggests that these materials probably exhibit high  $\text{CO}_2$  solubility—a desirable



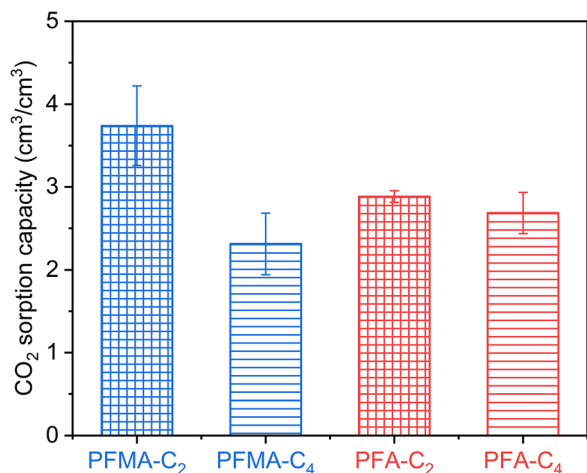
**Table 3** CO<sub>2</sub> permeability (*P*), solubility (*S*), and diffusion coefficients (*D*) for PFMA and PFA

	<i>T<sub>g</sub></i> (K)	<i>D</i> /10 <sup>-8</sup> (cm <sup>2</sup> s <sup>-1</sup> )	<i>S</i> (cm <sup>3</sup> cm <sup>-3</sup> )	<i>P</i> (Barrer)
PFA-C <sub>2</sub>	258	6.61 ± 0.28	2.82 ± 0.10	50 ± 3
PFA-C <sub>4</sub>	249	16.5 ± 0.5	2.61 ± 0.25	121 ± 4
PFMA-C <sub>2</sub>	332	1.45 ± 0.05	3.60 ± 0.48	14 ± 1
PFMA-C <sub>4</sub>	294	2.25 ± 0.11	2.57 ± 0.37	20 ± 1

Measured at 297 K.

property for gas separation applications.<sup>34,35</sup> The CO<sub>2</sub> sorption capacities of PFA and PFMA were evaluated using QCM. The Sauerbrey equation was used to calculate the mass of the deposited polymers and sorbed molecules in a certain atmosphere. The CO<sub>2</sub> sorption data are summarized in Table 3 and Fig. 7. Compared with the *n*-alkyl methacrylates, both PFA and PFMA exhibited higher CO<sub>2</sub> sorption capacities owing to stronger interactions between CO<sub>2</sub> and *R<sub>f</sub>* groups.

In addition, PFMA exhibited higher CO<sub>2</sub> sorption than PFA, which could be attributed to the additional unoccupied volume of the glassy polymers. The  $\alpha$ -methyl group hindered the chain rotation, which limited the efficient packing of the *R<sub>f</sub>* side chain. However, both PFMA and PFA exhibited a clear decrease in CO<sub>2</sub> sorption as the *R<sub>f</sub>* side-chain length increased from C<sub>2</sub> to C<sub>4</sub>. This reduction was attributed to increased van der Waals interactions between the longer *R<sub>f</sub>* chains, thereby weakening their interactions with CO<sub>2</sub>. Thus, *R<sub>f</sub>* chains longer than C<sub>8</sub> are expected to become semi-crystalline, exhibiting significantly lower gas sorption than the amorphous ones. This effect was also observed for the *n*-alkyl methacrylates with increasing side-chain length, as previously reported.<sup>36,37</sup> The highest CO<sub>2</sub> sorption capacity was observed in PFMA-C<sub>2</sub> (5.8 mg g<sup>-1</sup>), where the  $\alpha$ -methyl group and shorter C<sub>2</sub> *R<sub>f</sub>* chains synergistically maximized free volume and CO<sub>2</sub> interaction sites. The  $\alpha$ -methyl group disrupted packing efficiency, while the shorter *R<sub>f</sub>* chains minimized interchain interactions. In contrast, PFA-C<sub>4</sub> exhibited the lowest sorption (3.5 mg g<sup>-1</sup>) owing to more efficient packing and stronger *R<sub>f</sub>*-*R<sub>f</sub>* interactions. It is crucial to note that this high CO<sub>2</sub> affinity is a distinguishing feature of the

**Fig. 7** CO<sub>2</sub> sorption of PFA and PFMA calculated from QCM results.

fluorinated polymers. In their non-fluorinated counterparts, such as poly(*n*-alkyl methacrylates), gas sorption is significantly lower as it is primarily driven by weaker van der Waals forces. The enhanced solubility in PFA and PFMA is a direct consequence of the favorable CO<sub>2</sub>-*R<sub>f</sub>* interactions, as PFMA surpasses PFA owing to the disruption of packing efficiency by the  $\alpha$ -methyl group. Shorter *R<sub>f</sub>* chains (C<sub>2</sub>) optimized sorption by reducing interchain interactions, whereas longer chains (C<sub>4</sub>) diminished sorption due to enhanced *R<sub>f</sub>*-*R<sub>f</sub>* interactions. The  $\alpha$ -methyl group and shorter *R<sub>f</sub>* length contributed together in achieving the inefficient packing of *R<sub>f</sub>* to realize higher CO<sub>2</sub> sorption.

The gas permeability through a polymer membrane is generally expressed as a product of its solubility and diffusivity ( $P = S \times D$ ). The interplay between solubility, diffusivity, and glass transition temperature (*T<sub>g</sub>*) is complex, as structural features—such as the *R<sub>f</sub>* length—simultaneously influence the free volume, chain flexibility, and intermolecular interactions. For PFA, *P* rose from 50 Barrer (PFA-C<sub>2</sub>) to 121 Barrer (PFA-C<sub>4</sub>), driven by a significant *D* increase (6.6 to 16.5 × 10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup>) despite a slight *S* decrease (2.82 to 2.61 cm<sup>3</sup> cm<sup>-3</sup>). This indicates that the increased diffusivity, resulting from lower *T<sub>g</sub>* and higher free volume, outweighed any solubility reduction caused by *R<sub>f</sub>*-*R<sub>f</sub>* interactions. Compared with PFA, PFMA exhibited a significantly lower *P* value at comparable *R<sub>f</sub>* lengths. This reveals that the decreased chain mobility outweighed the pronounced *S* increase. This nuanced interplay highlights the challenge of optimizing *D* and *S* to achieve high gas permeability, thereby guiding the design of advanced fluorinated materials for CO<sub>2</sub> capture and gas separation membrane applications.

## Conclusions

In this work, we have established critical structure–property relationships governing CO<sub>2</sub> transport in PFA and PFMA polymers. Our findings demonstrate that while both polymer families show a strong affinity for CO<sub>2</sub>, their permeability is dictated by a delicate balance between solubility and diffusivity. The absence of an  $\alpha$ -methyl group in the PFA backbone enhances chain mobility, leading to higher diffusivity and, consequently, superior CO<sub>2</sub> permeability compared to the PFMA series. Meanwhile, extending the fluoroalkyl side-chain length acts as an internal plasticizer that lowers the glass transition temperature (*T<sub>g</sub>*) and boosts diffusivity, albeit at the expense of solubility due to side-chain aggregation. This structure-guided approach provides a foundation for developing next-generation fluorinated membranes with tunable gas transport properties, enabling their application in direct air capture (DAC), post-combustion CO<sub>2</sub> separation, and barrier materials for gas packaging and environmental sensing.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.



## Conflicts of interest

There are no conflicts to declare.

## Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its ESI.† Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

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