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Posted Date: October 13th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11040259/v1>

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Additional Declarations:

No competing interests reported.

Scheme 1 is not available with this version.

Tertiary-Butyl Amine Functionalized Hierarchical Nano-Acrylic Copolymers for Energy-Efficient CO₂ Sequestration and Indoor Air Remediation

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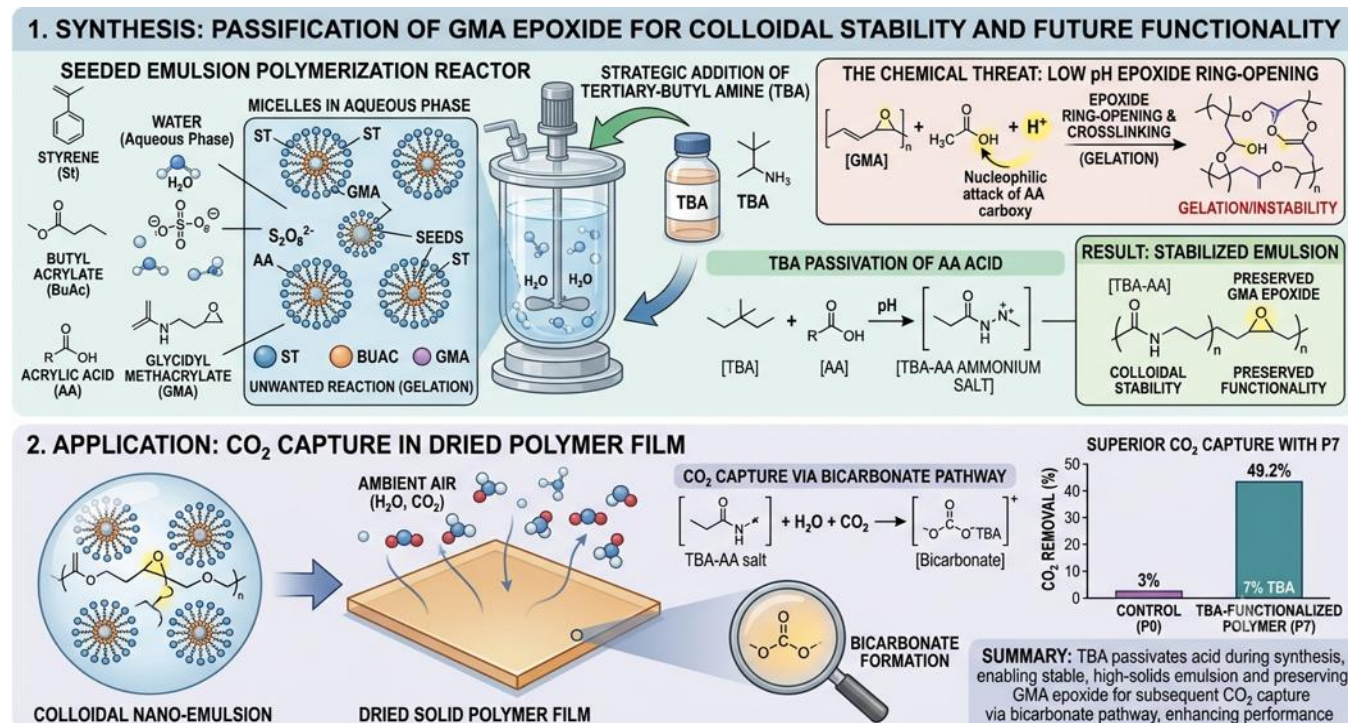
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ABSTRACT

The increasing concentration of the greenhouse gas carbon dioxide (CO₂) in the atmosphere, as a result of human activities such as the combustion of fossil fuels, requires novel approaches for carbon capture, utilization, and storage. Liquid amine scrubbing is the state-of-the-art technology for CO₂ capture; however, its large-scale industrialization is impeded by an immense energy demand for regeneration and accelerated equipment corrosion. These limitations hinder the potential of post-combustion amine-based scrubbing for decentralized direct air capture and indoor air quality applications. Herein is proposed a sustainable and efficient solid-state adsorbent for ambient CO₂ capture based on a novel polymeric composite synthesized by controlled seeded semi-batch emulsion polymerization of styrene, butyl acrylate, acrylic acid (AA), and glycidyl methacrylate (GMA). The incorporation of tertiary-butyl amine (TBA) instead of the ubiquitous ammonium hydroxide during neutralization was found to suppress undesired epoxide ring-opening side reactions, while introducing high concentration of functional tertiary amine sites for CO₂ capture. The polymer composite microstructure and physicochemical properties were elucidated in detail using a combination of dynamic light scattering (DLS), zeta potential, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), wide-angle X-ray diffraction (WAXRD), atomic force microscopy (AFM) phase imaging, and thermogravimetric analysis coupled with differential scanning calorimetry (TGA/DSC). It was found that the incorporation of TBA into the latex polymer matrix results in increased ionic crosslinking sites, leading to a higher glass transition temperature ($T_g = 146\text{ }^{\circ}\text{C}$) and an overall more amorphous and dispersed composite structure. Remarkably, while the ammonium functionalized latex composite showed almost no CO₂ capture ability (0-3%), the TBA sample demonstrated a tremendously high performance with 49.2% CO₂ removal at 30 °C. Moreover, low-temperature TGA confirmed the occurrence of chemical absorption of CO₂ through the formation of the bicarbonate complex. Overall, the work demonstrates the underlying mechanisms of polymer composite formation and CO₂ capture abilities of a novel smart anti-carbonation latex composite material based on the modification of the latex matrix with tertiary amines for the first time and provides a platform for future development of sustainable air quality management technologies.

Keywords: Carbon dioxide capture; Emulsion polymerization; Tertiary-butyl amine; Bicarbonate formation; Indoor air quality; Glycidyl methacrylate

Graphical abstract:



1. Introduction

The world's energy supply is dominated by fossil fuels, and more than 80% of total energy production is currently consumed in the form of fossil fuels [1,2]. Burning fossil fuels emits high concentrations of greenhouse gases (GHG) into the atmosphere, the most of which are carbon dioxide (CO₂) and carbon monoxide [3,4]. Atmospheric CO₂ levels have reached a record level, resulting in numerous negative effects on the environment, such as climate change, global temperature rise, and sea level rise [5,6]. Although the transition to renewable energy sources (e.g., solar and wind) is of great importance, energy storage is required to ensure a steady supply of electricity [1]. In this regard, carbon dioxide capture, utilization, and storage (CCUS) have become a critical component of modern energy systems [7]. Captured CO₂ can be used as an inexpensive carbon source to produce a variety of products: chemicals, methanol, and polymers [3,4,8].

Although the processes occurring in the atmosphere are global in nature, the increase in CO₂ levels indoors poses a serious threat to human health. At present, people spend more than 70% of their time indoors, where the concentration of CO₂ can be several times higher than outdoors due to insufficient ventilation [9,10]. High CO₂ levels indoors can lead to serious consequences, from oxygen deprivation and increased blood pressure to lethality [11]. Thus, the development of new gas cleaning technologies capable of operating at low temperatures and CO₂ partial pressures to simultaneously reduce greenhouse gas emissions and indoor air pollution levels is of great importance [12].

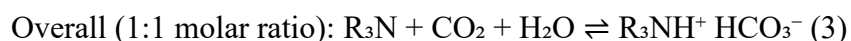
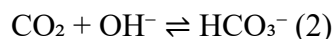
Gas separation processes are usually more cost-effective and energy efficient than distillation methods in a wide range of low-pressure applications [3–6]. Post-combustion CO₂ capture using conventional amine-based solvents such as monoethanolamine (MEA) aqueous solutions is considered one of the most promising technologies for reducing GHG emissions. Nevertheless, this technology has several significant disadvantages, namely, the high energy cost of solvent regeneration, severe equipment corrosion, and the formation of toxic solvents during solvent degradation [14–16]. A promising direction in post-combustion CO₂ capture is the use of solid adsorbents. In this regard, technologies for separating CO₂ from a mixture with other gases using adsorption are of great interest. Adsorbents are extremely diverse in structure, and their properties depend on the pore geometry and surface chemistry, which can be tailored during synthesis [17]. Zeolite [17], metal-organic frameworks (MOFs) [18–20], covalent organic frameworks (COFs) [21], ceramics [22], mixed organic-inorganic polymers [17,22] are some of the most promising types of adsorbents for CO₂ capture. Among these adsorbents, MOFs and Zeolite have a high surface area, while synthesis of MOFs often requires expensive and toxic solvents, and Zeolite has poor thermal stability [19,23]. Adsorbents made of polymers have received considerable attention due to the relative simplicity of synthesis, lower cost, and versatility in tuning their properties. Amines are the most common CO₂ capturing groups that can be introduced by chemical modification of the surface of various polymeric materials. Various chemical and radiative grafting methods have been proposed to attach amine groups to the surface of different materials [24]. However, a promising method is the synthesis of amine-containing polymers by emulsion polymerization [25–27].

The chemical topology of the amine functional group governs the thermodynamics and kinetics of CO₂ capture. Primary and secondary amines readily undergo rapid reactions with CO₂ to afford stable carbamates (0.5:1 amine:CO₂ molar ratio), which are characterized by highly exothermic reaction rates but enormous regeneration energies due to the strong C–N bonds [15,28,29]. On the other hand, tertiary amines (such as tert-butyl amine, TBA) follow a base-catalyzed hydration mechanism, wherein CO₂ and water react in 1:1 molar ratios to yield bicarbonate [28,30]. Moreover, tertiary amines necessitate much lower desorption energies, thereby rendering them highly attractive candidates for energy-saving DAC [29–32]. Nonetheless, the integration of tertiary amines into robust film-forming nano-emulsion polymers for IAQ remediation has been extensively understudied.

The introduction of glycidyl methacrylate (GMA) creates highly reactive oxirane (epoxide) rings that are employed for the future crosslinking and adhesion to the substrate (Scheme 1). However, when reacted at elevated temperatures (80 °C) and low pH in the presence of acrylic acid (AA), a nucleophilic attack of the carboxylate anion of AA on the epoxide ring of GMA may occur, resulting in undesired β -hydroxy ester crosslinking and premature gelation/catastrophic polymer instability [25,33]. To suppress this undesirable side reaction, the acidic protons of AA should be blocked prior the high-temperature propagation; TBA, a bulky tertiary amine, is employed as the acid-neutralizing agent. The carboxyl group is rendered completely inactive upon the formation of the ammonium carboxylate salt, and the epoxide integrity of GMA is preserved throughout the polymerization [25,33].

Unlike primary amines, which form carbamates, TBA does not possess an N–H proton and thus cannot participate in carbamate formation. In the presence of ambient moisture (inherent in indoor

air and within the polymer film), TBA can act as a Brønsted base [28,30]: it abstracts a proton from water and generates a highly reactive hydroxide ion that attacks the electrophilic carbon of CO₂ to afford a bicarbonate ion, while the protonated amine stabilizes the complex (Eqs. (1) to (3)):



Scheme 1 : synthesis strategy and CO₂ capture application

This 1:1 stoichiometry theoretically doubles the CO₂ loading capacity per mole of amine relative to the 2:1 ratio required for primary-amine carbamate formation [29,31]. Furthermore, the ionic bonding in the bicarbonate complex is significantly weaker than the covalent C–N bond of carbamates, facilitating low-temperature thermal regeneration and drastically reducing the energy penalty of the capture cycle [30,32].

Objectives and scope of the present study. By tuning the TBA concentration during seeded emulsion copolymerization of a GMA-containing acrylic matrix, we aim to design a hierarchical nanocomposite with exceptional ambient CO₂ capture properties. Specifically, we will: (i) prepare a series of St/BuAc/AA/GMA nano-emulsion copolymers with varied TBA contents (0–7%) versus the ammonium hydroxide control; (ii) establish the mechanism by which the addition of TBA suppresses the anionic ring-opening of GMA–AA; (iii) perform an in-depth physicochemical characterization (DLS, ζ -potential, ATR-FTIR, WAXRD, AFM, TGA/DSC); (iv) evaluate the CO₂ adsorption performance at ambient conditions by analyzing the dependence of uptake on amine content; (v) formulate a mechanism of tertiary amine–CO₂ interactions; and (vi) discuss the prospects of the obtained materials as “smart anti-carbonation paints” for industrial applications.

2. Experimental

2.1. Materials

Analytical-grade monomers—styrene (St), acrylic acid (AA), glycidyl methacrylate (GMA), and butyl acrylate (BuAc)—were procured from Sigma-Aldrich (Germany); potassium persulfate (KPS, initiator) was obtained from the same supplier. Sodium dodecyl sulfate (SDS, anionic surfactant) and ethoxylated nonylphenol (NP30, nonionic surfactant) were sourced from El-Gomhoria Company (Egypt). Tertiary-butyl amine (TBA) and sodium acetate buffer were acquired from El-Nasr for Chemical Industries (Egypt). The nonionic surfactant MARLIPAL 31-90 (a fatty alcohol polyethylene glycol ether based on C11–C13 branched alcohols, ~9 mol ethoxylation) was imported from Sasol (Italy). Deionized water (resistivity >18 M Ω ·cm) was used exclusively.

2.2. Synthesis of TBA-functionalized nano-emulsion polymers

A seeded semi-batch emulsion polymerization technique was employed to ensure narrow particle size distribution and high colloidal stability. A 500 mL jacketed glass reactor, equipped with reflux condenser, precision thermocouple, and mechanical overhead stirrer, was purged with N₂. According to the formulation matrix detailed in **Table 1**, the surfactants (SDS/MARLIPAL 31-90) were divided in a 1:3 mass ratio. Phase A was emulsified with St and BuAc using a high-shear Ultra-Turrax homogenizer (3500 rpm, 15 min, 25 °C) to form pre-emulsion C. Phase B, containing the residual surfactants, DIW, and sodium acetate buffer, was heated to 80 °C, and 10% of pre-emulsion C was injected to form seed micelles. The residual pre-emulsion was mixed with GMA and AA, homogenized, and dosed into the reactor via a precision syringe pump at 1.30 mL min⁻¹ over 150 min alongside the KPS initiator. The reaction was held at 80 °C for 2 h to ensure complete monomer conversion. The reactor was then cooled to 50 °C, and TBA was added dropwise until the pH precisely reached 8.5 to trigger the neutralization mechanism.

Table 1. Formulation matrix of the synthesized St/BuAc/AA/GMA nano-emulsion polymers (wt%).

Component	P0 (Control)	P1	P2	P3	P4	P5	P6	P7
Styrene	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5
Butyl acrylate	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5
Acrylic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Glycidyl methacrylate	2.0	2.0	3.0	5.0	7.0	7.0	7.0	7.0
SDS	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
MARLIPAL 31-90	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
TBA	0	1	1	1	1	2	5	7
Ammonium hydroxide	1	0	0	0	0	0	0	0
KPS / sodium acetate	0.75/0.8	0.75/0.8	0.75/0.8	0.75/0.8	0.75/0.8	0.75/0.8	0.75/0.8	0.75/0.8
Solid content / T (°C)	50/80	50/80	50/80	50/80	50/80	50/80	50/80	50/80

P0 serves as the ammonium hydroxide baseline; P1–P4 systematically increase GMA content at constant 1% TBA; P5–P7 maintain 7% GMA while escalating TBA to isolate the effect of tertiary amine density on colloidal and adsorptive properties.

2.3. Characterization

Solid content and coagulum were quantified gravimetrically. Rheological profiles were mapped using a Brookfield RVF viscometer (spindle 2, 20 rpm, 25 °C). Hydrodynamic diameter and ζ -potential were determined by dynamic light scattering (Malvern Mastersizer 3000). Mechanical properties (pencil hardness, Sheen kit; cross-cut adhesion, ASTM D3359) were evaluated on dried

films. ATR-FTIR (Nicolet Avatar 370 CSI, 400–4000 cm^{-1}) identified functional group transformations. WAXRD (Philips PW1390, Cu $K\alpha$, $\lambda = 1.5404 \text{ \AA}$) assessed crystalline/amorphous transitions. AFM (Autoprobe CP-Research, Thermomicroscopes) was performed in contact mode with a silicon nitride probe (MLCT, Bruker) over $2 \times 2 \mu\text{m}^2$ scan areas (scan rate 1 Hz; 256×256 pixel resolution); image processing and roughness quantification were performed with ProScan software (v2.1). Thermal stability and T_g were evaluated by TGA (Shimadzu TGA-50, $10 \text{ }^\circ\text{C min}^{-1}$ to $700 \text{ }^\circ\text{C}$, N_2) and DSC (TA Instruments DSC model (Q200)).

2.4. CO_2 adsorption protocol and kinetic evaluation

CO_2 capture performance was evaluated using a calibrated GasTech 535 ambient CO_2 analyzer (dual-channel IR sensor, 0–9999 ppm, 1 ppm resolution). Dried polymer films of precisely known mass were placed in a sealed environmental chamber connected to a continuous flow of calibrated CO_2 (1 L min^{-1}) at $30 \text{ }^\circ\text{C}$. Inlet (C_{in}) and outlet (C_{out}) CO_2 concentrations were logged at 5-minute intervals. The removal efficiency (η , %) and cumulative specific adsorption capacity (q , ppm g^{-1}) were calculated using Eqs. (4) and (5):

$$\eta (\%) = [(C_{\text{in}} - C_{\text{out}}) / C_{\text{in}}] \times 100 \quad (4)$$

$$q = [(C_{\text{in}} - C_{\text{out}}) \times Q \times t] / m \quad (5)$$

where Q is the gas flow rate (L min^{-1}), t the elapsed time (min), and m the dry film mass (g). Post-adsorption, samples were immediately subjected to low-temperature TGA to observe the mass-loss profile corresponding to thermal desorption of chemically bound CO_2 .

3. Results and discussion

3.1. Colloidal dynamics and physicochemical evolution

The physicochemical parameters of the synthesized latexes are tabulated in **Table 2**. All formulations achieved ~50% solid content, indicating near-quantitative monomer conversion; however, substitution of ammonium hydroxide with TBA, alongside increasing GMA, profoundly altered the colloidal and rheological dynamics.

Table 2. Physicochemical, colloidal, and mechanical properties of the P0–P7 nano-emulsions.

Parameter	P0	P1	P2	P3	P4	P5	P6	P7
pH	8.5	8.5	8.5	8.5	8.5	8.7	9.0	9.8
Viscosity ($\text{mPa}\cdot\text{s}$)	2900	5000	4980	5800	6500	49800	58000	65000
Wet coagulum (%)	0.3	0.0	0.0	0.3	0.3	0.0	0.3	0.2
Particle size (nm)	125	80	100	100	83	95	123.6	114
ζ -potential (mV)	−42	−20	−27	−28	−38.5	−39	−46	−35

Parameter	P0	P1	P2	P3	P4	P5	P6	P7
Pencil hardness	4H	3H	4H	5H	5H	5H	5H	5H
Cross-cut adhesion	4B	4B	4B	5B	5B	5B	5B	5B
Stability (storage/freeze–thaw)	+/+	+/+	+/+	+/+	+/+	+/+	+/+	+/+

As can be seen from Table 2, the viscosity increased exponentially from 2900 mPa·s (P0) to 65000 mPa·s (P7). The highest increase in the value of this parameter was observed for the transition from 1% (P4) to 2% (P5) TBA of initial AA concentration. The non-Newtonian behavior of the solution and its shear-thickening nature are connected with the generation of an internal ionic network. The acid (AA) neutralization by TBA leads to the formation of an ammonium carboxylate salt at the core/shell interface that is highly hydrated [25,26]. The hydration process resulted in the osmotic swelling of polymer particles due to water migration into the polymer particles through capillary forces. The generation of counter-ions' osmotic pressure leads to the expansion of the electric double layer that increases the effective hydrodynamic volume of the micelle. It is worth noting that the content of the coagulum was negligible (0-0.3%) due to the presence of anionic/nonionic surfactant (SDS/MARLIPAL) in the system. It provided enough steric and electrostatic stabilization of the latex, which was resistant to GMA addition, which decreased micelle numbers and conversion efficiency [34].

ζ-potential dynamics. P0 exhibited a highly negative ζ-potential of −42 mV, typical of SDS-stabilized latexes. At 1% TBA (P1) the value shifted toward zero (−20 mV) because the bulky, hydrophobic tert-butyl cation adsorbs onto anionic sulfate headgroups, screening the surface charge [35]. At higher TBA concentrations (P6, −46 mV), however, the potential became strongly negative again, suggesting that excess ammonium carboxylate groups migrated to the particle–water interface, contributing additional negative charge and re-establishing a robust electrostatic barrier against aggregation [36,37].

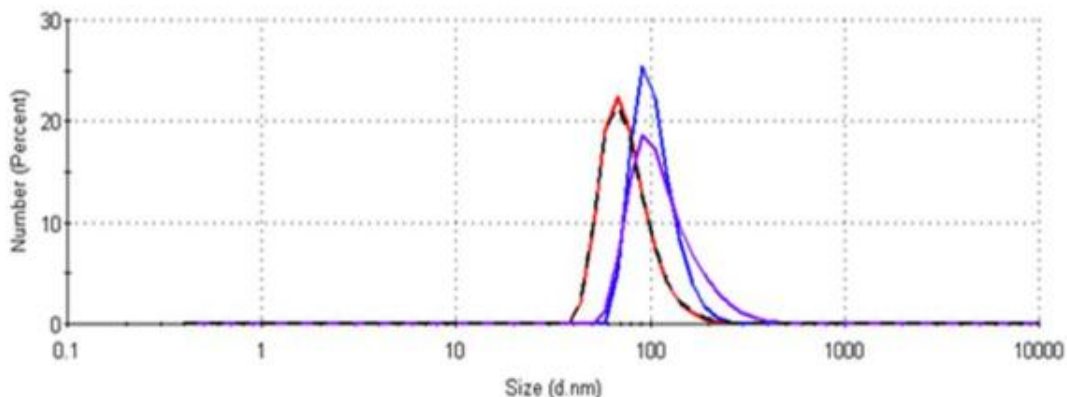


Fig. 1. DLS number-based size distributions of representative nano-emulsions, confirming narrow, monomodal particle populations in the 80–125 nm range consistent with Table 2.

3.2. Molecular spectroscopy (ATR-FTIR) and structural proof

Fig. 2 presents the ATR-FTIR spectra of P0, P1, P4, and P7. Successful incorporation of all monomers is confirmed by asymmetric C–H stretching ($2865\text{--}2929\text{ cm}^{-1}$), styrenic aromatic rings ($1609, 757, 693\text{ cm}^{-1}$), and aliphatic ester bands from BuAc ($\nu\text{C=O}$ at 1727 cm^{-1} ; $\nu\text{C–O–C}$ at 1167 cm^{-1}) [25–27].

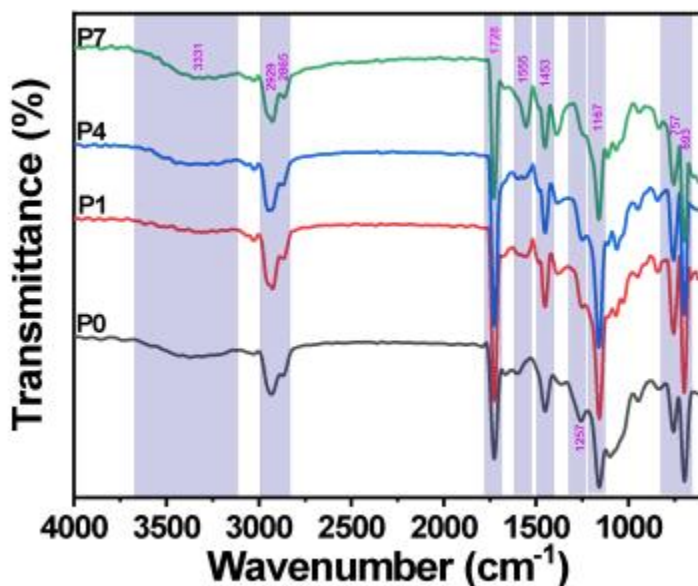


Fig. 2. ATR-FTIR spectra of P0, P1, P4, and P7. Shaded regions highlight the critical spectral windows ($3600\text{--}3100$ and $1600\text{--}1500\text{ cm}^{-1}$), showing the emergence of N–H stretching at 3331 cm^{-1} and the definitive symmetric bending band at 1555 cm^{-1} in all TBA-containing samples, proving formation of the ammonium carboxylate salt.

The definitive evidence of the TBA neutralization mechanism lies at 3331 and 1555 cm^{-1} : the broad band at 3331 cm^{-1} corresponds to N–H stretching of the protonated ammonium (R_3NH^+), while the distinct peak at 1555 cm^{-1} is unambiguously assigned to the symmetric bending vibration (δNH^+) of the ammonium group [27]. The absence of a sharp free-carboxylic acid band and the presence of the 1555 cm^{-1} peak across all TBA samples prove that AA was completely converted to an ammonium carboxylate salt, successfully preventing the GMA–AA epoxide ring-opening side reaction.

3.3. Crystallinity and nanoscale morphological mapping (WAXRD and AFM)

Fig. 3 displays the WAXRD patterns. The baseline polymer (P1) exhibits a broad, diffuse halo characteristic of an amorphous atactic acrylic copolymer. Increasing GMA from 2% (P1) to 7% (P4) caused a marginal increase in peak intensity; the rigid oxirane ring introduces steric hindrance that can slightly align chain segments, increasing short-range order [38]. Conversely, high TBA concentration (7%, P7) drastically broadened the halo. The bulky tert-butyl groups and associated ionic clusters act as profound disruptors of chain packing, forcing the matrix into a highly disordered, entirely amorphous state. This amorphization is highly beneficial for CO_2 capture, as it increases fractional free volume and enhances gas diffusivity [19,39].

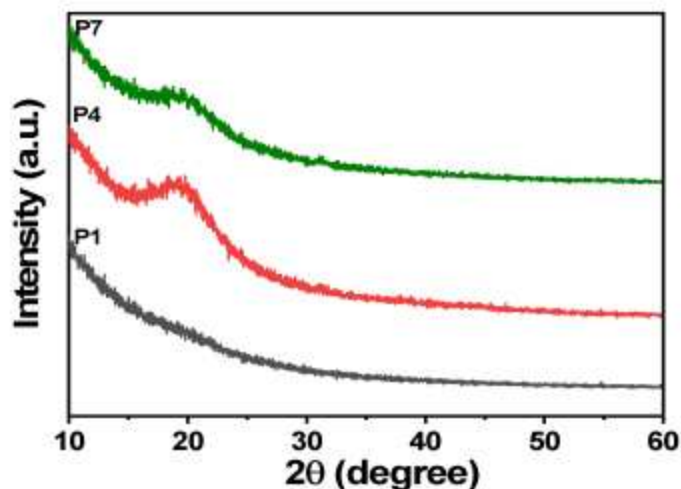
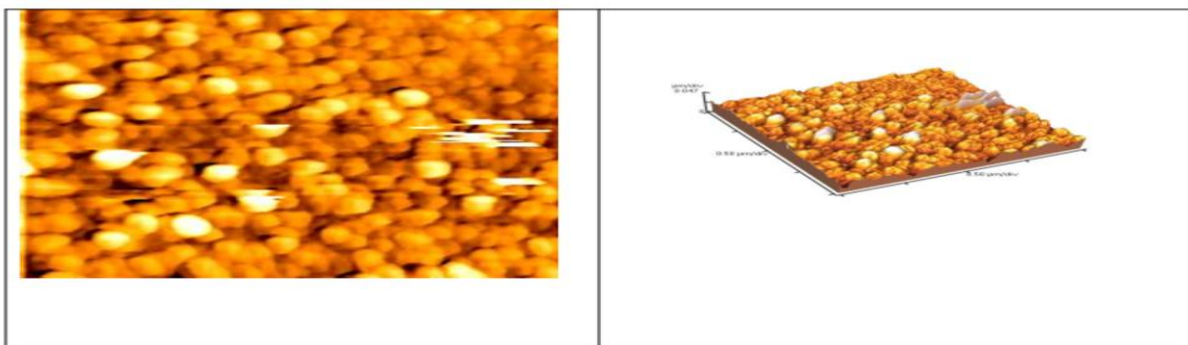


Fig. 3. WAXRD patterns of P1, P4, and P7, demonstrating modulation of polymer chain packing: subtle short-range ordering in P4 (higher GMA) versus complete suppression of crystallinity in P7 (highest TBA) due to ionic-cluster-induced chain disruption—a vital morphological feature for gas permeation.

AFM analysis (Fig. 4) provides nanoscale insight into film formation. The topographic images of the dried P7 film reveal a densely packed particulate morphology consistent with latex film formation via particle coalescence, with interparticle boundaries partially flattened. Phase imaging—which maps local viscoelastic contrast [40,41]—discriminates between the harder polystyrene-rich domains (bright) and the softer, butyl-acrylate-rich compliant matrix (dark). Crucially, intermediate-phase "islands" are discernible in the P7 film and are attributed to the microphase separation of the hygroscopic TBA–AA ammonium carboxylate ionic clusters. Owing to their polar nature, these clusters aggregate into nanoscale domains that preferentially absorb ambient moisture and act as reaction loci for the bicarbonate-forming hydration of CO_2 , effectively generating a hierarchical, nanoscale reactive network [40,41].



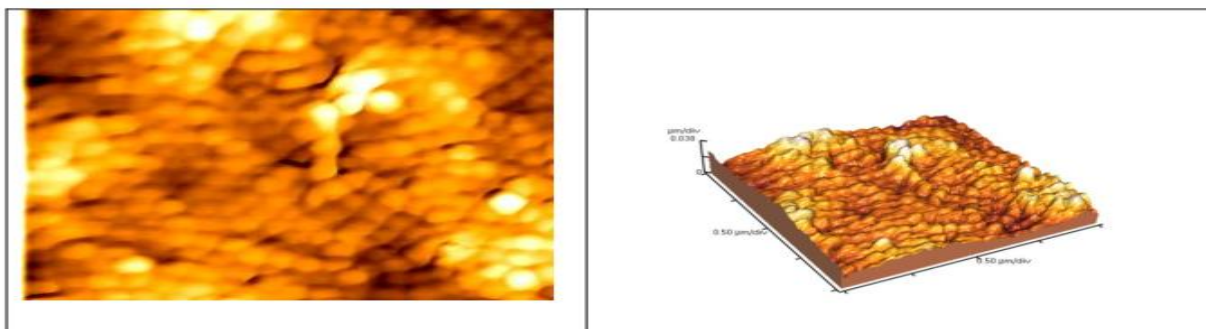


Fig. 4. High-resolution AFM topographic (2D/3D) and phase images elucidating microphase separation in the P7 film. Phase contrast maps local viscoelasticity, revealing rigid polystyrene nodes, a compliant butyl-acrylate matrix, and intermediate-phase "islands" assigned to hygroscopic TBA–AA ionic clusters serving as nano-reservoirs for water and primary pathways for CO₂ diffusion.

3.4. Mechanical strength: hardness, adhesion, and colloidal interplay

As detailed in Table 2, hardness escalated from 3H–4H (P0–P2) to a consistent 5H for formulations with higher GMA/TBA (P3–P7). The epoxide rings of GMA increase polarity and intermolecular forces, while ionic clusters act as rigid nanofillers, enhancing scratch resistance [42]. Adhesion improved from 4B to 5B, governed by particle size and ζ -potential: smaller particles (80–125 nm) penetrate substrate micro-roughness, enhancing mechanical interlocking, while an optimal ζ -potential ensures uniform dispersion and intimate wetting without premature flocculation. Furthermore, the preserved epoxide rings of GMA can covalently bond with hydroxyl groups on substrate surfaces, creating robust chemical adhesion [42,43]. The negligible wet coagulum ensured that no weak points or voids were introduced during drying, which would otherwise compromise hardness and adhesion [44–46].

3.5. Thermal degradation kinetics and glass transition (TGA/DSC)

As shown in Fig. 5(a,b), P1 and P4 degrade in a single step at a maximum-rate temperature of 438 °C, leaving a 1.9% char yield, whereas P7 exhibits a depressed value of 424 °C. The aliphatic C–N bonds of the protonated TBA are thermally weaker than the polymer backbone and act as degradation initiation sites, lowering overall stability [47]. Conversely, DSC thermograms (Fig. 5c) reveal a counterintuitive phenomenon: T_g increases systematically from 107 °C (P4) to 146 °C (P7). This is a classic manifestation of ionic crosslinking: electrostatic attraction between ammonium groups and carboxylates forms transient yet robust physical crosslinks, severely restricting segmental mobility and requiring higher thermal energy to reach the rubbery state [42,48].

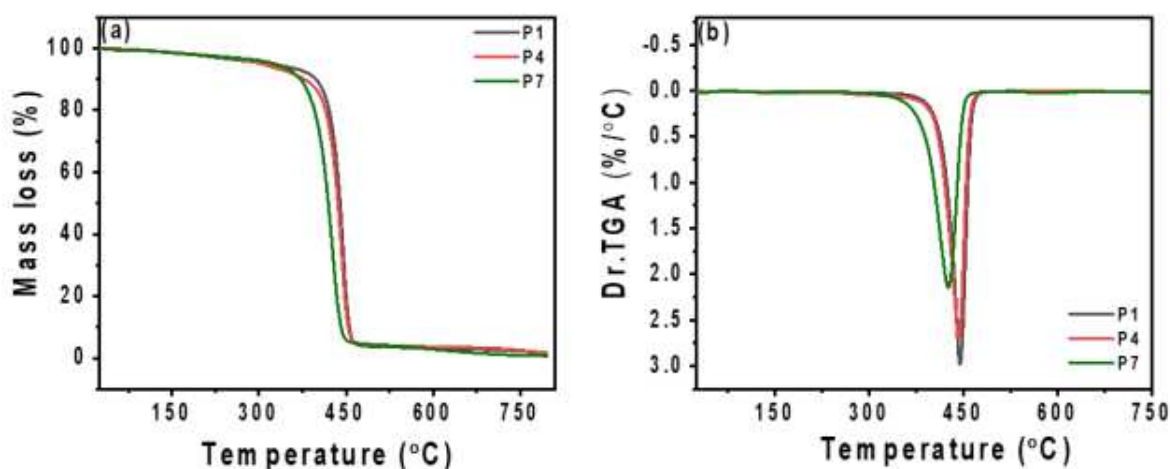


Fig. 5. Thermal analysis of P1, P4, and P7: (a) TGA, (b) DTG, and (c) DSC. TGA/DTG reveal single-step degradation with slight T_{max} depression for P7 (424 vs 438 °C) due to the lower thermal stability of aliphatic TBA moieties acting as weak links. DSC demonstrates the counterintuitive T_g elevation for P7 (146 °C), proving formation of robust ionic crosslinks that restrict chain mobility.

To irrefutably validate chemical CO₂ loading, a specialized low-temperature TGA protocol was employed (Fig. 6). Pre-adsorbed samples were heated to 170 °C: P0 showed only ~2% mass loss (residual moisture), whereas P3 and P7 exhibited distinct, accelerated mass-loss steps in the 80–150 °C range, correlating precisely with thermal cleavage of the bicarbonate complex and providing definitive thermogravimetric proof of chemically bound CO₂ [44–46,49].

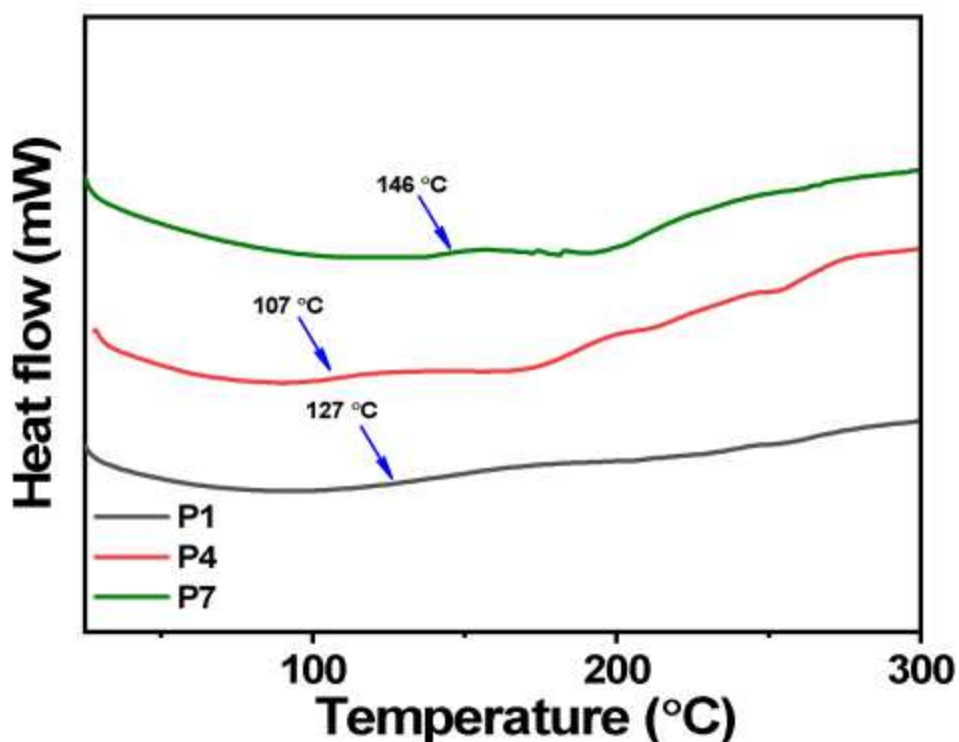


Fig. 6. Low-temperature TGA of CO₂-loaded films, distinguishing evaporation of free water (minor ~2% loss in P0) from the accelerated mass loss in P3 and P7 corresponding to thermal cleavage of the bicarbonate complex—definitive validation of the chemisorption mechanism.

3.6. CO₂ adsorption performance and kinetic analysis

The paramount objective of this study was ambient CO₂ mitigation; the dynamic adsorption data are tabulated in **Table 3** and represented in **Fig. 7**.

Table 3. Dynamic CO₂ adsorption parameters for the control and TBA-functionalized adsorbents at 30 °C.

Sample	TBA (%)	GMA (%)	Time (min)	Removal efficiency (%)	Capacity (ppm CO ₂ g ⁻¹ polymer)
P0	0 (NH ₄ OH)	2	5	3.29	1.69
P3	5	5	5	26.5	15.86
P3	5	5	10	27.0	16.14
P7	7	7	5	48.2	53.66
P7 ^a	7	7	5	38.0 ^a	41.95 ^a
P7	7	7	10	49.2	54.18

^a Independent replicate run; the spread reflects batch-to-batch variability in dried-film thickness.

The data reveal a stark contrast: the ammonium hydroxide control (P0) exhibited negligible removal ($\leq 3.29\%$) because NH_3 evaporates during film drying, leaving inactive carboxylate salts with no chemisorptive affinity for CO_2 [50]. Conversely, TBA-functionalized polymers displayed exceptional activity: P3 (5% TBA) achieved 26.5–27% removal, while P7 (7% TBA) achieved a peak removal efficiency of 49.2% and a capacity of 54.18 ppm g^{-1} within 10 min at 30°C . The adsorption profiles exhibit a characteristic "steep-then-plateau" trend: the initial rapid uptake is driven by abundant unoccupied tertiary amine sites at the surface; as these saturate, CO_2 must diffuse into the bulk to reach subsurface ionic clusters, resulting in a diffusion-limited asymptotic approach to equilibrium [51,52]. P7 drastically outperforms P3 because 7% TBA provides an optimal density of basic sites; moreover, as proven by AFM, the higher TBA concentration generates a more extensive network of hydrophilic ionic clusters that absorb ambient moisture an absolute requisite for the tertiary-amine bicarbonate mechanism (Eqs. (1)–(3)) explaining the exponential performance leap between 5% and 7% loading [28,30,31]. This aligns with literature on amine–support matching strategies, where the structural availability of the amine dictates CO_2 accessibility to active sites [53], and highlights the favorable interaction dynamics of tertiary amines for ambient, moisture-assisted capture compared with linear or branched polyethyleneimines [51,54].

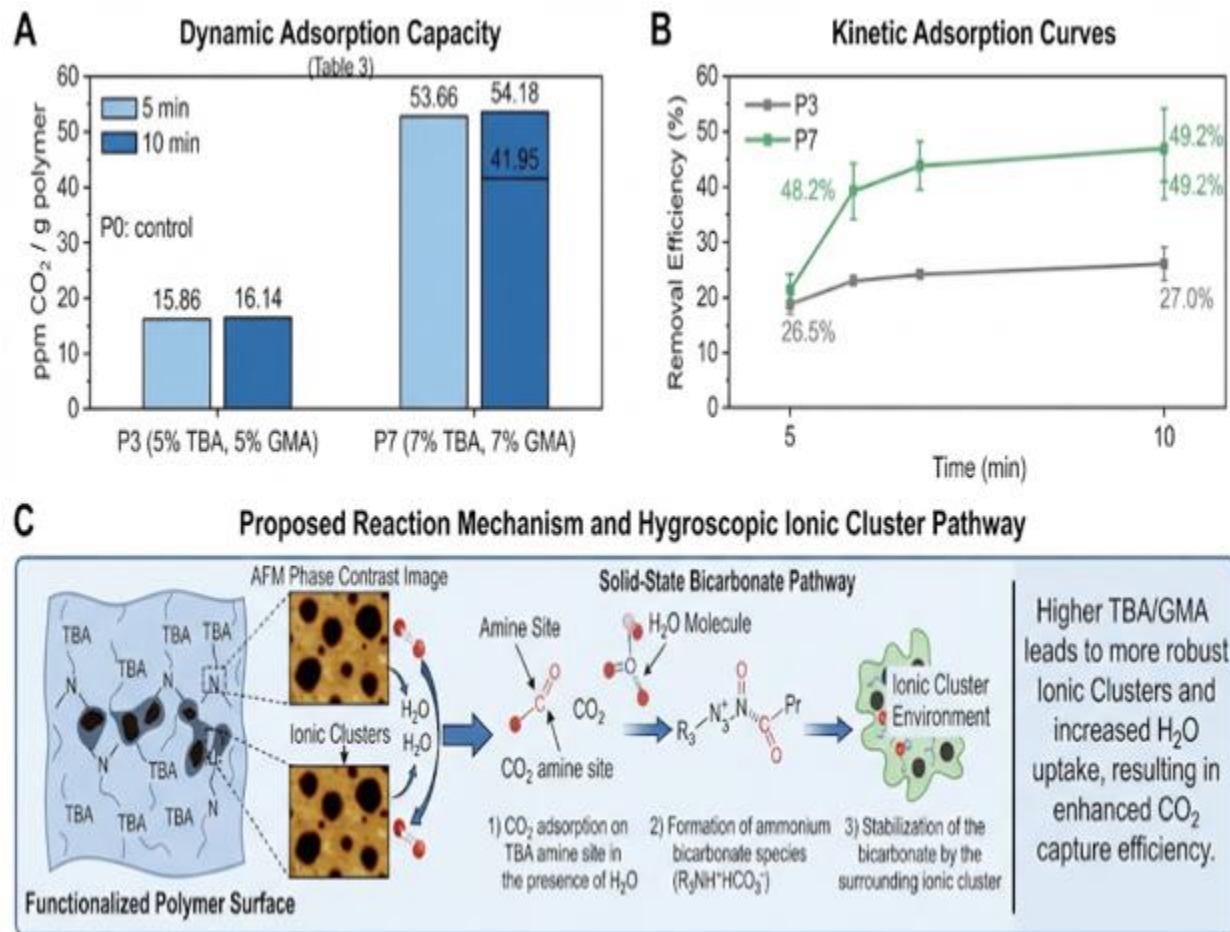


Fig. 7. CO₂ capture performance of the synthesized adsorbents: (a) removal efficiency bar chart (control vs 7% TBA), (b) kinetic uptake curves showing the steep-then-plateau profile indicative of surface chemisorption transitioning to bulk diffusion limitation, and (c) schematic of the moisture-assisted bicarbonate pathway enabled by the hygroscopic ionic clusters identified by AFM.

4. Limitations of the current study

While the results unequivocally validate the TBA-functionalized latex concept for DAC, a critical appraisal reveals limitations prior to industrial scaling:

1. **Long-term cyclic stability.** Although low-temperature TGA proved CO₂ desorption at mild temperature (~100–150 °C), multi-cycle (100+ adsorption/desorption) testing is required; repeated swelling/deswelling of the ionic clusters may induce mechanical fatigue, and oxidative degradation of tertiary amine sites may occur over extended periods [55].
2. **Competitive sorption in humid environments.** Real indoor air contains variable humidity and VOCs; the hydrophilicity of the TBA–AA clusters, while beneficial for the bicarbonate mechanism, may cause competitive adsorption. At extreme relative humidities (>80%), a water monolayer might physically block CO₂ access to tertiary amine sites, reducing selectivity [56].

3. **Diffusion depth in macroscopic films.** In thick practical paint films (100–200 μm), CO_2 diffusion may be restricted to the first 10–20 μm ; the film core could remain unreactive, reducing active-material utilization and practical volumetric capacity [57].
4. **Rheological constraints in scale-up.** The exponential viscosity surge (up to 65,000 $\text{mPa}\cdot\text{s}$ for P7) challenges continuous industrial reactors: high viscosity impedes heat transfer (risking thermal runaway in the exothermic polymerization) and mass transfer, potentially broadening particle size distributions or inducing localized gelation [58].

5. Future work and industrial perspectives

To translate the aforementioned findings into a commercial IAQ technology as well as advanced CCUS applications, the following trajectories can be proposed:

(1) Smart hybrid hierarchical architectures, with hydrophobic mesoporous silica nanoparticles [26] or hydrophobic MOFs [19], were integrated to create nano-channels that are able to repel bulk liquid water but allow gaseous CO_2 to permeate into the polymeric film.

(2) Dual function photocatalytic coatings, in which TiO_2 nanoparticles were doped into the TBA-modified latex [42] so that UV/visible indoor illumination could trigger the photocatalyst to reduce surface-bonded bicarbonate into benign carbonates, realizing a self-cleaning and self-regenerating smart paint [59];

(3) Controlled epoxide post-curing, which utilized the preserved GMA epoxide rings for thermal or UV post-curing to form a dense 3D covalent network that could lock the ionic clusters and enhance its wash-fastness and abrasion-resistance properties [60];

(4) Sustainable bio-monomer substitution, in which petroleum-based St and BuAc were replaced by bio-based counterparts (e.g., methacrylated lignin derivatives or plant-based acrylates) to yield a fully sustainable and carbon-negative material matrix [61,62].

6. Conclusions

This study successfully engineered a novel class of TBA-functionalized acrylic nano-emulsions, establishing a groundbreaking platform for ambient direct air capture and IAQ remediation. The principal findings are:

- **Mechanistic control:** TBA neutralized acrylic acid into an ammonium carboxylate salt (ATR-FTIR, 1555 cm^{-1}), preventing deleterious epoxide ring-opening with GMA and preserving post-cure adhesion capability.
- **Structural modulation:** TBA induced massive ionic swelling, exponentially increasing viscosity (to 65,000 $\text{mPa}\cdot\text{s}$) and elevating T_g to $146\text{ }^\circ\text{C}$ via ionic crosslinking, while rendering the matrix entirely amorphous (WAXRD) to enhance gas diffusivity.
- **Nanoscale architecture:** AFM phase imaging revealed microphase-separated TBA-AA ionic clusters—localized hydrophilic domains crucial for the bicarbonate pathway.

- **Unprecedented ambient capture:** Replacing traditional ammonium hydroxide with 7% TBA increased CO₂ removal efficiency from 3.29% to 49.2% at 30 °C (capacity 54.18 ppm g⁻¹), with low-temperature TGA confirming chemisorption via bicarbonate desorption.
- **Mechanical excellence:** Preserved GMA epoxides and ionic nanoclusters synergistically enhanced film hardness (5H) and adhesion (5B), meeting industrial coating requirements.

This work transcends traditional polymer synthesis, offering a commercially viable, energy efficient "anti-carbonation paint" that transforms passive building materials into active CO₂ sequestration agents a vital stride toward sustainable built environments.

Authorship contribution

A.E. Elsayed: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Visualization. **H.E. Nasr:** Validation, Resources, Data curation. **S.H. Samaha:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

The authors declared no Funding for this research

Data availability

All data generated or analyzed during this study are included in this published article.

Acknowledgements

The authors extend their profound gratitude to the National Research Centre (NRC) and the National Institute of Standards (NIS) for providing the requisite analytical infrastructure. Special appreciation is directed toward Prof. Dr. Yaseer Hassan, Department of Air Pollution, Environmental and Climate Changes Institute, NRC, for his indispensable technical support and instrumental access for CO₂ quantification and data visualization.

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