



## Hydrocarbon ladder polymers with ultrahigh permselectivity for membrane gas separations

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## Title: Hydrocarbon Ladder Polymers with Ultrahigh Permselectivity for Membrane Gas Separations

**Authors:** Holden W. H. Lai<sup>1a</sup>, Francesco M. Benedetti<sup>2a</sup>, Jun Myun Ahn<sup>1b</sup>, Ashley M. Robinson<sup>1</sup>, Yingge Wang<sup>3</sup>, Ingo Pinnau<sup>3</sup>, Zachary P. Smith<sup>2\*</sup>, Yan Xia<sup>1\*</sup>

### Affiliations:

<sup>1</sup>Department of Chemistry, Stanford University, Stanford, California 94305, United States.

<sup>2</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States.

<sup>3</sup>Advanced Membranes and Porous Materials Center, Chemical Engineering Program, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, KSA

<sup>a</sup>Present address: Osmoses Inc., 501 Massachusetts Avenue, Cambridge, MA 02139, United States

<sup>b</sup>Present address: Vertex Pharmaceuticals Incorporated, 50 Northern Avenue Boston, MA 02210 United States

\*Correspondence to: [zpsmith@mit.edu](mailto:zpsmith@mit.edu); [yanx@stanford.edu](mailto:yanx@stanford.edu).

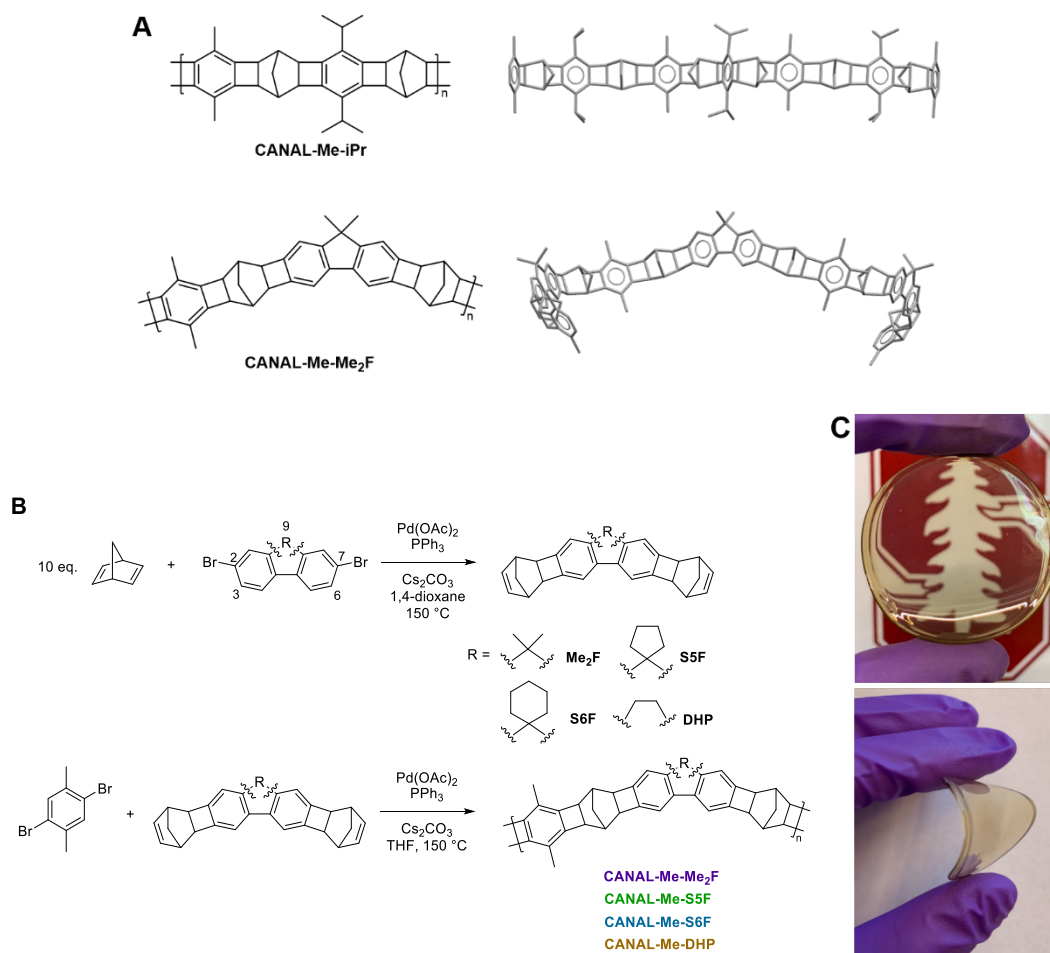
**Abstract:** Membranes have the potential to substantially reduce energy consumption of industrial chemical separations, but their implementation has been limited due to a performance upper bound, the trade-off between permeability and selectivity. While recent developments of highly permeable polymer membranes have advanced the upper bounds for various gas pairs, these polymers typically exhibit limited selectivity. We report a class of hydrocarbon ladder polymers that can achieve both high selectivity and high permeability in membrane separations for many industrially relevant gas mixtures, and their corresponding films exhibit excellent mechanical and thermal properties. Tuning the ladder polymer backbone configuration was found to have a profound effect on the separation performance and aging behavior.

**One Sentence Summary:** Tuning ladder polymer backbone configuration results in highly selective and permeable membrane gas separations.

**Main Text:** Industrial chemical separations account for 15% of the world's energy consumption (1). Compared to traditional separation methods such as distillation and absorption, membrane processes can be up to ten times more energy-efficient (1). However, a major limitation for membrane-based gas separations has been the well-known trade-off between permeability and selectivity of membrane materials, resulting in performance upper bounds (2). Commercial membranes usually have moderate selectivity but low permeability. Solution-processable polymers of intrinsic microporosity (PIMs) have emerged as attractive membrane materials. The rigid and contorted PIM backbones lead to frustrated chain packing in the solid state, resulting in abundant fractional free volume, and thus, ultrahigh permeability relative to traditional polymers

(3-5). PIMs define the upper bounds for nearly all gas separations (6, 7). Despite these promising recent advances, it remains a challenge to design PIMs with high selectivity, which is essential for the implementation of membranes in industrially relevant applications. For example, CO<sub>2</sub>/CH<sub>4</sub> selectivity >40 and H<sub>2</sub>/CH<sub>4</sub> selectivity >50 are needed for natural gas processing and hydrogen recovery, respectively, to meet process specifications (8). Moreover, experimental mixed-gas CO<sub>2</sub>/CH<sub>4</sub> separation performance for PIM membranes is far below the pure-gas upper bound limit that is based on calculated ideal selectivities (8). In order to design polymer membranes for natural gas and biogas upgrading, as well as other gas and vapor separations, it is essential to evaluate membrane performance through mixed-gas permeation experiments at pressures relevant to real processes.

We developed a family of microporous ladder polymers with rigid backbones of fused norbornyl benzocyclobutene repeat units via catalytic arene-norbornene annulation (CANAL) polymerization from readily available chemicals (9-11). These hydrocarbon polymers have glass transition temperatures that exceed their thermal decomposition temperature (>400 °C). The original CANAL polymers that were made from the polymerization of norbornadiene and *p*-dibromobenzene derivatives have a ribbon-like ladder geometry with approximately two-dimensional (2D) contortions (Figure 1A, top). Films of these microporous polymers exhibited high permeability, but their selectivity was low for gas separation applications (11). By tuning the backbone configuration, we discovered a series of three-dimensionally (3D) contorted CANAL ladder polymers (Figure 1A, bottom) that form mechanically robust films with a combination of ultrahigh selectivity and permeability. These 3D contorted CANAL polymers were synthesized using 2,7-dibromofluorenes or 2,7-dibromo-9,10-dihydrophenanthrene and norbornadiene as building blocks, providing a unique polymer configuration that led to the beneficial property sets.



**Fig. 1.** Molecular structures and films of CANAL ladder polymers. (A) Simulated (molecular mechanics) structures of a ribbon-like 2D ladder polymer, CANAL-Me-iPr (top), and a 3D ladder polymer, CANAL-Me-Me<sub>2</sub>F (bottom). (B) Synthesis of CANAL-fluorene and CANAL-dihydrophenanthrene monomers (top) and polymers (bottom). (C) Photos of a 50- $\mu\text{m}$  CANAL-Me-Me<sub>2</sub>F film.

One distinct advantage of CANAL chemistry is that many aromatic bromides can be used as monomer building blocks. We envisioned that introducing fluorene or dihydrophenanthrene units would confer additional backbone contortions to CANAL ladder polymers, thus further frustrating chain packing and potentially modulating the polymer microporosity. We synthesized such CANAL polymers via a two-step procedure. The 2,7-dibromofluorene derivatives were first reacted with excess norbornadiene (NBD) (5 equiv. relative to aryl bromide) in the presence of a palladium catalyst to yield ladder dinorbornenes **Me<sub>2</sub>F**, **S5F**, **S6F**, and **DHP**, which then underwent efficient and clean CANAL polymerization with *p*-dibromo-*p*-xylene to form ladder polymers CANAL-Me-Me<sub>2</sub>F, CANAL-Me-S5F, CANAL-Me-S6F, and CANAL-Me-DHP (Figure 1B), in high molecular weights with  $M_w = 67\text{--}170$  kDa as determined by gel permeation chromatography (GPC) light scattering analysis (Figure S1). These polymers exhibited high surface areas ( $870\text{--}1190$   $\text{m}^2\text{g}^{-1}$ ) and high thermal stability ( $T_{d,5\%} > 450$  °C) (Table S1).

Mechanically robust films (50–60  $\mu\text{m}$  thick) of all the polymers can be easily prepared by solution casting from chloroform (Movie S1). After the films were pretreated to remove residual

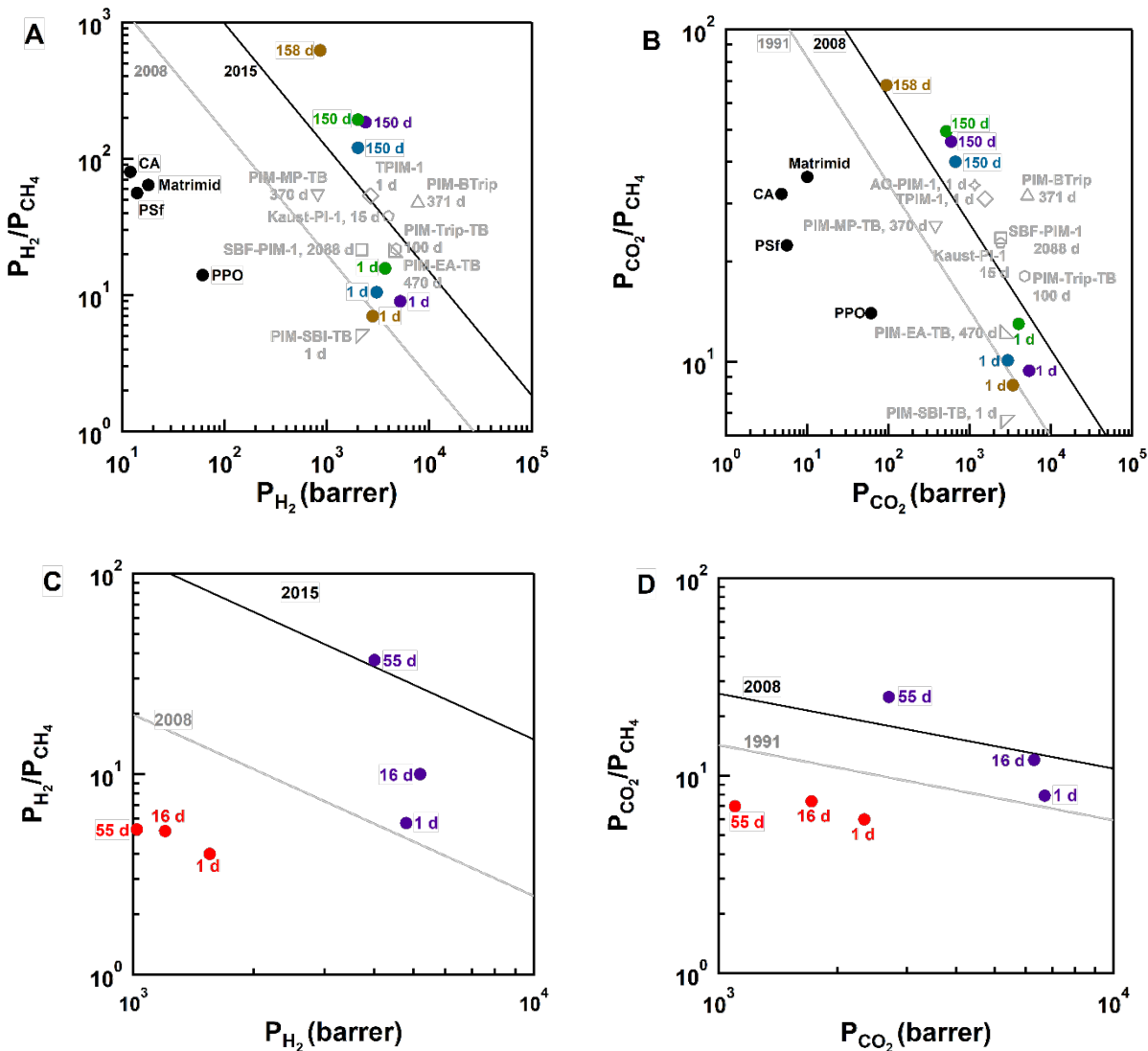
casting solvent and erase processing history using conditions common for PIMs (heating in vacuo at 120 °C for 24 h, followed by soaking in methanol, and then air drying), we performed pure-gas permeation experiments using gases in this order: H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> (T = 35 °C, p = 1 bar). Fresh films of CANAL-Me-Me<sub>2</sub>F exhibited high permeabilities but only moderate selectivities (Table S2). Surprisingly, upon aging, separation performance of CANAL-Me-Me<sub>2</sub>F improved significantly. Physical aging is commonly observed for PIMs and is a process that reduces excess free volume as the polymer chains densify into more compact packing states (12). Aging of PIMs typically leads to greatly decreased permeability and moderately increased selectivity, often following the upper bound trade-off relationships or slightly improving their performance relative to the upper bound (13). In contrast, aging of 3D CANAL polymers improved performance for several industrially relevant gas pairs by boosting selectivity, including H<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/CH<sub>4</sub> (Figure 2A–B), H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO<sub>2</sub>, and O<sub>2</sub>/N<sub>2</sub> (Figure S4–5, Table S2).

For CO<sub>2</sub>/CH<sub>4</sub> separation, CANAL-Me-Me<sub>2</sub>F offers twice the selectivity and 100 times the permeability compared to cellulose acetate, a widely used commercial membrane material (14). Compared to another commercial membrane material, polysulfone (14), CANAL-Me-Me<sub>2</sub>F is two orders of magnitude more permeable and three times more selective for H<sub>2</sub>/CH<sub>4</sub> separation. With H<sub>2</sub> permeability >2000 barrer and H<sub>2</sub>/CH<sub>4</sub> selectivity of 185, the H<sub>2</sub>/CH<sub>4</sub> performance of aged CANAL-Me-Me<sub>2</sub>F exceeds that of other PIMs (Figure 2A), which typically have H<sub>2</sub>/CH<sub>4</sub> selectivity <50. Aged CANAL-Me-Me<sub>2</sub>F also exhibited exceptional CO<sub>2</sub>/CH<sub>4</sub> selectivity of ~50 and high CO<sub>2</sub> permeability of ~600 barrer (Figure 2B).

Other CANAL-fluorene polymers with cyclic substituents, CANAL-Me-S5F and CANAL-Me-S6F, and CANAL-Me-DHP all showed ultrahigh performance upon aging, similar to that of CANAL-Me-Me<sub>2</sub>F (Figure 2 and S4). This finding suggests that the unusual aging behavior is general among 3D CANAL polymers. Compared to CANAL-fluorene polymers, CANAL-Me-DHP became even more selective, reaching CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/CH<sub>4</sub> selectivities of 68 and 621, respectively, while maintaining high CO<sub>2</sub> and H<sub>2</sub> permeabilities of 94 and 860 barrer, respectively, after 158 days of aging. The H<sub>2</sub>/CH<sub>4</sub> selectivity of CANAL-Me-DHP also exceeds that of non-solution-processable thermally rearranged polymers (15) and graphene (16). CANAL-Me-DHP also has much higher selectivity for H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO<sub>2</sub>, and O<sub>2</sub>/N<sub>2</sub> compared to other PIMs (Figure S4).

We did not observe the same aging trend and enhanced performance for our previously reported CANAL polymers with similar hydrocarbon structures but a 2D geometry, such as CANAL-Me-iPr, which showed little or no gain in selectivity and decreased permeability upon aging (Figure 2C–D). This further suggests the effect of ladder chain configurations is critical for the observed behavior and performance. The substantially different aging profiles between 2D and 3D CANAL polymers prompted us to investigate the origin of improved selectivities for CANAL-Me-Me<sub>2</sub>F. We determined diffusion (*D*) and solubility (*S*) coefficients based on the solution–diffusion model ( $P = DS$ ) (17), which revealed similar gas transport behavior for the fresh CANAL-Me-Me<sub>2</sub>F, CANAL-Me-iPr samples (Table S3), and other PIMs (18). As CANAL-Me-Me<sub>2</sub>F and CANAL-Me-iPr aged, solubility coefficients remained relatively constant. However, in contrast to CANAL-Me-iPr, diffusion coefficients of larger gases in CANAL-Me-Me<sub>2</sub>F, such as N<sub>2</sub> and CH<sub>4</sub>, decreased significantly more than those of smaller gases, such as CO<sub>2</sub> and O<sub>2</sub> (Figure S7A). For example, after 55 days of aging, the diffusion coefficient of CH<sub>4</sub> decreased ~90%, while that of O<sub>2</sub> decreased ~60% (Table S3). The constant solubility coefficients during aging suggest that the total free volume of polymers remained relatively stable. However, the large

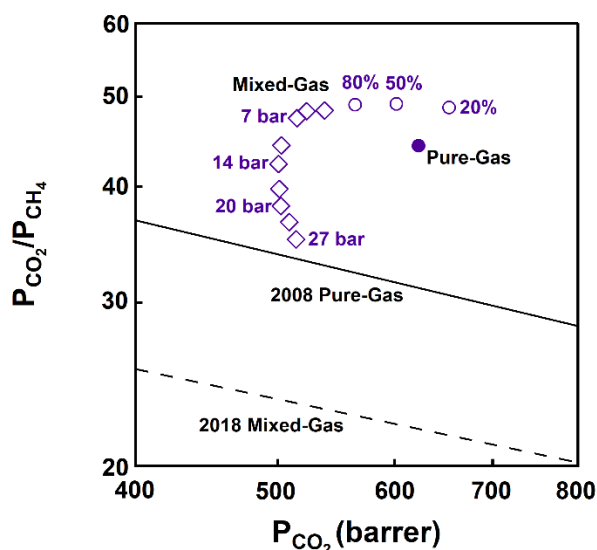
decrease in diffusion coefficients for larger gases suggests that the connections between free volume elements, or “bottlenecks”, are narrowing as aging occurs to restrict transport of larger gases (i.e., gases larger than N<sub>2</sub> with a kinetic diameter of 3.64 Å) without significantly affecting the transport of smaller gases (smaller than O<sub>2</sub> with a kinetic diameter of 3.46 Å), thus leading to enhanced size selectivity over time. These results are further supported through Brandt model analysis by comparing activation energies of diffusion as a function of gas diameters squared, which demonstrate that aged CANAL-Me-Me<sub>2</sub>F has a narrower distribution of interchain spacing than other aged high-performance PIMs and the pre-aged CANAL-Me-Me<sub>2</sub>F sample (Figure S7B and Table S8). In contrast, for CANAL-Me-iPr, permeabilities for all gases decreased by roughly the same relative extent, leading to small changes in selectivity (Figure 2C–D). Thus, our results suggest that 3D backbone contortions of CANAL polymers are essential for the exceptionally high selectivity.



**Fig. 2.** Pure-gas permeation properties of 50–60  $\mu\text{m}$  thick CANAL-Me-Me<sub>2</sub>F (●), CANAL-Me-S5F (●), CANAL-Me-S6F (●), and CANAL-Me-DHP (●) relative to the (A) H<sub>2</sub>/CH<sub>4</sub> and (B) CO<sub>2</sub>/CH<sub>4</sub> upper bounds. CANAL films in figures A and B were heated at 120 °C under vacuum for 24 h, soaked in liquid methanol for 24 h, and then air dried for 24 h. State-of-the-art PIMs (open symbols, duration of aging noted in days, see figure S12 for structures) (3-7, 19-24) and commercial membrane materials (filled black symbols, cellulose acetate (CA), polysulfone (PSf), polyphenylene oxide (PPO)) (14) are plotted for comparison. Pure-gas permeation properties of 110–116  $\mu\text{m}$  thick CANAL-Me-Me<sub>2</sub>F (●) and CANAL-Me-iPr (●) relative to the (C) H<sub>2</sub>/CH<sub>4</sub> and (D) CO<sub>2</sub>/CH<sub>4</sub> upper bounds. CANAL films in figures C and D were heated at 120 °C under vacuum for 24 h. All CANAL films were tested at 35 °C and 1 bar.

We evaluated the CO<sub>2</sub>/CH<sub>4</sub> mixed-gas permeation of CANAL-Me-Me<sub>2</sub>F with 20–50–80% CO<sub>2</sub> at 2 bar total pressure (Figure 3, open circles). For all three compositions, the selectivity remained at 49, surpassing that of the pure-gas selectivity likely due to the role of competitive sorption (25). We then evaluated the mixed-gas permeation properties of CANAL-Me-Me<sub>2</sub>F in 50/50 CO<sub>2</sub>/CH<sub>4</sub> mixtures with increasing pressure. The CO<sub>2</sub>/CH<sub>4</sub> mixed-gas selectivity remains

>35 even at 14 bar CO<sub>2</sub> partial pressure, placing the mixed-gas performance of CANAL-Me-Me<sub>2</sub>F far above the 2018 mixed-gas upper bound (8). Similarly, the CO<sub>2</sub>/CH<sub>4</sub> mixed-gas performance of CANAL-Me-DHP also exceeds the 2018 mixed-gas upper bound (Figure S9–10).



**Fig. 3.** Mixed-gas permeation properties of CANAL-Me-Me<sub>2</sub>F at 35 °C (50 μm thick, aged 190 days). Pure-gas ( $p = 1$  bar, filled circle), variable-composition CO<sub>2</sub>/CH<sub>4</sub> mixed-gas (total  $p = 2$  bar, 20–50–80% CO<sub>2</sub>, open circles), and variable-pressure 50/50 CO<sub>2</sub>/CH<sub>4</sub> mixed-gas permeation results (total  $p = 3$ –27 bar, open diamonds) relative to the 2008 pure-gas (2) and 2018 mixed-gas (8) upper bounds.

Based on the observed contrasting aging behavior and separation performance, we speculate that different hydrocarbon ladder configurations can profoundly affect the chain packing and the distribution and connectivity of free volume elements. While gas adsorption isotherm and X-ray scattering experiments are commonly used to characterize the porosity of microporous materials, these techniques do not capture the distribution and connectivity of the smallest free volume elements, which are believed to account for the diffusion bottleneck. It remains a challenge to experimentally and computationally probe the off-equilibrium packing of rigid contorted polymers. Nevertheless, our observations suggest new opportunities to selectively control transport bottlenecks via tuning the molecular design of membrane polymers for many energy-intensive chemical separations.

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## Supplementary Materials:

Materials and Methods

Figures S1-S24

Tables S1-S11

Movie S1

References (26-36)