Underlying Reaction Mechanisms Support Narrowing Exemptions of ODS and HFC Feedstocks Under the Montreal Protocol

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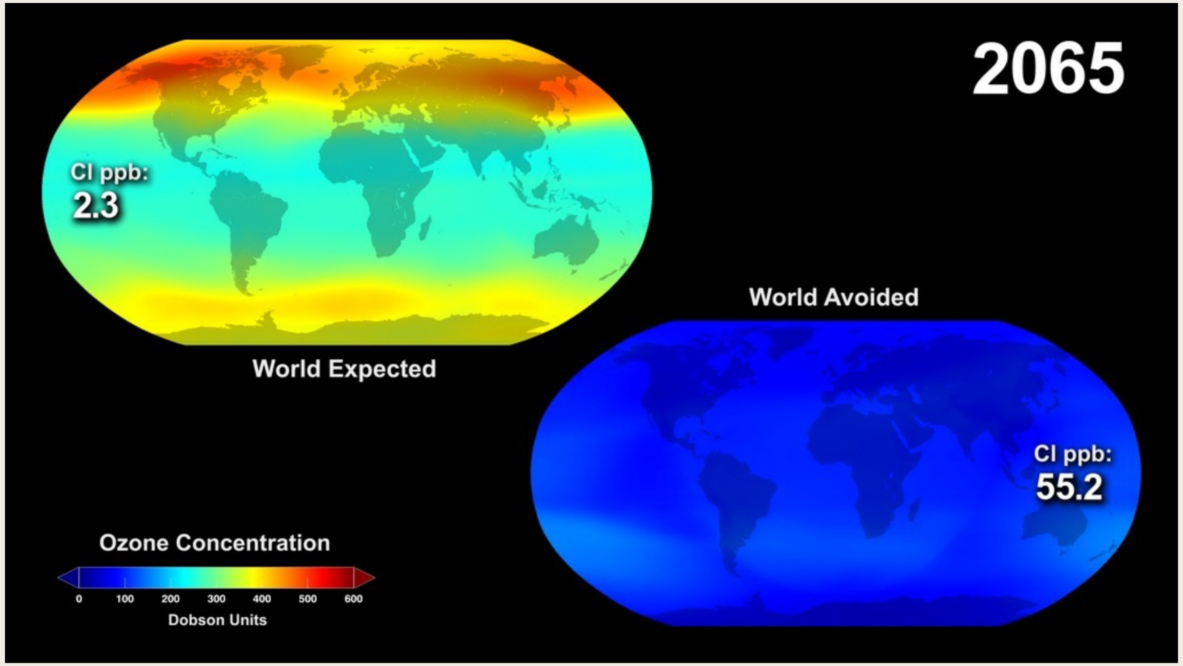
Introduction

- Montreal Protocol
  - *Protect Earth against the harmful effects of ultraviolet radiation.*
  - *Eliminate production of about* ***98%*** *of the ozone-depleting substances (ODSs).*
  - *Put the stratospheric ozone layer on the path to recovery by about* ***2065****.*
  - *Essential exemption:*
    - Feedstocks had been assumed to present an insignificant threat to the environment; experience has shown that this is incorrect.
    - Montreal Protocol may be further amended to control feedstock use and resultant plastics production.



Box 1: Criteria for essentiality and conditions for authorizing essential use (paragraph 1 (a) and (b), Decision IV/25, 4th Meeting of the Parties (1992))

Use of a controlled substance should qualify as essential only if:

- It is necessary for health, safety or is critical for the functioning of society (encompassing cultural and intellectual aspects); and
- There are no available technically and economically feasible alternatives or substitutes that are acceptable from the standpoint of environment and health.

Production and consumption, if any, of controlled substances for essential uses should be permitted only if:

- All economically feasible steps have been taken to minimize the essential use and any associated emission of the controlled substance; and
- The controlled substance is not available in sufficient quantity and quality from existing stocks of banked or recycled controlled substances, also bearing in mind the developing countries' need for controlled substances.

Source: https://svs.gsfc.nasa.gov/4272
https://ozone.unep.org/sites/default/files/2020-06/Briefing_note_on_exemptions.pdf

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Narrowing feedstock exemptions under the Montreal Protocol has multiple environmental benefits

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The Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) can be further strengthened to control ozone-depleting substances and hydrofluorocarbons used as feedstocks to provide additional protection of the stratospheric ozone layer and the climate system while also mitigating plastics pollution. The feedstock exemptions were premised on the assumption that feedstocks presented an insignificant threat to the environment; experience has shown that this is incorrect. Through its adjustment procedures, the Montreal Protocol can narrow the scope of feedstock exemptions to reduce inadvertent and unauthorized emissions while continuing to exempt production of feedstocks for time-limited, essential uses. This upstream approach can be an effective and efficient complement to other efforts to reduce plastic pollution. Existing mechanisms in the Montreal Protocol such as the Assessment Panels and national implementation strategies can guide the choice of environmentally superior substitutes for feedstock-derived plastics. This paper provides a framework for policy makers, industries, and civil society to consider how stronger actions under the Montreal Protocol can complement other chemical and environmental treaties.

ozone-depleting substances | ODS and HFC feedstocks | plastics pollution | ocean pollution | Montreal Protocol

The Montreal Protocol on Substances that Deplete the Ozone Layer (Montreal Protocol) (1) protects Earth against the harmful effects of ultraviolet (UV) radiation, which causes skin cancer and cataracts, supresses the human immune system, damages agricultural crops and ecosystems, and degrades materials such as plastics and paint. It also protects the climate system, because most ozone-depleting substances (ODSs) are potent greenhouse gases (GHGs), and because UV radiation can diminish the terrestrial capacity of plants as carbon sinks (2).

The Montreal Protocol and the underlying Vienna Convention for the Protection of the Ozone Layer are widely regarded as the most effective environmental treaties yet created. Over its 34 y of operation, the Montreal Protocol has eliminated production of about 98% of the ODSs and put the stratospheric ozone layer on the path to recovery by about 2,065 (3–5). At the same time, phasing out ODSs has avoided GHG emissions that otherwise could have equaled or exceeded the emissions of carbon dioxide (CO_2) (6). The Protocol has provided additional climate mitigation by preventing UV radiation from damaging terrestrial carbon sinks (2).

Using their existing authority, the parties to the Montreal Protocol have the opportunity to narrow the exemption for feedstocks, which initially were assumed to pose an insignificant threat to the environment (1, 7, 8). Narrowing the feedstock exemption would provide additional protection of the

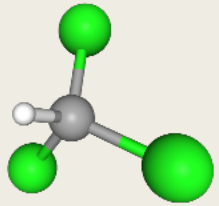
Source: Andersen et al. “Narrowing feedstock exemptions under the Montreal Protocol has multiple environmental benefits.” *Proceedings of the National Academy of Sciences of the United States* 118.49 (2021).

General Synthesis Pathway of PTFE

Chloroform → HCFC-22 → Tetrafluoroethylene (TFE) → Polytetrafluoroethylene (PTFE)

$$CHCl_3 + HF \xrightarrow[80°C]{SbF_3} CHClF_2 + \text{byproducts}$$

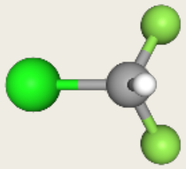
Chloroform HCFC-22



Chloroform

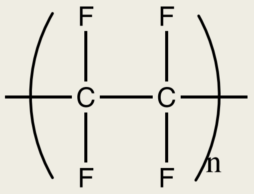
$$CHClF_2 \xrightarrow[1\ atm]{750°C\ -\ 950°C} CF_2{=}CF_2 + \text{byproducts}$$

HCFC-22 TFE

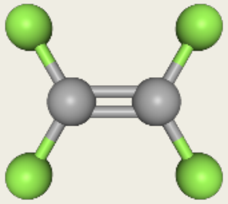


HCFC-22

$$CF_2{=}CF_2 \xrightarrow[\substack{80°C \\ 20\ atm}]{\text{initiator: ammonium persulfate}}$$



TFE PTFE



TFE

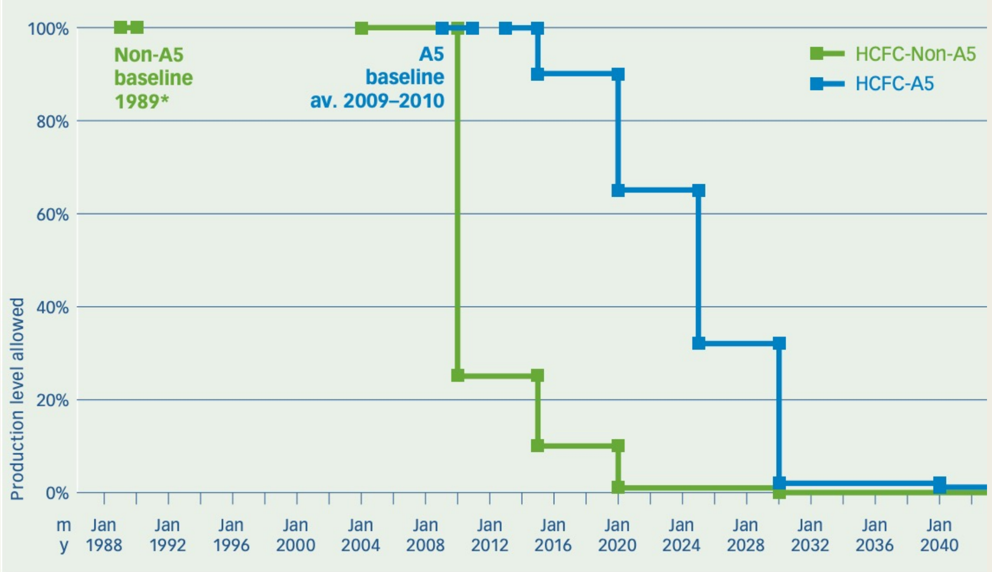
HCFC-22

The Montreal Protocol on Substances that Deplete the Ozone Layer, Annex C– Group I

Usage: refrigerant, foam blowing agent and feedstock

Non-Article 5 parties		Article 5 parties	
Baseline	**Average of 1989 HCFC production + 2.8 per cent of 1989 CFC* production and 1989 HCFC consumption + 2.8 per cent of 1989 CFC* consumption**	**Baseline**	**Average 2009–2010**
Freeze	January 1, 2004, at the baseline for production	Freeze	January 1, 2013
		10 per cent reduction	January 1, 2015
75 per cent reduction	January 1, 2010	35 per cent reduction	January 1, 2020
90 per cent reduction	January 1, 2015	67.5 per cent reduction	January 1, 2025
100 per cent reduction	January 1, 2020, and thereafter – allowance of 0.5 per cent of baseline production until January 1, 2030 for the uses defined in Article 2F paragraph 6(b) and – possible essential use exemptions	100 per cent reduction	January 1, 2030, and thereafter – allowance of 2.5 per cent of baseline production when averaged over ten years 2030–2040 until January 1, 2040 for the uses defined in Article 5 paragraph 8 *ter* (e) (ii) and – possible essential use exemptions

* Annex A Group I



* Baseline calculated as average of 1989 HCFC production + 2.8 per cent of 1989 CFC production and 1989 HCFC consumption + 2.8 per cent of 1989 CFC consumption

Ozone-depletion potential (ODP): 0.024-0.034

Global warming potential ($GWP_{100\text{-}y}$): 1760

Byproduct HFC-23 $GWP_{100\text{-}y}$: 12,690

Source: https://ozone.unep.org/sites/default/files/Handbooks/MP-Handbook-2020-English.pdf

PTFE

- **~45%** of the total fluoropolymer market in 2019
- Apply in automotive, textile, construction, and other sectors
- Release harmful polymer processing aids such as PFOA, PFNA during manufacturing
- Release hazardous substances such as trifluoroacetic acid under high temperature

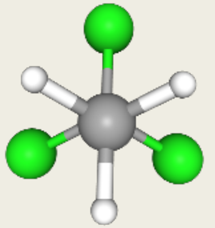
Source: https://www.chukoh.com/products/tube/ptfe-large-diameter/

General Synthesis Pathway of PVDF

1,1,1-trichloroethane → HCFC-142b → Vinylidene Fluoride (VDF) → Polyvinylidene Fluoride (PVDF)

$$CH_3CCl_3 + HF + CH_2{=}CF_2 \xrightarrow[\substack{60°C - 120°C \\ 5 - 20\ bar}]{\text{antimony compounds}} CCl_2FCH_3 + CH_3CClF_2 + CH_3CF_3 + \text{byproducts}$$

1,1,1-trichloroethane HCFC-142b



1,1,1-trichloroethane

Pathway 1

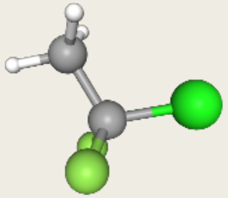
$$CH_3CClF_2 \xrightarrow[400°C]{\text{N-doped ordered mesoporous carbons}} CH_2{=}CF_2 + HCl$$

HCFC-142b VDF

Pathway 2

$$CH_3CClF_2 \xrightarrow{\text{high temperature}} CH_2{=}CF_2 + HCl$$

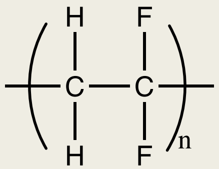
HCFC-142b VDF



HCFC-142b

Emulsion

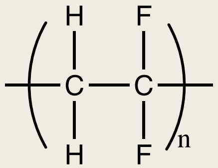
$$CH_2{=}CF_2 \xrightarrow[\substack{60°C - 125°C \\ 27bar - 55bar}]{\text{initiator: organic peroxide or persulfate}}$$



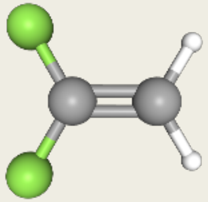
VDF PVDF

Suspension

$$CH_2{=}CF_2 \xrightarrow[\substack{20°C - 60°C \\ 70bar - 100bar}]{\text{initiator: organic peroxide or persulfate}}$$



VDF PVDF



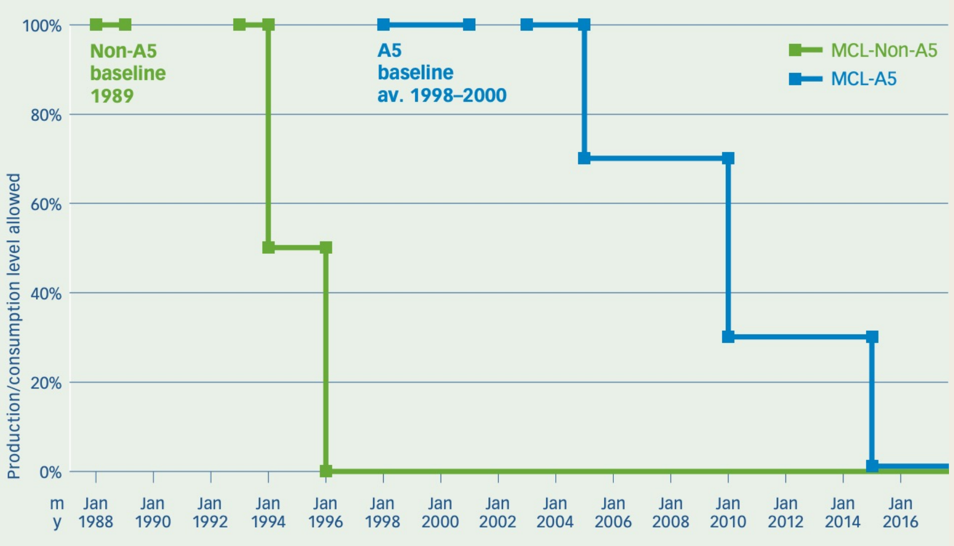
VDF

1,1,1-trichloroethane

The Montreal Protocol on Substances that Deplete the Ozone Layer, Annex B– Group III

ODP: 0.1

Non-Article 5 parties		Article 5 parties	
Baseline	1989	Baseline	Average of 1998–2000
Freeze	January 1, 1993	Freeze	January 1, 2003
50 per cent reduction	January 1, 1994	30 per cent reduction	January 1, 2005
100 per cent reduction	January 1, 1996 (with possible essential use exemptions)	70 per cent reduction	January 1, 2010
		100 per cent reduction	January 1, 2015 (with possible essential use exemptions)



Source: https://ozone.unep.org/sites/default/files/Handbooks/MP-Handbook-2020-English.pdf

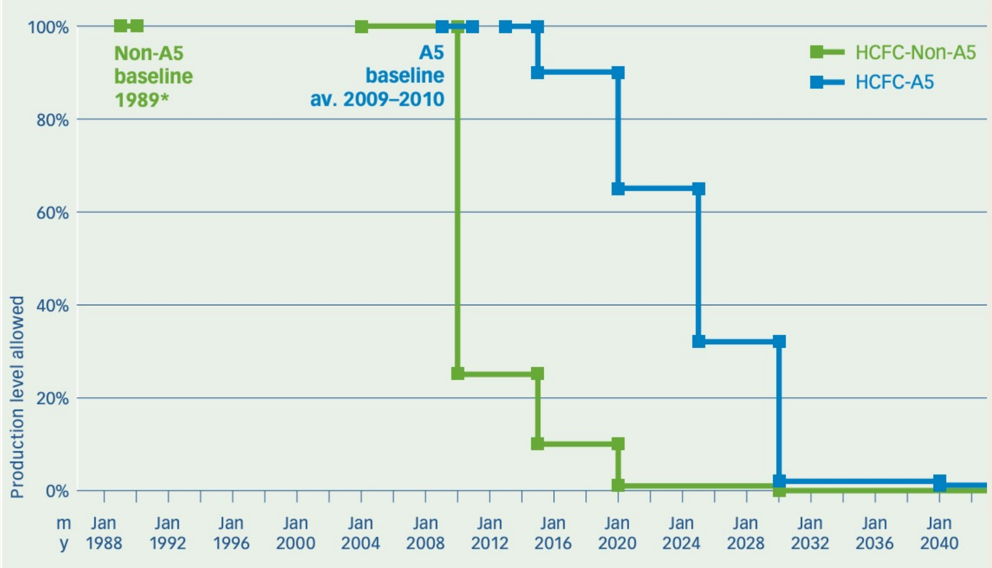
HCFC-142b

The Montreal Protocol on Substances that Deplete the Ozone Layer Annex C– Group I

Usage: refrigerant, foam blowing agent and feedstock

Non-Article 5 parties		Article 5 parties	
Baseline	Average of 1989 HCFC production + 2.8 per cent of 1989 CFC* production and 1989 HCFC consumption + 2.8 per cent of 1989 CFC* consumption	Baseline	Average 2009–2010
Freeze	January 1, 2004, at the baseline for production	Freeze	January 1, 2013
		10 per cent reduction	January 1, 2015
75 per cent reduction	January 1, 2010	35 per cent reduction	January 1, 2020
90 per cent reduction	January 1, 2015	67.5 per cent reduction	January 1, 2025
100 per cent reduction	January 1, 2020, and thereafter – allowance of 0.5 per cent of baseline production until January 1, 2030 for the uses defined in Article 2F paragraph 6(b) and – possible essential use exemptions	100 per cent reduction	January 1, 2030, and thereafter – allowance of 2.5 per cent of baseline production when averaged over ten years 2030–2040 until January 1, 2040 for the uses defined in Article 5 paragraph 8 *ter* (e) (ii) and – possible essential use exemptions

* Annex A Group I



* Baseline calculated as average of 1989 HCFC production + 2.8 per cent of 1989 CFC production and 1989 HCFC consumption + 2.8 per cent of 1989 CFC consumption

ODP: 0.057

$GWP_{100\text{-}y}$: 1980

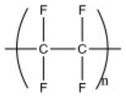
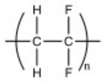
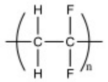
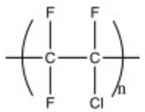
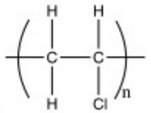
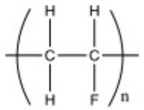
Source: https://ozone.unep.org/sites/default/files/Handbooks/MP-Handbook-2020-English.pdf

PVDF

- **~14%** of the total fluoropolymer market in 2019
- Apply in electronic, chemical, and energy-related industries
- Potential harms are similar to PTFE

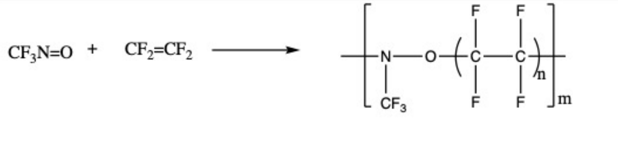
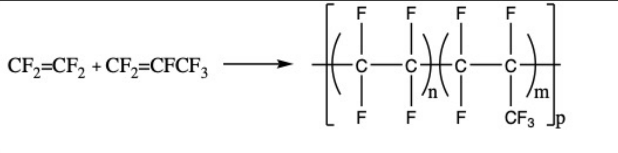
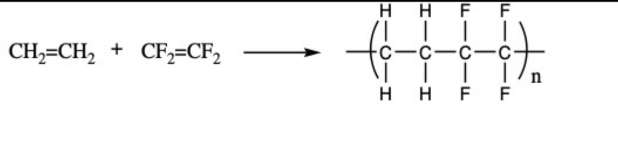
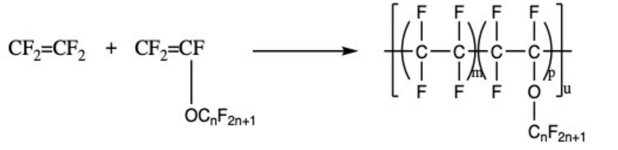
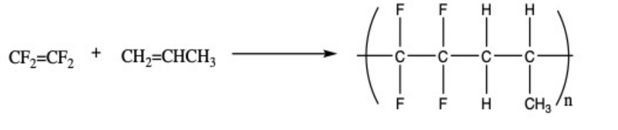
Source: https://polymerdatabase.com/Polymer%20Brands/PVDF.html
https://www.punepolymer.com/pvdf-products.html

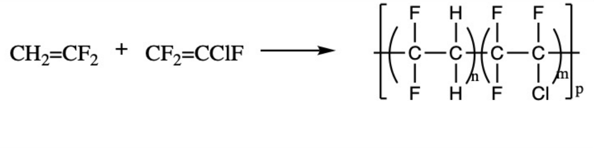
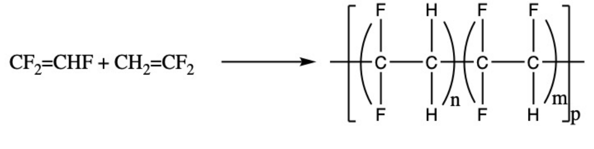
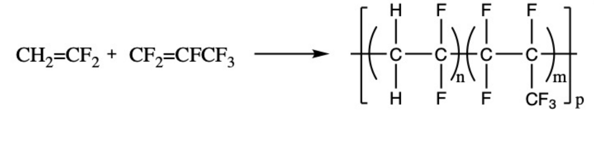
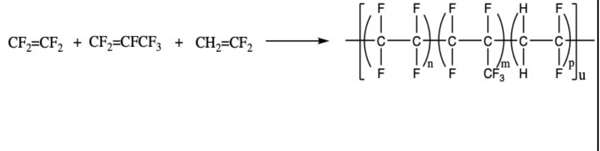
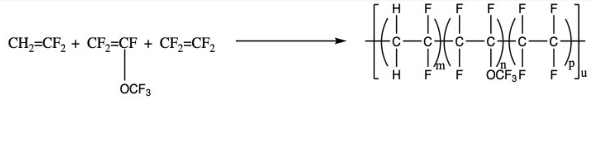
ODS and HFC Feedstocks to Polymers Built on a Singular Type of Monomers (examples)

ODS and HFC feedstocks	End products functioning as plastics	Reaction pathways
HCFC-22	PTFE	HCFC-22 to tetrafluoroethylene (TFE): $CHClF_2 \xrightarrow[1\ atm]{750°C\ -\ 950°C} CF_2{=}CF_2 + byproducts$ TFE to PTFE: $CF_2{=}CF_2 \xrightarrow[80°C,\ 20\ atm]{initiator:\ ammonium\ persulfate}$ 
HCFC-142b, HFC-143a	Polyvinylidene fluoride, or PVDF	HCFC-142b to vinylidene fluoride (VDF): Pathway 1 $CH_3CClF_2 \xrightarrow[400°C]{N\text{-}doped\ ordered\ mesoporous\ carbons} CH_2{=}CF_2 + HCl$ Pathway 2 $CH_3CClF_2 \xrightarrow{high\ temperature} CH_2{=}CF_2 + HCl$ (The specified temperature is different among published papers.) HFC-143a to VDF $CH_3CF_3 \xrightarrow{750°C\ -\ 910°C} CH_2{=}CF_2 + byproducts$ VDF to PVDF Pathway 1 (Emulsion) $CH_2{=}CF_2 \xrightarrow[60°C\ -\ 125°C,\ 27bar\ -\ 55bar]{initiator:\ organic\ peroxide\ or\ persulfate}$  Pathway 2 (Suspension) $CH_2{=}CF_2 \xrightarrow[20°C\ -\ 60°C,\ 70bar\ -\ 100bar]{initiator:\ organic\ peroxide\ or\ persulfate}$ 
CFC-113	PCTFE	CFC-113 to chlorotrifluoroethylene (CTFE) Pathway 1: $CClF_2CCl_2F \xrightarrow{500°C\ -\ 600°C} CF_2{=}CClF + Cl_2$ Pathway2: $CClF_2CCl_2F \xrightarrow[50°C\ -\ 100°C]{Zn/MeOH} CF_2{=}CClF + ZnCl_2$ CTFE to PCTFE $CF_2{=}CFCl \xrightarrow[10°C\ -\ 70°C,\ 4bar\ -\ 20bar]{initiator:\ potassium\ persulphate}$ 
VC*	Polyvinyl chloride, or PVC	$CH_2{=}CHCl \xrightarrow[65°C,\ 10\ atm]{initiator:\ AIBN}$ 
HFC-152a	Polyvinyl fluoride, or PVF	HFC-152a to vinyl fluoride (VF) $CH_3CHF_2 \xrightarrow[250°C\ -\ 325°C,\ atmospheric\ pressure]{MgF_2/\beta\text{-}AlF_3\ or\ ZnF_2/\beta\text{-}AlF_3} CH_2{=}CHF + HF$ VF to PVF $CH_2{=}CHF \xrightarrow[25°C\ -\ 100°C,\ 25atm\ -\ 100atm]{initiator:\ AIBN}$ 

Source: Andersen et al. “Narrowing feedstock exemptions under the Montreal Protocol has multiple environmental benefits.” ***Proceedings of the National Academy of Sciences of the United States*** 118.49 (2021).

ODS and HFC Feedstocks to Polymers Built on Multiple Monomers (examples)

HCFC-22	Nitroso rubbers (an example)	
HCFC-22	Fluorinated ethylene propylene copolymer (FEP)	
HCFC-22	Ethylene tetrafluoroethylene copolymer (ETFE)	
HCFC-22	Perfluoroalkoxy copolymer (PFA)	
HCFC-22	Poly(TFE-*alt*-propylene (P)) (AFLAS®)	

HCFC-142b, HFC-143a, CFC-113	Poly(VDF-*co*-CTFE) (Dyneon®)	
HCFC-142b, HFC-143a	Poly(VDF-*co*- TrFE)	
HCFC-142b, HFC-143a	Poly(VDF-*co*-hexafluoropropylene (HFP)) (Viton® A)	
HCFC-142b, HFC-143a, HCFC-22	Poly(VDF-*ter*-TFE-*ter*-HFP) (Viton® B)	
HCFC-142b, HFC-143a, HCFC-22	Poly[VDF-*ter*-TFE-*ter*-(perfluoromethyl vinyl ether) (PMVE)] (Viton® GLT)	

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Growth Rate of Plastics

$$Compound\ annual\ growth\ rate\ (CAGR) = (\frac{EV}{BV})^{\frac{1}{n}} - 1$$

where:
EV = Ending value
BV= Beginning value
n=Number of years

	Beginning value	Ending value	n	CAGR %
Fluoropolymer 2020-2025	2020: 395.83 kt	2025: 511.74 kt	5 yr	5.3%
Total plastic 2020-2025	2020: 381 Mt	2025: 439 Mt	5 yr	2.9%

Proposed Future Steps

- **Parties** of Montreal Protocol provide more detailed and accurate reporting of feedstock production
- **Scientific Assessment Panel** (SAP) estimates the atmospheric impact of narrowing the feedstock exemptions
- **Technology and Economic Assessment Panel** (TEAP) identifies and catalogs substitutes for plastics currently made with ODS and HFC feedstocks

Potential Achievements

- By estimate, reduce up to 6% of the total plastics production
  - *5% by controlling fluoropolymer production*
  - *1% by controlling VC- and PVC-related production*

- Inspire environmental authorities to use other international agreements to help mitigate the plastics pollution issue at the production stage.

Thank you !

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