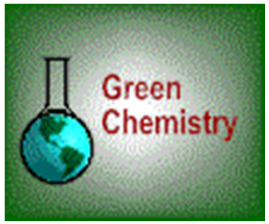
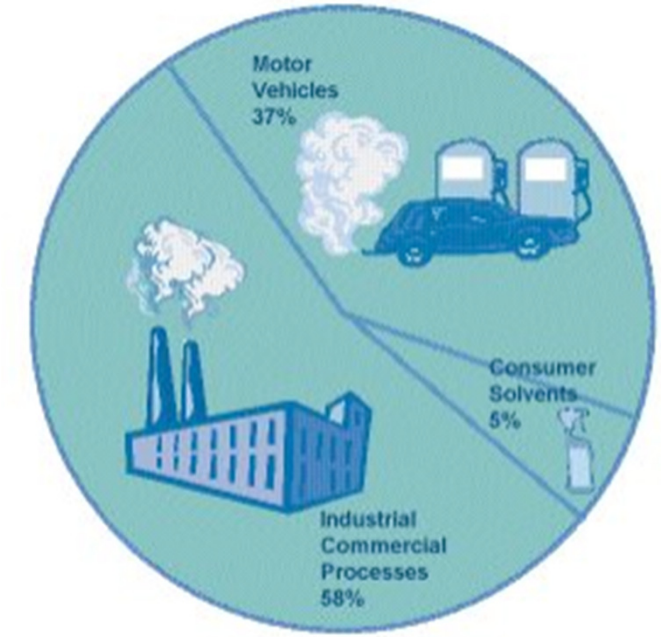
Design and Application of Surfactants for Carbon Dioxide; Making Carbon Dioxide a Better Solvent in an Effort to Replace Solvents that Damage the Environment



Volatile Organic Compounds and Halogenated Organic Compounds



Sources of VOC

- xylene
- toluene
- benzene
- methylene chloride
- chloroform
- isopropyl alcohol

from epa web site
(http://www.epa.gov/oar/oaqps/gooduphigh/)

Uses of Volatile Organic Compounds and Halogenated Organic Compounds

- **Industrial types of cleaning**
  - **flux removal**
  - **oil and grease removal from metal parts**
  - **garment cleaning**

- **Household products**
  - **stains and varnishes**
  - **paint thinner**
  - **fingernail polish remover**
  - **adhesives**
  - **furniture polish**
  - **hair spray**

VOCs and Ozone Production

VOCs + NO_x + sunlight ⟶ ⟶ O_3 + HNO_3 + organic compounds

from epa web site (http://www.epa.gov/oar/oaqps/gooduphigh/)

Halogenated Organic Compounds

- **Carbon based compounds that contain halogen atoms such as fluorine, chlorine, and bromine.**

- **They include the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs).**

Chlorofluorocarbons (CFCs)

- **Widely used for many applications**
  - **refrigerants, propellants for aerosol, and blowing agents**
  - **industrial cleaning**
- **Chemically unreactive, nontoxic and nonflammable**
- **Known to decompose in the stratosphere under the influence of high energy UV radiation (UV-C)**
- **These decomposition products catalyze reactions that deplete the stratospheric ozone layer**
- **Significant increases in the intensity of harmful UV radiation reaching the surface of the earth results**

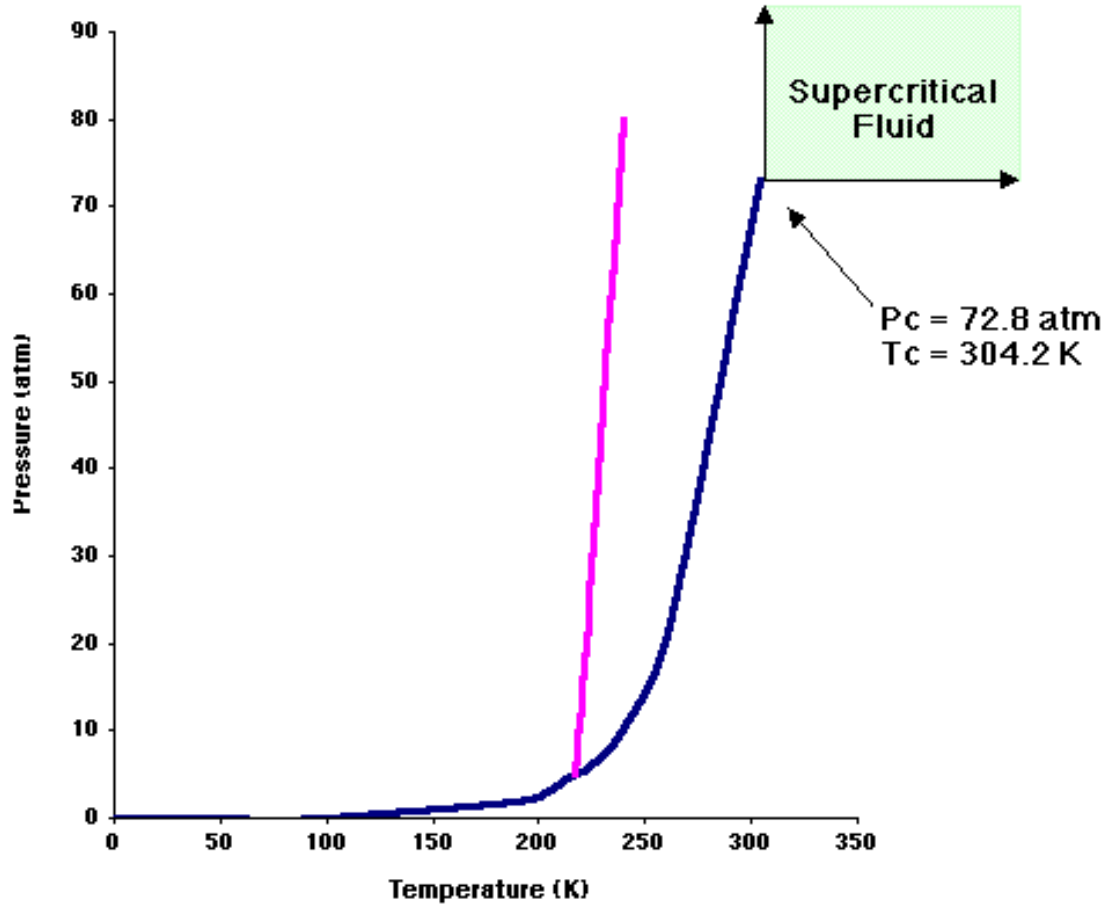
Hydrochlorofluorocarbons

- HCFCs are being used as temporary replacements for CFCs.
- HCFCs do not have as great an ozone layer depleting potential.
- The carbon hydrogen bond in HCFCs makes them much more reactive than CFCs so…
- the vast majority of the HCFC molecules are destroyed in the troposphere.
- This prevents most of the HCFC molecules from rising into the stratosphere where they too would act to deplete the ozone layer.

Carbon Dioxide: An Alternative Solvent

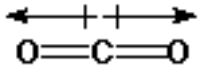
- **Preferable to VOCs and Halogenated Organic Compounds**
- **Nonflammable, nontoxic, and chemically unreactive**
- **Available as a cheaply recovered byproduct from the production of ammonia and from natural gas wells**
- **The used carbon dioxide can easily be recovered, purified, and reused.**

Supercritical CO_2



Solubility of Substances in CO_2

- Carbon dioxide a non polar molecule since the dipoles of the two bonds cancel one another.



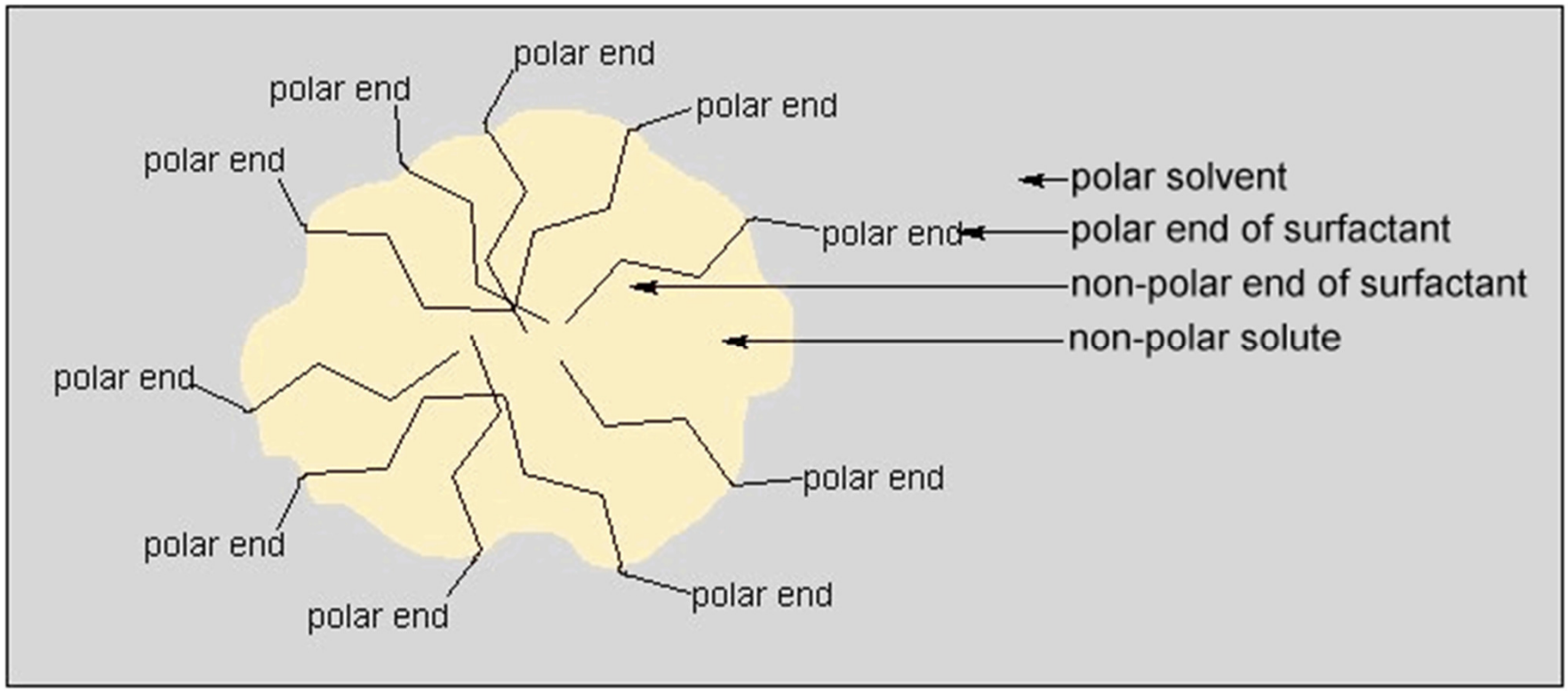
- Carbon dioxide will dissolve smaller non polar molecules
  - hydrocarbons having less than 20 carbon atoms
  - other organic molecules such as aldehydes, esters, and ketones

- But it will not dissolve larger molecules such as oils, waxes, grease, polymers, and proteins, or polar molecules.

Surfactants

- A molecule that contains a polar portion and a non polar portion.
- A surfactant can interact with both polar and non polar molecules.
- A surfactant increases the solubility of the otherwise insoluble substances.
- In water, surfactant molecules tend to cluster into a spherical geometry
  - non polar ends on the inside of the sphere
  - polar ends on the outside
- These clusters are called micelles

Micelle Structure of a Surfactant



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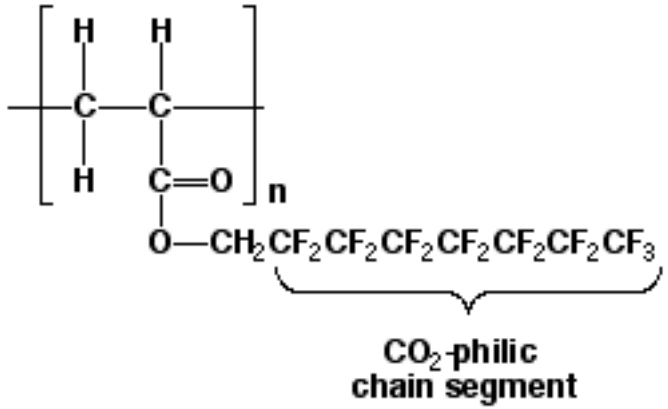
A Surfactant for Liquid or Supercritical Fluid CO_2

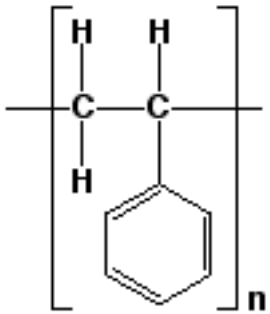
- **Must have both CO_2-philic (CO_2 loving) and CO_2 -phobic functionality.**

- **In 1994, Joseph M. DeSimone of the University of North Carolina and North Carolina State University published his discovery that polymers such as that shown below are soluble in liquid or supercritical CO_2.**



Polymers

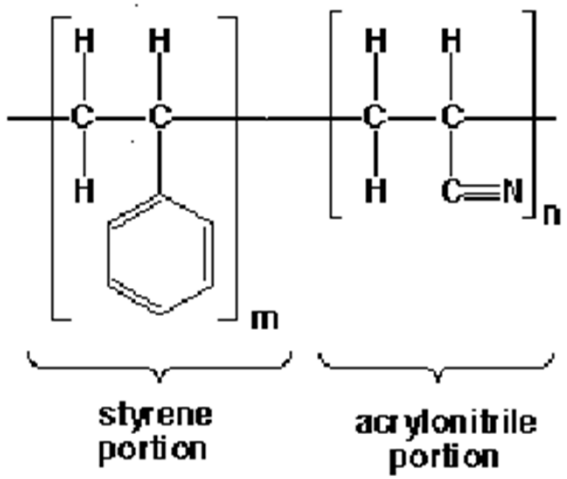
- **Molecule with a high molar mass (typically 10,000 to 10^6)**
- **Polystyrene is an example:**



- **n is the number of times the structure in brackets repeats itself (on average)**
- **n is called the number average degree of polymerization and is usually ≥ 1000**

Copolymers

- A copolymer contains two different types of repeat units within the same polymer chain.
- A copolymer is not a blend of two different polymers, but instead the two monomers are covalently bonded along the length of the chain.
- Example of a copolymer of styrene and acrylonitrile:



Possible Copolymer Sequencing Arrangements

Using ‘S’ to represent the styrene monomers and ‘A’ to represent the acrylonitrile monomers:

- **Random Copolymer**

  SASASAASASSAS

- **Block Copolymer**

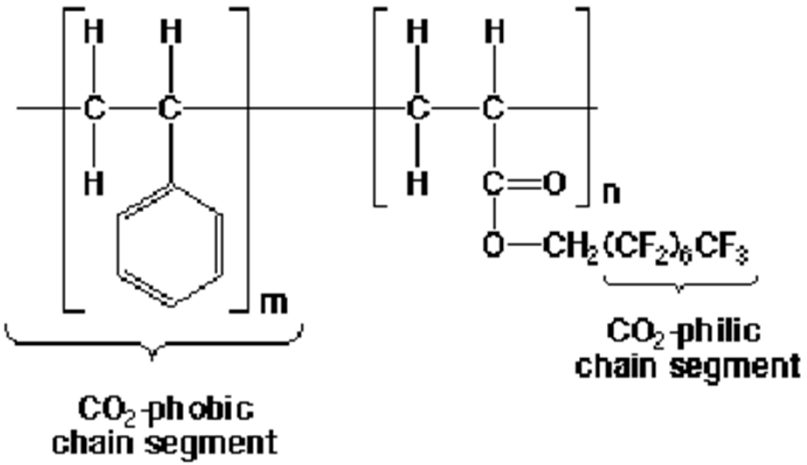
  SSSSSSAAAAAAA

- **Alternating Copolymer**

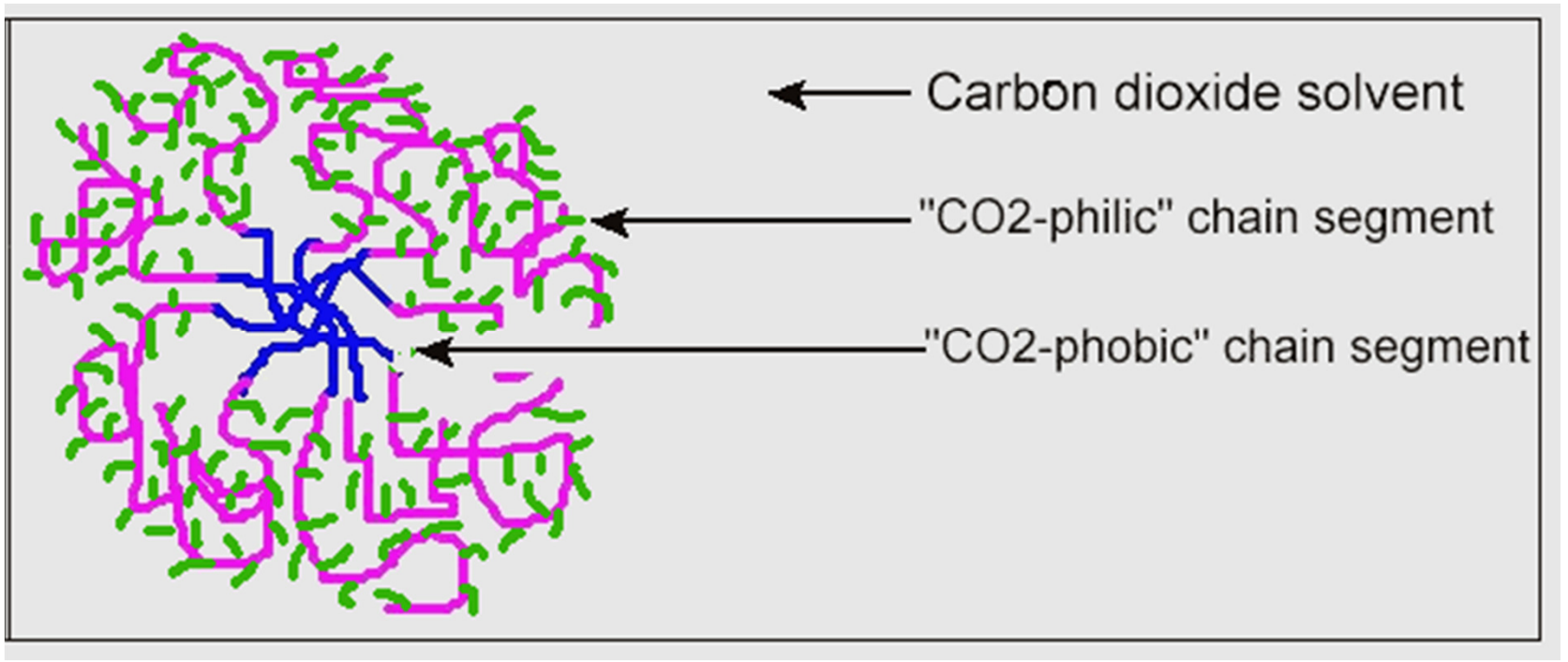
  SASASASASASASA

Block Copolymers are Used to make a Surfactant for CO_2

- DeSimone synthesized copolymers with a CO_2-phobic portion and a CO_2-philic portion.



Micelle Structure for a CO_2 Surfactant



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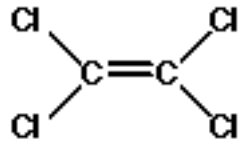
Current Use of CO_2 Surfactants--Green Chemistry in *ACTION*

- **The dry cleaning industry typically uses the solvent perchloroethylene (PERC), as the cleaning agent.**



- **344 million lb of PERC were produced in the United States in 1998.**

- **The dry cleaning industry uses approximately 50% of the PERC produced each year ~ 172 million pounds of the solvent.**

Current Use of CO_2 Surfactants--Green Chemistry in *ACTION*

- **EPA has classified PERC as a groundwater contaminant and a potential human health hazard.**
- **PERC is a suspected human carcinogen and a known rodent carcinogen.**
- **Breathing PERC for short periods of time can adversely affect the central nervous system.**
- **These effects are not likely to occur though at levels of PERC that are normally found in the environment, but people who work in the dry cleaning industry have the greatest risk for exposure.**

Current Use of CO_2 Surfactants--Green Chemistry in *ACTION*

- **Micell Technologies, a company founded in 1995, has made the CO_2 surfactant technology available commercially.**
- **Micell's Micareô system is a commercial washing machine that utilizes CO_2 and a CO_2 surfactant instead of PERC, thereby eliminating the need for PERC.**
- **The franchise, Hangers, uses this technology.**

The Micare™ System

Current Use of CO_2 Surfactants--Green Chemistry in *ACTION*

- **Micell Technologies also developed technology known as the Micleanô system.**
- **Cleans oils and greases from metal components.**
- **This eliminates the need for halogenated cleaning solvents.**

Professor DiSimone won AWARDS!

- ☺ **Presidential Green Chemistry Challenge Award in 1997 for his discovery and development of the CO_2 surfactants**
- ☺ **Governor's Award for Excellence**
- ☺ **National Science Foundation's Young Investigator Award**
- ☺ **Presidential Faculty Fellow Award**
- ☺ **He and Micell Technologies also received the R&D 100 Award for their Micareô dry cleaning system**
  - * **recognized as being one of the "100 most technologically significant new products and processes of the year."**