NOVA SCHOOL OF
SCIENCE & TECHNOLOGY

Ciência dos Materiais A

Ana Rita C. Duarte

aduarte@fct.unl.pt

Funcionamento da cadeira

- 1 Teste – 12 de Dezembro – 3ª feira 8.00 – 9.30
- Trabalhos práticos
  - Lab 1
  - Lab 2

Avaliação

60% parte teórica

40% parte prática

- 30% Relatórios dos trabalhos práticos
- 10% Trabalho – polímeros do dia a dia

Funcionamento da cadeira

- Trabalhos práticos:

    - Lab 1 - Identificação de polímeros através de testes fisico-químicos (relatório entregue no **final da aula prática**)
    - Lab 2 - Avaliação das propriedades térmicas de várias amostras (relatório entregue no **moodle** até dia **14 de Dezembro**

- Entrega do trabalho polímeros do dia a dia **27 Novembro** (**moodle**)

Bibliografia

1. Fred W. Billmeyer, Jr., Textbook of Polymer Science, Wiley Interscience, 3ª Ed., 1984

2. F. Rodriguez, Principles of Polymer Systems, McGraw-Hill, 3ª Ed., 1983

3. Paul J. Flory, Principles of Polymer Chemistry, Cornell University Press, 10ª Ed., 1978

4. J. M. G. Cowie, Polymers: Chemistry and Physics of Modern Materials, Intertex Books, 2ª Ed., 1993

5. I. M. Campbell, Introduction to Synthetic Polymers, Oxford Science Publications, 3ª Ed., 1997

6. S. R. Sandler, W. Karo, J. Bonesteel, E.M. Pearce, Polymer Synthesis and Characterization, A Laboratorial Manual, Academic Press, 1998

7. Brandrup, Immergut, Polymer Handbook, John Wiley & Sons, 4ª Ed., 1999

O que é um polímero?

Polímeros na vida quotidiana

O “ABC da vida plastificada”. © Planeta Tangerina

Exercícios

Polímero ou não…

Sal	Esferovite	DNA
Cabelo	Unhas de gel	Ferro
Açúcar	Papel	Neon
Nylon	Vinagre	Músculos
Bicarbonato de sódio	Seda	Slime
Vidro	Lã	Polietileno
Madeira	Ouro	Prata

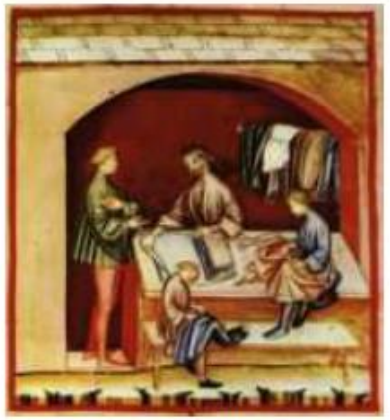
TED TALK:

From DNA to Silly Putty, the diverse world of polymers

Jan Mattingly

https://ed.ted.com/lessons/from-dna-to-silly-putty-the-diverse-world-of-polymers-jan-mattingly

Perspectiva histórica



Silk wearing (XIV century)

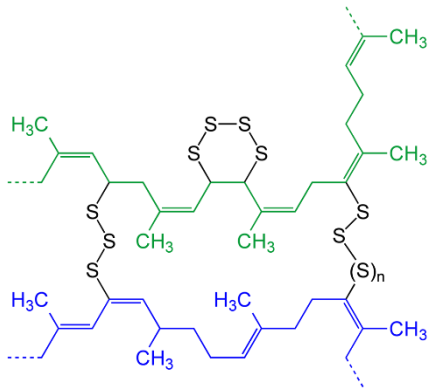
- **Polímeros naturais**, isto é, não produzidos pelo homem são usados há vários séculos. São exemplos a seda e a lã.
- Serviram como base de várias indústrias e para trocas comerciais entre civilizações, das quais e tão bem conhecida a rota da seda.

Kneaded rubber and common eraser

- **Borracha**, era usada pelos povos da América do Sul para produzir capas impermeabilizantes.
- 1770 – foi criada a primeira aplicação comercial da borracha, para apagar lápis

1830 – a era das aplicações industriais dos polímeros inicia-se

Charles Goodyear – descobre o processo de vulcanização da borracha – reticulação das cadeias poliméricas de borracha natural com enxofre



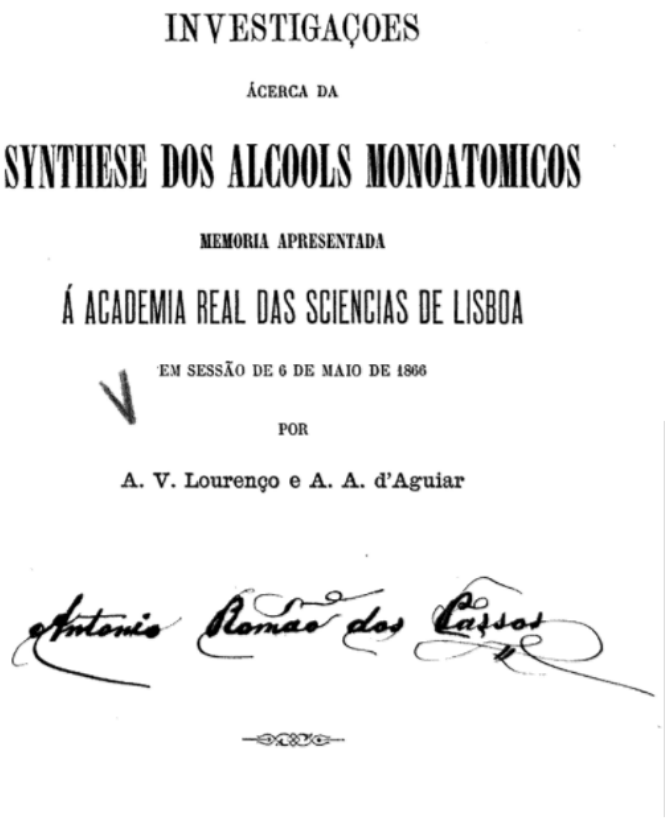
Charles Macintosh – desenvolveu os casacos impermeáveis, revestindo os tecidos com borracha, a partir da dissolução da borracha em nafta.


Charles Macintosh

Mackintosh shop - Burlington Arcade

1863 – Agostinho Vicente Lourenço - Um português na história dos polímeros

Médico, nascido em Goa. Defende a sua tese de doutoramento em Química Orgânica e é reportado o primeiro exemplo de uma reação de polimerização por condensação.



INVESTIGAÇOES

ÁCERCA DA

SYNTHESE DOS ALCOOLS MONOATOMICOS

MEMORIA APRESENTADA

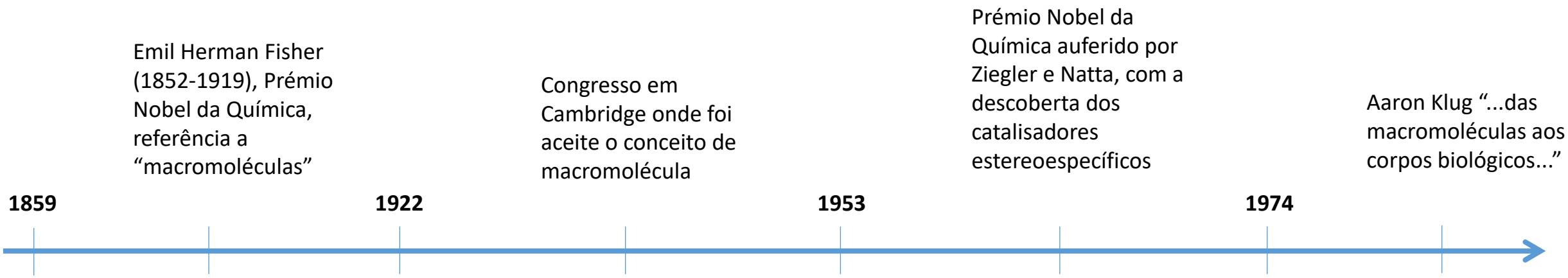
Á ACADEMIA REAL DAS SCIENCIAS DE LISBOA

EM SESSÃO DE 6 DE MAIO DE 1866

POR

A. V. Lourenço e A. A. d'Aguiar

Breve cronologia de ciência de polímeros



1900-1929

1909
Casein plastics, derived from milk, developed by Erinoid

1910
Stockings made of viscose (CA) begin to be manufactured in Germany

1915
Queen Mary sees casein products at the British Industries Fair and orders several pieces of jewellery made from it

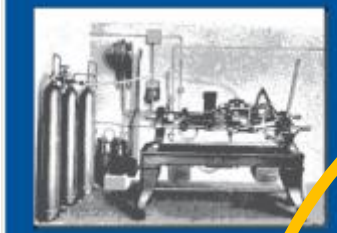
1916
Rolls Royce begins to use phenol formaldehyde in its car interiors and boasts about it

1919
Eichengrun produce first cellulose acetate moulding powder

1921
Beginning of rapid growth of phenolic mouldings especially for electrical insulation, with addition of phenolic laminates in 1930

1922
Staudinger published his work recognising that plastics are composed of long chain molecules leading to a Nobel prize in 1935

1924
Rossiter at British Cyanide develops urea-thiourea formaldehyde resins, subsequently commercialised as the first water white transparent thermosetting moulding powder

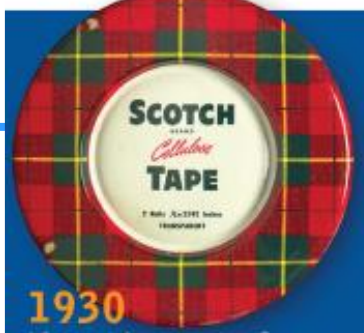


1926
Eckert and Ziegler patent first commercial modern plastics injection moulding machine

1926
Harrods host first display of coloured thermosetting plastics tableware produced by Brookes and Adams, The Streetly Manufacturing Company and Thomas De La Rue and Co.

1929
Bakelite Ltd receives its largest ever order for phenolic moulding powder for the casing of the Siemens telephone

1930s



1930
'Scotch' tape, the first transparent sticky tape invented in US by 3M Company

1932
Screw pre-plasticisation in injection moulding patented

1933
BPF founded on the 21st December 1933. First Chairman, Charles Waghorne of Insulators Limited

1933
Fawcett and Gibson at ICI discover polyethylene

1933
Crawford at ICI develops first commercial synthesis of poly(methyl methacrylate)

1935
Troester in Germany produce first extruder designed for thermoplastics

1937
First commercial production of polystyrene by IG Farben, Germany

1935
Carothers and DuPont patent nylon

1936
First production of aircraft canopies made from 'Perspex'

1937
Columbo and Pasquetti in Italy produce first twin-screw extruder machine

1938
First toothbrush with nylon tufts manufactured

1938
Full scale production of nylon 6 fibre begins in United States

1938
Plunkett (DuPont) discovers PTFE

1939
first commercial production of polyethylene in UK by ICI

1939
outbreak of war – strategic stockpiles of materials

1940s

1940
First production of PVC in UK

1940s
Polyethelene used as radar cable insulation

1940
DuPont introduces polyacrylonitrile (PAN), an early engineering product

1941
Whinfield and Dickson, of the Calico Printer's Association of Manchester, patent polyethylene terephthalate (PET); followed by the creation of the first polyester fiber called 'Terylene'

1944
Bakelite Handgrenade widely used by British Troops in Normandy

1943
First pilot plant for polytetrafluoroethylene (PTFE); to be marketed under trade mark 'Teflon'

1942
'Super Glue' (methyl cyanoacrylate) first discovered by Dr Harry Coover, Eastman Kodak

1945
The production of the LDPE Sqezy bottle by Monsanto caused a rapid expansion of the industry with containers produced to replace glass bottles for shampoos and liquid soaps.

1947
Formica melamine faced decorative laminates introduced into the UK

1948
Introduction of 12" long playing records made from PolyVinyl Chloride (PVC)

1948
George de Mestral invents Velcro, patented in 1955

1948
Acrylonitrile-butadiene-styrene (ABS) produced

1949
High impact polystyrene introduced as a commercial plastic

1949
First Airfix self-assembly model produced (Ferguson Tractor) initially made of cellulose acetate and later polystyrene

1949
Launch in US of Tupperware made from low density polyethylene

1949
'Lycra' based on polyurethane, invented by DuPont

1950s

1950
ICI opens new factory at Redcar to produce 'Terylene'

1950s
Introduction of acrylonitrile-butadiene-styrene (ABS) copolymers

1951
Festival of Britain

1953
Commercialisation of polyester fibres introduces the concept of 'drip dry' and 'non-iron'

1954
Polystyrene foam introduced by Dow Chemical Co.

1955
First production of high density polyethylene in UK

1950s
The polyethylene bag makes its first appearance

1956
DuPont files patents for first acetals (POM)

1956
Reliant Regal 111, first commercially successful all glass-reinforced-plastic bodied car goes on sale

1956
Eero Saarinen's 'Tulip Chair' launched, consisting of a seat made of glass-fibre-reinforced plastic

1957
The hoop is reinvented as the 'Hula Hoop' by Knerr & Medlin, Wham-O Toy Company

1957
First production of polypropylene by Montecatini using Ziegler-Natta catalysts

1958
First production of polycarbonates (Bayer and General Electric)

1958
Lego patents its stud and block coupling system and produces toys of cellulose acetate, later Acrylonitrile-butadiene-styrene polymer

1959
Barbie Doll unveiled by Mattel at American International Toy Fair

1960s-70s

Early 1960s introduction of water-based acrylic paints

1960 Ethylene-vinyl acetate co-polymers launched by DuPont

1962 DuPont launches polyimide films and

1962 Silicone gel breast implants pioneered successfully

1965 'Kevlar' is first developed by DuPont and used in tyres

1966 Blow moulded fuel tanks introduced

1970 First Yellow HDPE pressure pipes for gas introduced into UK by Wavin/British Gas

1967 Polyvinyl Chloride (PVC) 'Blow' chair designed by Scolaria, De Pas and Lomazzi, manufactured by Zanotta

1969 Neil Armstrong plants a nylon flag on the moon

1973 Martin Cooper, a Motorola researcher and executive, designs the first ever mobile phone

1973 Polyethylene terephthalate beverage bottles introduced

1976 Plastics in its great variety of forms becomes the most used type of material in the world

1977 Polyaryletheretherketone (PEEK) was first prepared by ICI

1979 First PVC-U double glazed windows installed in the UK

1980s-90s

1980 First production of linear low density polyethylene

1980 First Blue HDPE pressure pipes for potable water introduced into UK

1983 The slim plastics Swatch watch made of 51 components, mainly plastics

1988 Introduction of triangular recycling symbols relating to plastics

1994 'Smart car' with lightweight flexible integrally coloured polycarbonate panels introduced

1982 First artificial heart made mainly of polyurethane, implanted in a human

1983 ICI and Bayer launch PEEK, PPS (polyphenyene sulphide), and PES (polyether sulphone)

1987 BASF in Germany produces a polyacetylene that has twice the electrical conductivity of copper

1989 first light-emitting polymers (poly-ethyne) discovered in Cambridge

1989 The Gravimetric Batch Blender is invented by Steve Maguire revolutionising the industry and bringing affordable gravimetric blending to processors.

1990 ICI launches 'Biopol', the first commercially available biodegradable plastic

1991 Dyson's vacuum cleaner launched in Japan

1998 Free standing Zanussi 'Oz' fridge, with insulation and outer skins made in one process from polyurethane foam, introduced

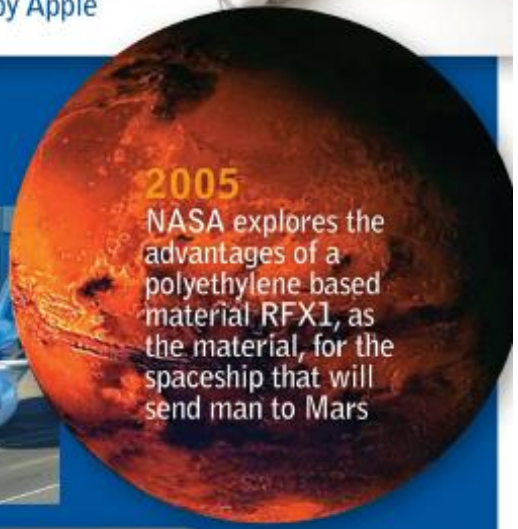
2000-10

2000s
Nano-Technology applied to polymer and composite applications

2001
iPod dreamed up by Tony Fadell, an independent inventor, developed by Apple

2000
First commercial metallocene catalysed polyolefins introduced

2005
Polycond project established to look at the potential of conductive polymers



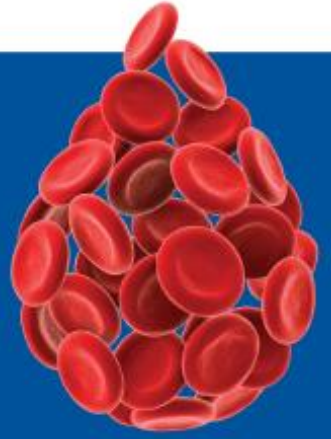
2005
NASA explores the advantages of a polyethylene based material RFX1, as the material, for the spaceship that will send man to Mars

2008
Airbus 380, comprising 22% carbon-fibre reinforced plastics, flies into Heathrow

2009
Boeing 787 (nicknamed 'Boeing's Plastic Dream') comes into service, its skin is made up of 100% Plastic composites with plastic making up 50% of all materials in the plane

2010
The Amazon Kindle is an e-reader made with a resilient plastic outer body case. Kindle is used to read e-books newspapers, magazines, blogs and other digital media

2010+



Bullet Proof Polymer
Scientists at Rice University, Texas have created a new super polymer material that can stop a 9mm bullet and seal the hole behind it

Plastics Blood
Developed by the University of Sheffield to mimic haemoglobin, for use in trauma situations where blood is needed quickly

Solar Powered Flight

The Solar Impulse plane's structure, made from roughly 90% polymer-matrix-composite materials, achieved the first solar-powered intercontinental flight in 2012

Plastic Solar Cells
A polymer solar cell that can produce electricity from sunlight by the photovoltaic effect provides a lightweight, disposable and inexpensive alternative to traditional solar panels

Implantable Polymers
Medical grade and implantable biomaterials such as PEEK will be used in neurological applications to help control epilepsy, Parkinson's disease and brain trauma

Commercial Space Flights
Lightweight carbon composite materials will be crucial in the realisation of sub-orbital tourist spaceflights

3D Printed Body Parts
Using plastic materials such as PMMA car parts can be printed at home and doctors can produce replica livers or kidneys for transplant patients

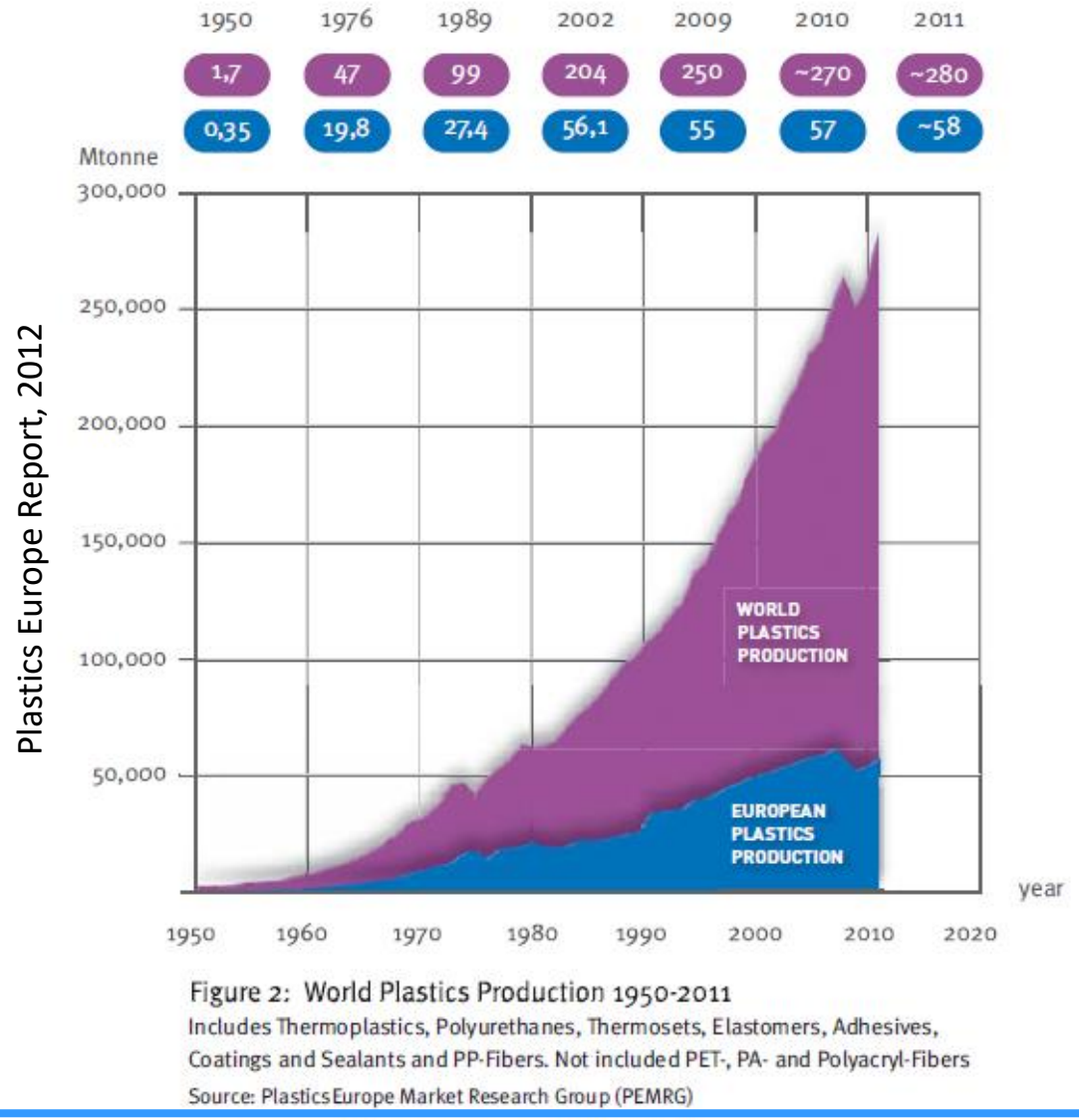
Flexible Plastic Screens
Organic light-emitting diodes are placed on plastic foil to create electronic devices with flexible displays

Driverless Cars
In the future all driverless vehicles will be almost entirely constructed from plastic parts due to the light weighting properties they provide

CONTRIBUTORS BY:
PHS, Science Museum, Sylvia Katz, Colin Williamson, Colin Richardson, Susan Mossman, John Russel, Ralph Kay, Deborah Jaffe

FURTHER INFORMATION:
BPF, PHS, Science Museum, Victoria and Albert Museum, Design Museum, Cornelius Collection of Toys, Bletchley Park, Bakelite Museum

World plastics production



Plastics Europe Report, 2012

Figure 2: World Plastics Production 1950-2011
Includes Thermoplastics, Polyurethanes, Thermosets, Elastomers, Adhesives, Coatings and Sealants and PP-Fibers. Not included PET-, PA- and Polyacryl-Fibers
Source: PlasticsEurope Market Research Group (PEMRG)

Nos últimos 10 anos produziu-se mais plástico que nos 100 anos anteriores!

6 maiores tipos de plásticos em termos de volume de mercado:

- polietileno – baixa densidade (PE-LD), ou alta densidade (PE-HD)
- polipropileno (PP)
- policloreto de vinilo (PVC)
- poliestireno sólido (PS), expandido (PS-E)
- polietileno tereftalato (PET)
- poliuretano (PUR)

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Perspectiva histórica

Plastics Europe Report, 2012

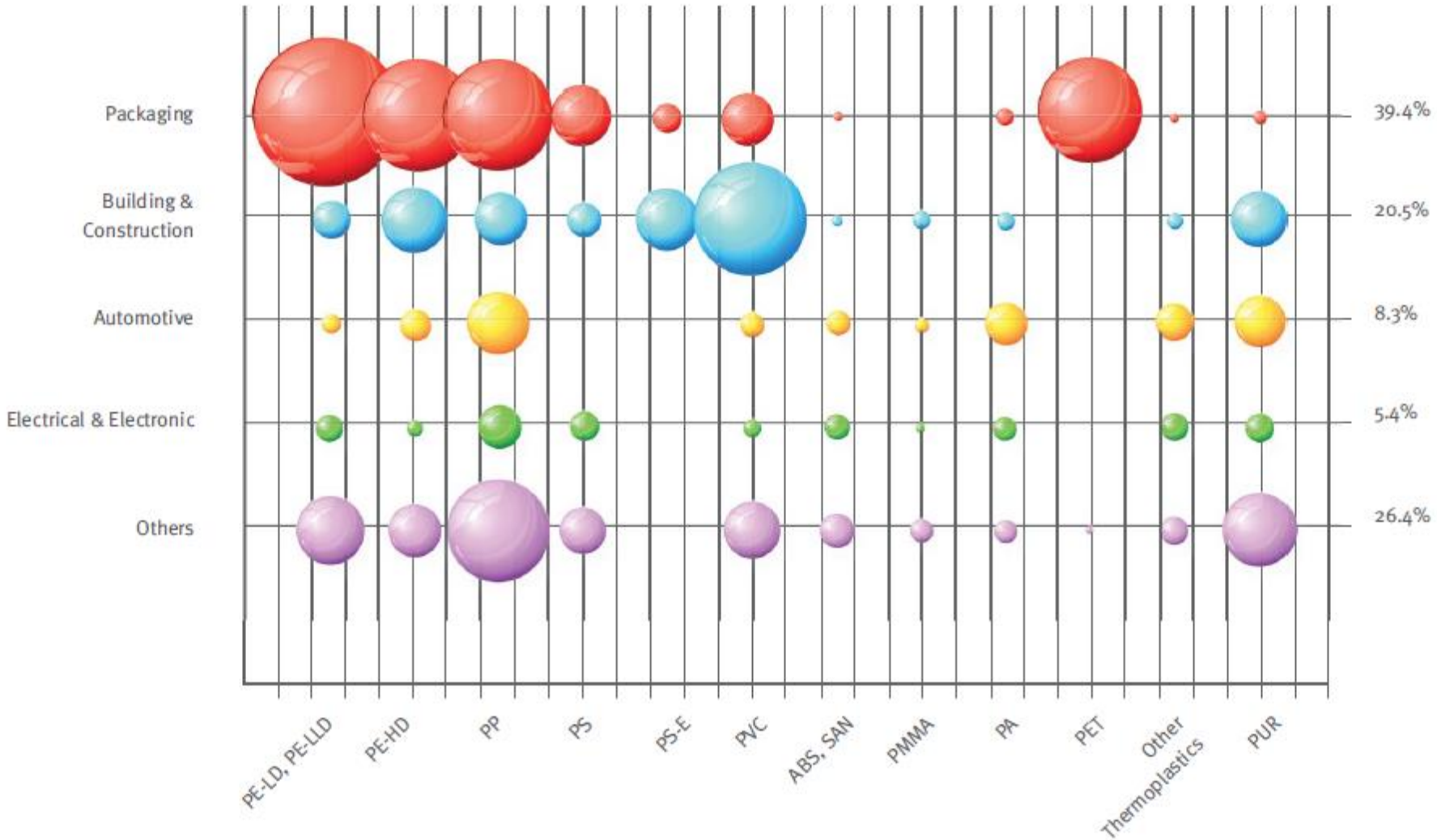


Figure 6: European Plastics Demand* by Segment and Resin Type 2011

Source: PlasticsEurope Market Research Group (PEMRG)

* EU-27+N/CH incl. Other Plastics (~5.7 Mtonne)

Perspectiva histórica

Chart 1. Annual percent changes in the January PPI's for Crude Petroleum, Organic Chemicals, and Plastics Products

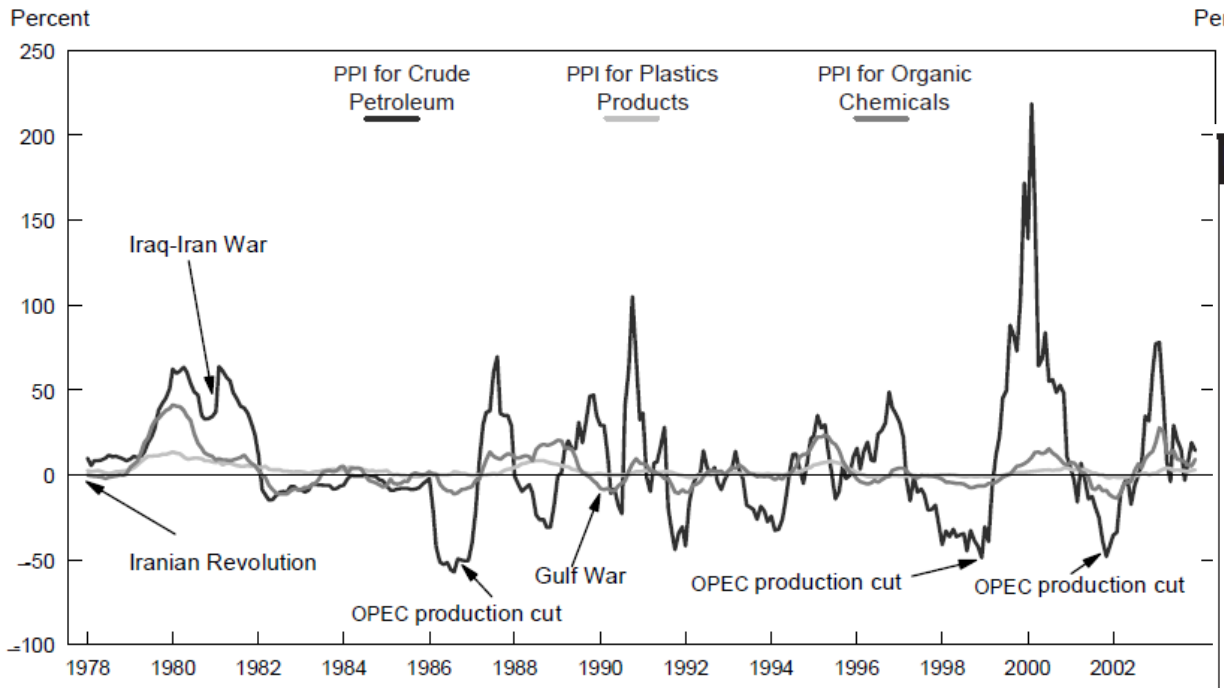


Exhibit 1. Accelerations, peaks, and troughs, crude petroleum, organic chemicals, and plastics products, 1978–2003

Supply shock	Acceleration	Peak	Trough
Crude petroleum			
Iranian Revolution/ Iran-Iraq War	December 1978	January 1980	April 1982
OPEC production cut, 1986	September 1986	August 1987	October 1988
Gulf War	August 1990	October 1990	October 1991
OPEC production cut, 1999	March 1999	February 2000	November 2001
OPEC production cut, 2001	December 2001	February 2003	—
Organic chemicals			
Iranian Revolution/ Iran-Iraq War	July 1978	January 1980	September 1982
OPEC production cut, 1986	September 1986	January 1989	April 1990
Gulf War	June 1990	November 1990	November 1991
OPEC production cut, 1999	April 1999	July 2000	February 2002
OPEC production cut, 2001	March 2002	February 2003	—
Plastics products			
Iranian Revolution/ Iran-Iraq War	August 1978	January 1980	March 1983
OPEC production cut, 1986	March 1987	August 1988	April 1990
Gulf War	October 1990	February 1991	February 1992
OPEC production cut, 1999	April 1999	November 2000	March 2002
OPEC production cut, 2001	April 2002	April 2003	—

Jonathan C. Weinhagen, Petroleum-to-Plastics Price Transmission, 2006

Exercícios

Quais os factores que influenciam o preço de venda de um polímero?

O preço dos polímeros é um dos factores que influencia o preço final de um produto acabado. No entanto outros factores podem influenciar o preço final. Indica por ordem crescente de dependência do custo do polímero os seguintes itens:

- Caixote do lixo de polietileno
- Meias de nylon
- Pente de nylon
- Pneu de automóvel
- Óculos de sol de acetato de celulose

Quais os factores que influenciam o preço de venda de um polímero?

Outros factores incluem:

- Aditivos ou outros ingredientes
- Custo de mão de obra
- Design
- Embalagem
- Distribuição

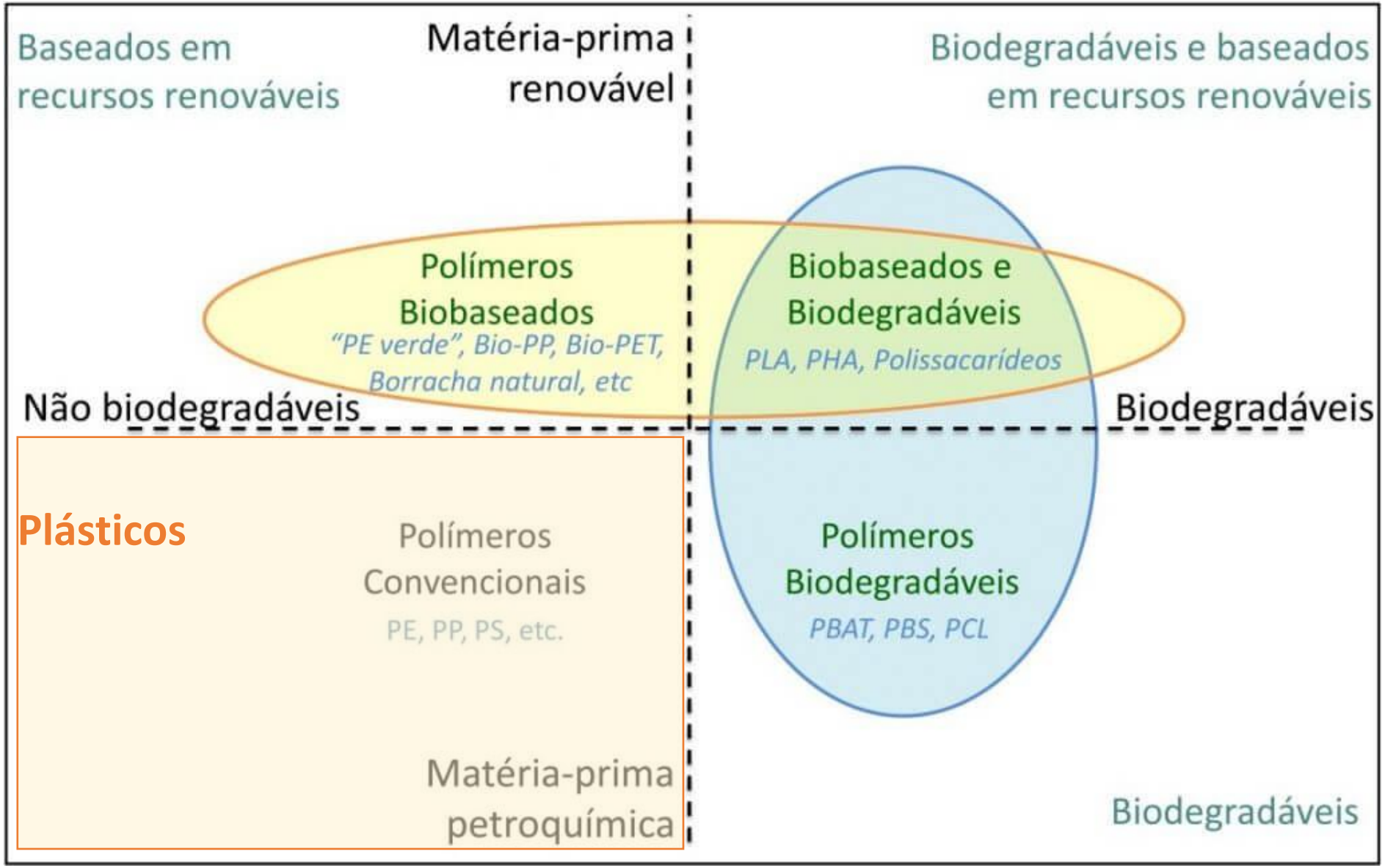
3. Caixote do lixo de polietileno
4. Meias de nylon
5. Pente de nylon
2. Pneu de automóvel
1. Óculos de sol de acetato de celulose

Vivemos rodeados de polímeros, mas já paramos para pensar sobre como é feito por exemplo um copo de café, qual é o material mais indicado, quais são as propriedades que tem que ter para ser adequado à função que vai desempenhar?

https://www.youtube.com/watch?v=xoIbPGFjQmM

Qual é a diferença entre um polímero e um plástico?

Classificação de polímeros



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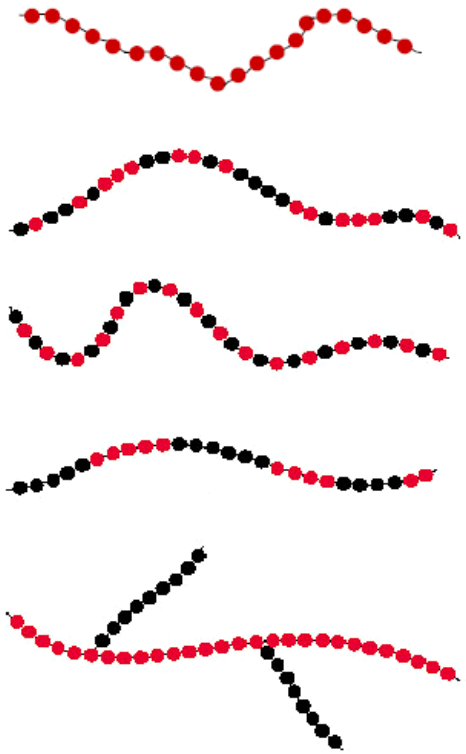
Definições e nomenclatura

Definições e Nomenclatura

Polímero – conjunto de unidades moleculares ligadas covalentemente entre si

Monómero – unidade repetitiva da cadeia macromolecular



Homopolímero – unidades repetitivas todas iguais

Copolímero aleatório

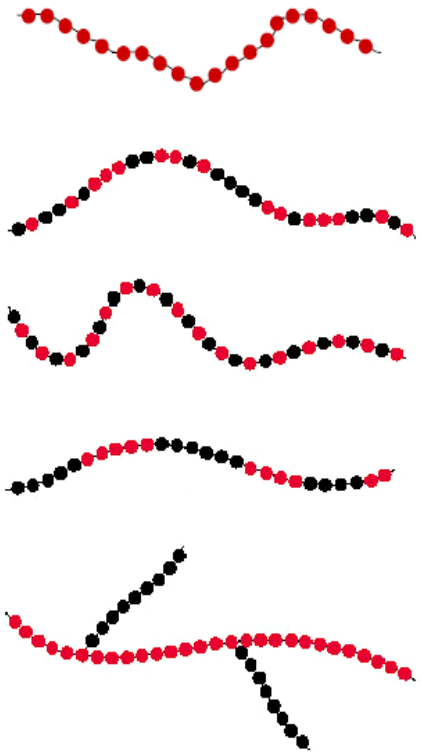
Copolímero alternado

Copolímero de blocos

Copolímero ramificado ou exertado

Copolímero – polímero formado por unidades repetitivas diferentes ligadas entre si covalentemente

Produção de copolímeros – surge da necessidade de produzir polímeros com propriedades específicas não conseguidas com a mistura física dos dois homopolímeros A e B



	Propriedades
Homopolímero	
Copolímero aleatório	Propriedades intermédias entre os homopolímeros A e B
Copolímero alternado	Propriedades ± intermédias entre os homopolímeros A e B
Copolímero de blocos	Propriedades intermédias entre os homopolímeros A e B,dependendo do tamanho das sequências/blocos de A e B
Copolímero ramificado ou exertado	Modificação das propriedades do homopolímero A

Exercícios

1. O que são homopolímeros e copolímeros?
2. Quais as diferenças entre copolímero aleatório e copolímero alternado.
3. Qual a motivação para a produção de copolímeros em substituição aos correspondentes homopolímeros?

Exercícios

4. Polímeros formados por mais de um tipo de unidade monomérica são chamados copolímeros. Um exemplo é o Nylon-66, no qual as unidades repetitivas são formadas por 1,6-diaminohexano (H2N(CH2)6NH2) e por ácido adípico (HOOC(CH2)4COOH).

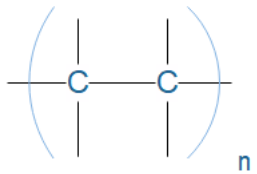
1 AAAABBBB 2 ABABABABAB 3 AABAABAB 4

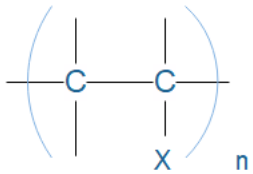
Identifique nas figuras de 1 a 4 os tipos de copolímeros formados pelos monómeros A e B.

A) 1 — ramificado, 2 — bloco, 3 — alternado e 4 — aleatório.
B) 1 — bloco, 2 — ramificado, 3 — aleatório e 4 — alternado.
C) 1 — bloco, 2 — alternado, 3 — aleatório e 4 — ramificado.
D) 1 — aleatório, 2 — bloco, 3 — ramificado e 4 — alternado.
E) 1 — alternado, 2 — ramificado, 3 — bloco e 4 — aleatório.

Nomenclatura

Etileno  monómero

 polímero



X	
—H	Polietileno
—CH_3	Polipropileno
—Cl	Policloreto de vinilo
	Poliestireno

Homopolímeros

Nomenclatura IUPAC

Poli (designação IUPAC da unidade repetitiva com a estrutura exacta)
Poly (designação IUPAC da unidade repetitiva com a estrutura exacta)

Ex: Poly (oxyspiro[3.5]nona-2,5-dien-7,1-ylene-4-cyclohexen-1,3-ylene)

Nomenclatura geral

Poli (nome do monómero) Poli (nome do monómero sem parêntesis)

Ex: Poli(propileno), Polipropileno, Polietileno
Abreviatura: PP PE

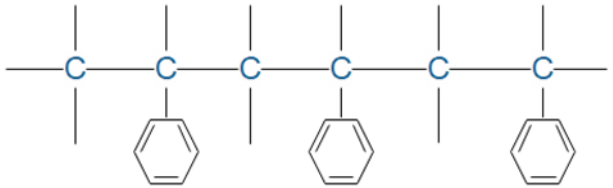
PVC - polyvinylchloride, policloreto de vinilo

PMMA – polymethylmethacrylate, polimetacrilato de metilo, poli(metacrilato de metilo)

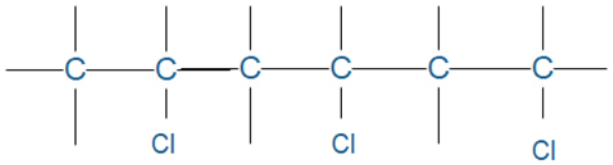
Nomes comerciais
NYLON – poliamida
TEFLON- politetrafluoretileno
TERYLENE – poliéster
PLEXIGLÁS – polimetacrilato de metilo
KEVLAR - poliaramida

5. Desenha uma secção de três unidades repetitivas dos seguintes polímeros:

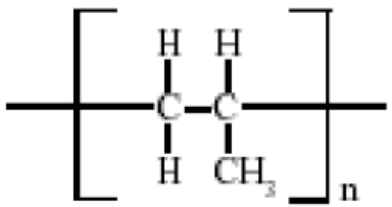
Poliestireno



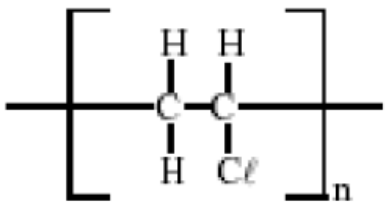
Policloreto de vinilo



6. Considere as fórmulas destes dois polímeros.



I

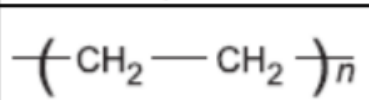
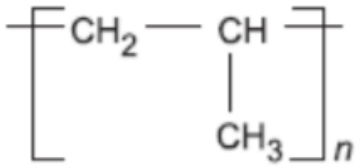
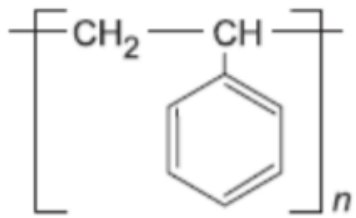
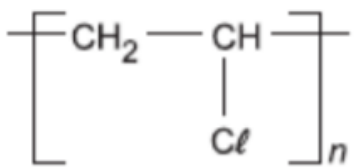


II

Os monómeros correspondentes aos polímeros **I** e **II** são, **respectivamente**,

A) propano e cloroetano.
B) propano e cloroeteno.
C) propeno e cloroetano.
D) propeno e cloroeteno.

7. Na tabela, são apresentadas algumas características de quatro importantes polímeros.

Polímero	Estrutura Química	Aplicações
X		Copos, sacos de plástico, embalagens de garrafas
Y		Fibras, cordas, assentos de cadeiras
Z		Embalagens descartáveis de alimentos, pratos
W		Tubos, filmes para embalagens

7.1. Polipropileno, poliestireno e polietileno são, respectivamente, os polímeros:

a) X, Y e Z.

b) X, Z e W.

c) Y, W e Z.

d) Y, Z e X.

e) Z, Y e X

7.2. Identifica o polímero W

Polímero ou não…

Sal	Esferovite	DNA
Cabelo	Unhas de gel	Ferro
Açúcar	Papel	Neon
Nylon	Vinagre	Músculos
Bicarbonato de sódio	Seda	Slime
Vidro	Lã	Polietileno
Madeira	Ouro	Prata