THEORETICAL AND EXPERIMENTAL EXPLORATION OF ORGANIC SYNTHESIS ROUTES TO OBTAIN NATURAL RUBBER ANALOGUES

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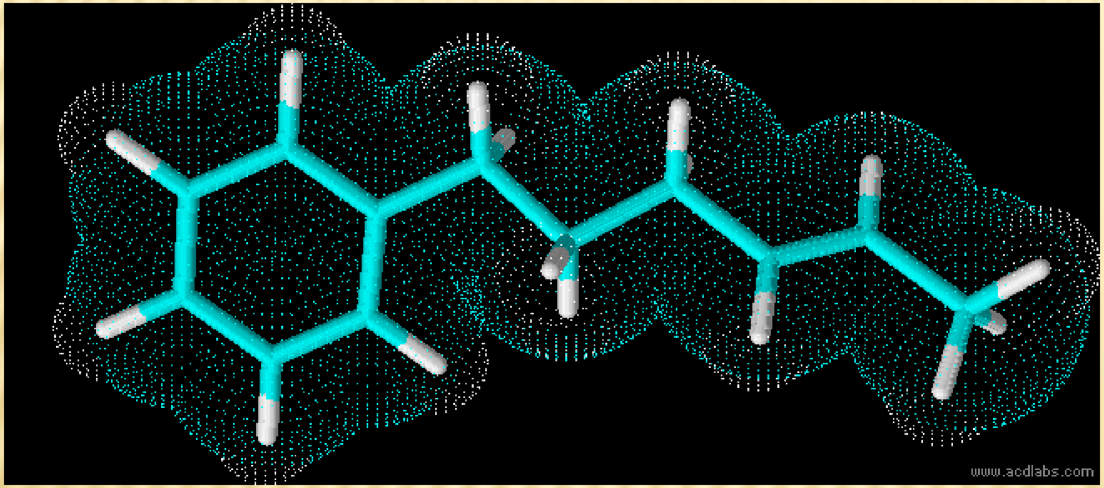
INTRODUCTION



ISSUE

National Industry requires synthetic compounds with a high molecular weight to replace natural rubber with its elasticity, resistency, softness and resilience properties among others.

It has theoretical tools that are not normally used in the national industry when the predictability potential they have is not known. The use of these tools in leading countries, has encouraged the development of these new technologies and their application to this industry could prompt more lights on how to improve processes.

In this work, the polymers synthesis processes are taken from dienes to obtain compounds similar to E-polyisoprene or natural rubber as a starting point for a theoretical study, using a semi-empirical calculation method and the theory of punctual groups applied to chemistry.

JUSTIFICATION

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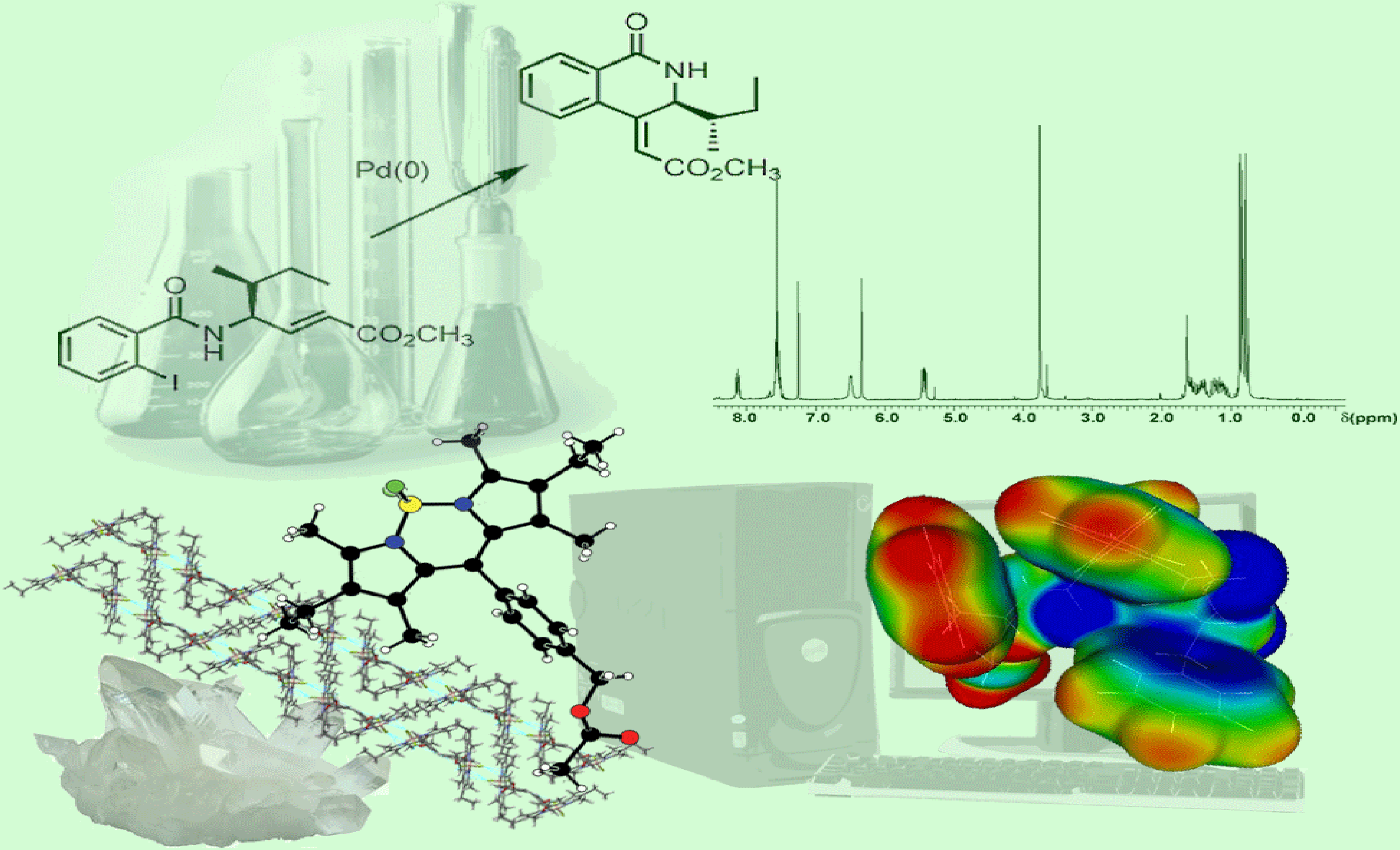


OBJECTIVES

- **General**

  To explore in a theoretical and experimental way, possible organic synthesis routes to obtain one or more compounds with analogous properties to natural rubber.

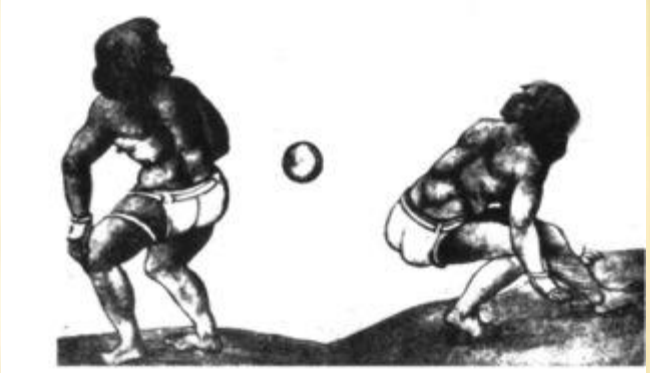
- **Specific**

- Design of synthesis routes for different monomeric units involved in the polymer obtainment.
- Theoretical determination of conditions to obtain the polymer(s) of interest.
- Design of synthesis routes for the polymer(s) of interest.
- Synthesis of polimer(s) of interest based on theoretical and computational studies previously carried out.

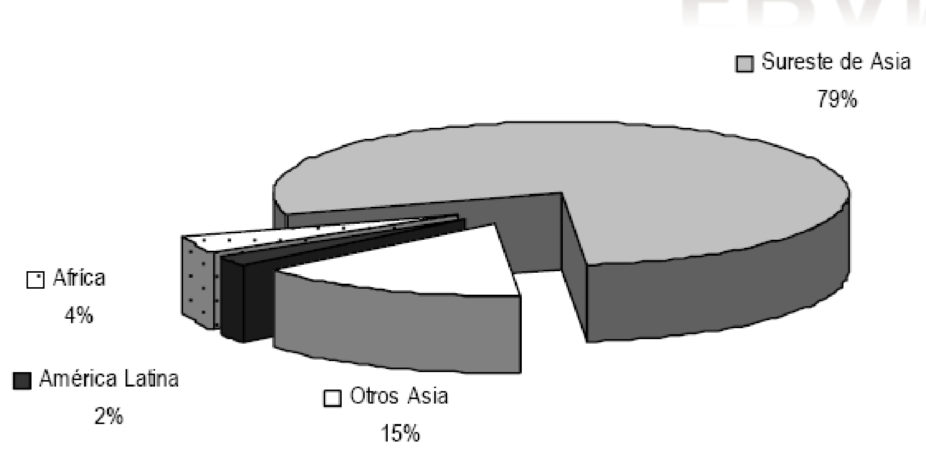
FRAMEWORK

- Natural Rubber
  - Used by ancient Mesoamerican

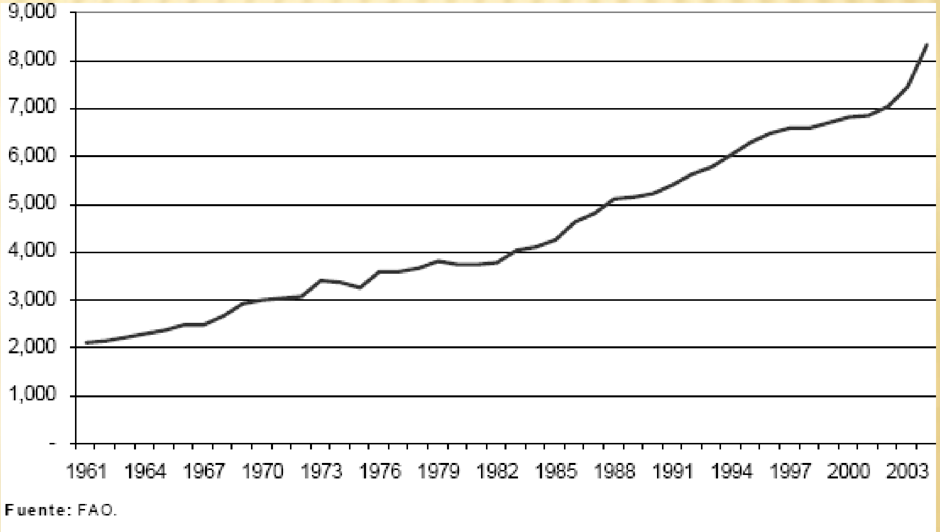
Elastic castile



FRAMEWORK

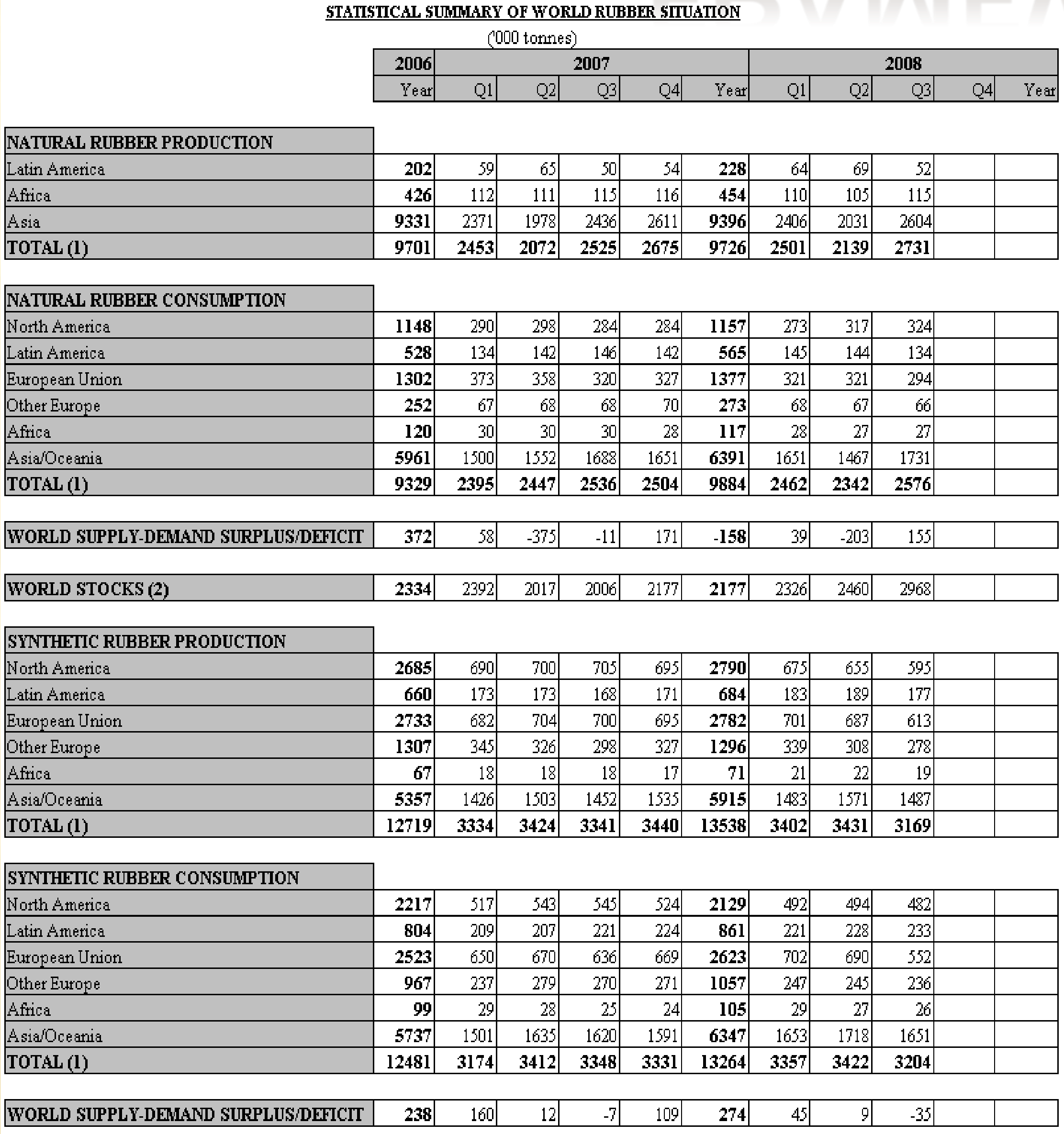


Taken from *International Rubber Study Group. Distribution of natural rubber global production in 2004*.



Ftaken from *http://www.rubberstudy.com/statistics-quarstat.aspx.* Statistics summary of world rubber situation

FRAMEWORK



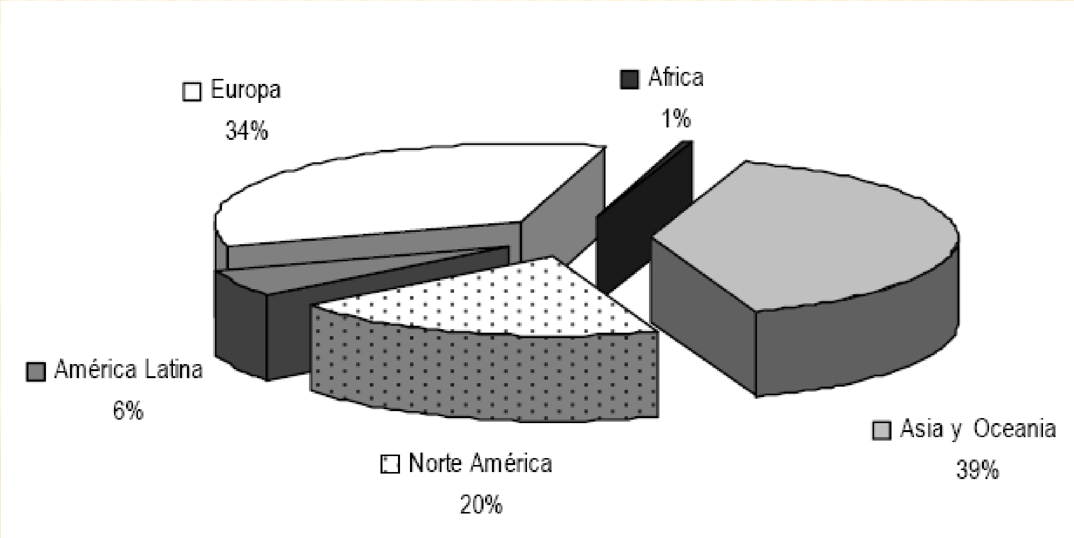
STATISTICAL SUMMARY OF WORLD RUBBER SITUATION

('000 tonnes)

	2006	2007					2008				
	Year	Q1	Q2	Q3	Q4	Year	Q1	Q2	Q3	Q4	Year
NATURAL RUBBER PRODUCTION											
Latin America	**202**	59	65	50	54	**228**	64	69	52		
Africa	**426**	112	111	115	116	**454**	110	105	115		
Asia	**9331**	2371	1978	2436	2611	**9396**	2406	2031	2604		
TOTAL (1)	**9701**	**2453**	**2072**	**2525**	**2675**	**9726**	**2501**	**2139**	**2731**		
NATURAL RUBBER CONSUMPTION											
North America	**1148**	290	298	284	284	**1157**	273	317	324		
Latin America	**528**	134	142	146	142	**565**	145	144	134		
European Union	**1302**	373	358	320	327	**1377**	321	321	294		
Other Europe	**252**	67	68	68	70	**273**	68	67	66		
Africa	**120**	30	30	30	28	**117**	28	27	27		
Asia/Oceania	**5961**	1500	1552	1688	1651	**6391**	1651	1467	1731		
TOTAL (1)	**9329**	**2395**	**2447**	**2536**	**2504**	**9884**	**2462**	**2342**	**2576**		
WORLD SUPPLY-DEMAND SURPLUS/DEFICIT	**372**	58	-375	-11	171	**-158**	39	-203	155		
WORLD STOCKS (2)	**2334**	2392	2017	2006	2177	**2177**	2326	2460	2968		
SYNTHETIC RUBBER PRODUCTION											
North America	**2685**	690	700	705	695	**2790**	675	655	595		
Latin America	**660**	173	173	168	171	**684**	183	189	177		
European Union	**2733**	682	704	700	695	**2782**	701	687	613		
Other Europe	**1307**	345	326	298	327	**1296**	339	308	278		
Africa	**67**	18	18	18	17	**71**	21	22	19		
Asia/Oceania	**5357**	1426	1503	1452	1535	**5915**	1483	1571	1487		
TOTAL (1)	**12719**	**3334**	**3424**	**3341**	**3440**	**13538**	**3402**	**3431**	**3169**		
SYNTHETIC RUBBER CONSUMPTION											
North America	**2217**	517	543	545	524	**2129**	492	494	482		
Latin America	**804**	209	207	221	224	**861**	221	228	233		
European Union	**2523**	650	670	636	669	**2623**	702	690	552		
Other Europe	**967**	237	279	270	271	**1057**	247	245	236		
Africa	**99**	29	28	25	24	**105**	29	27	26		
Asia/Oceania	**5737**	1501	1635	1620	1591	**6347**	1653	1718	1651		
TOTAL (1)	**12481**	**3174**	**3412**	**3348**	**3331**	**13264**	**3357**	**3422**	**3204**		
WORLD SUPPLY-DEMAND SURPLUS/DEFICIT	**238**	160	12	-7	109	**274**	45	9	-35		

Synthetic Rubber

- C.Schonbein (1846) Nitrocellulose
- A.Hofmann (1907) First synthetic rubber (Conjugated dienes)
- World war two ID Increase of new polymers
- Did not replace natural rubber completely
  - Radial tires, footwear, condoms



Taken from *International Rubber Study Group. . Distribution of natural rubber global production in 2004*..

Polimerization types

- Condensation

Polyester

- Ionic
  - Anionic

Poly(acrylonitrile)

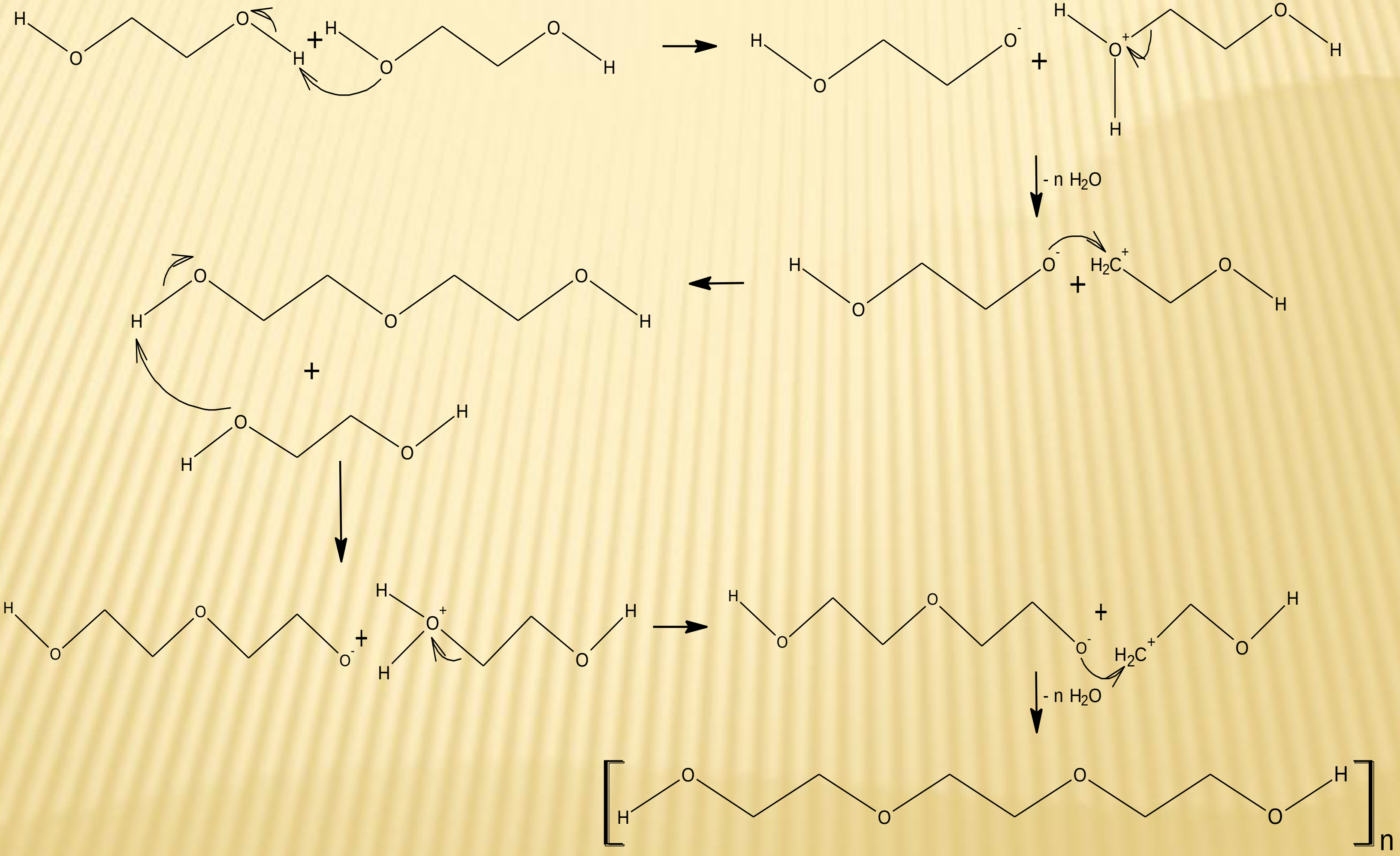
  - Cationic

Poly(isobutene)

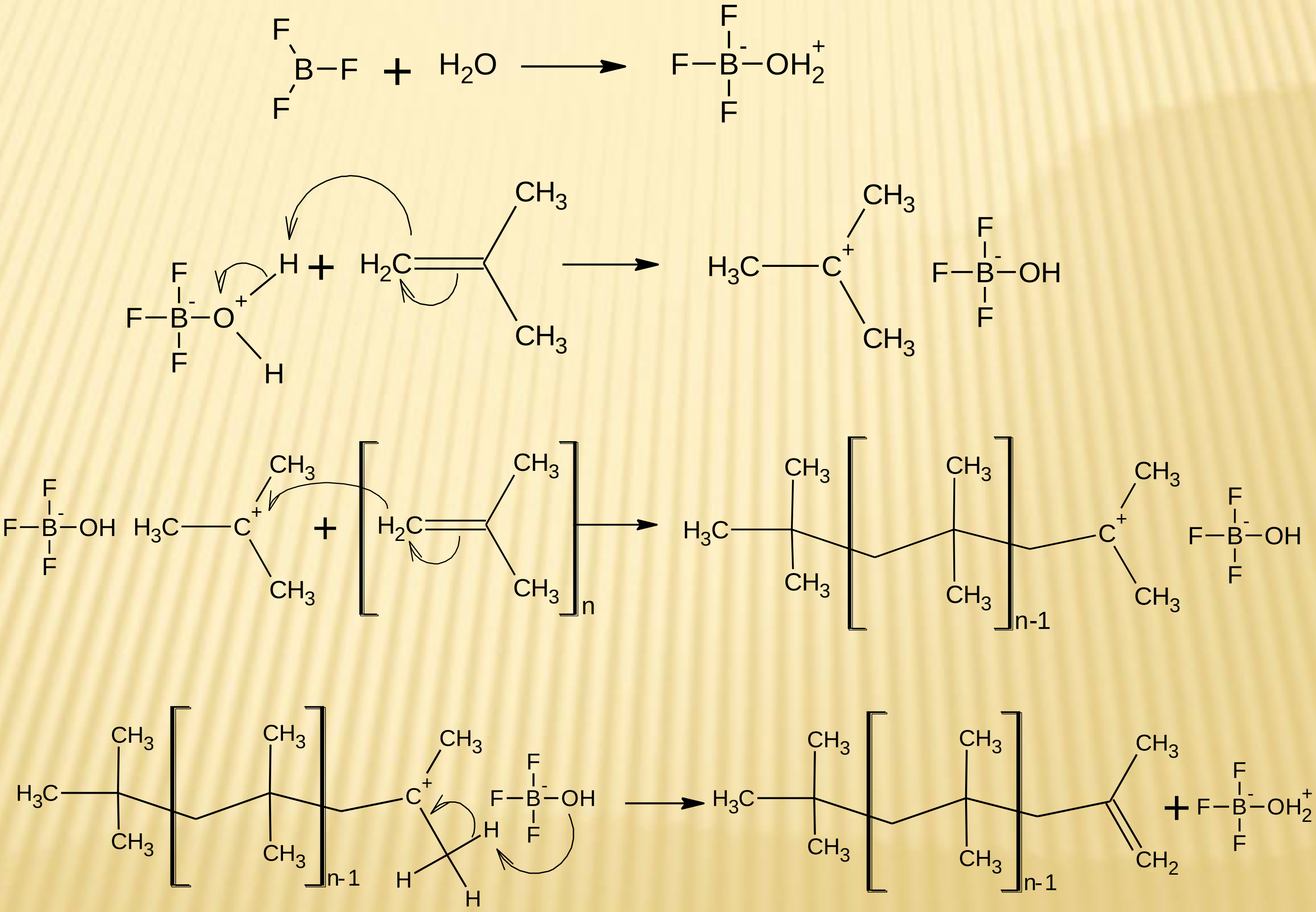
- Free Radicals

Synthetic rubber

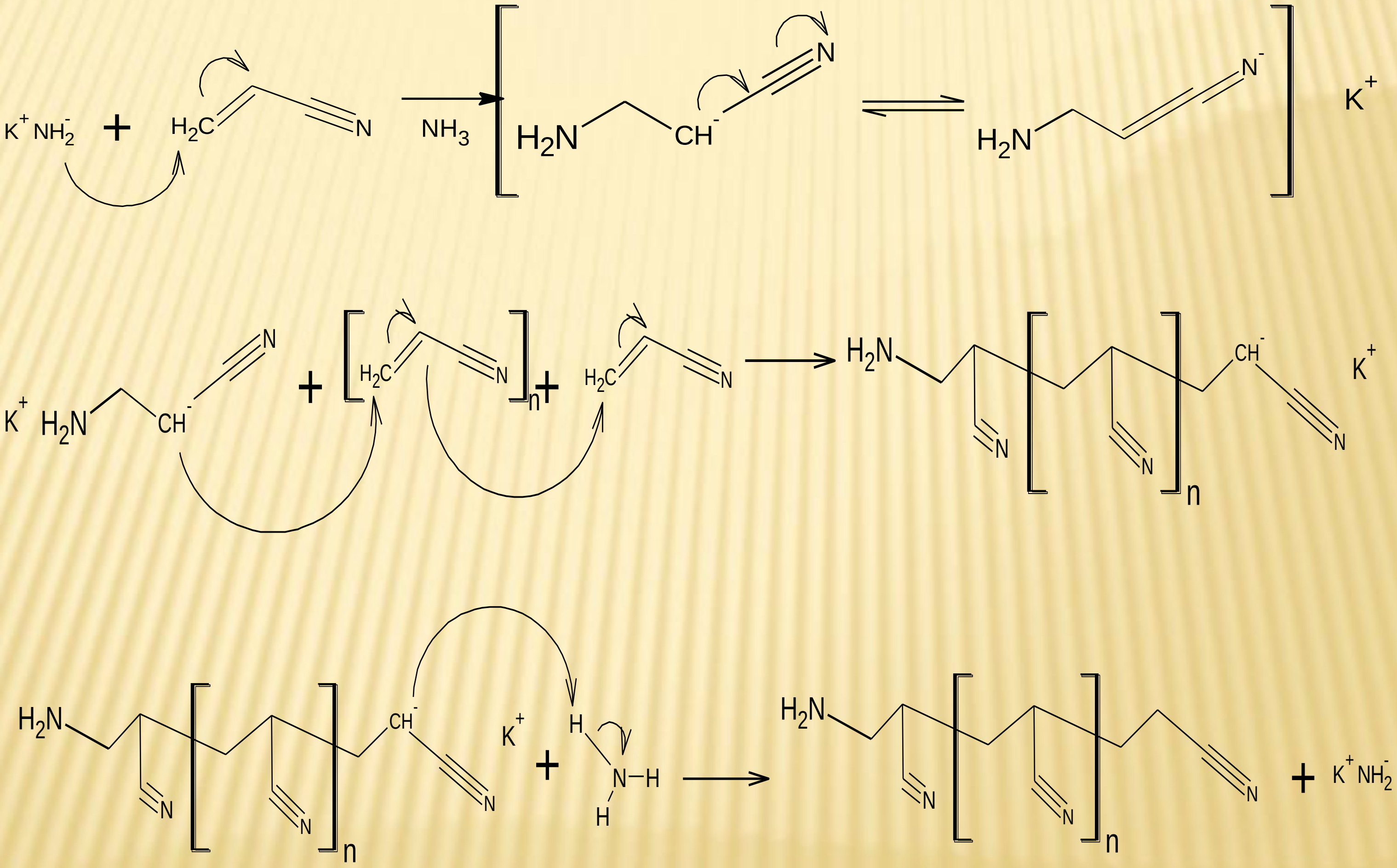
Condensation



Cationic



Anionic


$K^+ NH_2^-$
+
H_2C
N
NH_3
H_2N
CH^-
N
H_2N
N^-
K^+
K^+
H_2N
CH^-
N
+
H_2C
N
n
+
H_2C
N
H_2N
N
N
n
CH^-
N
K^+
H_2N
N
N
n
CH^-
N
K^+
+
H
N–H
H
H_2N
N
N
n
N
+
$K^+ NH_2^-$

Polymerization Means

- Emulsion

SBR

- Suspension

Poly(Vinylacrylate)

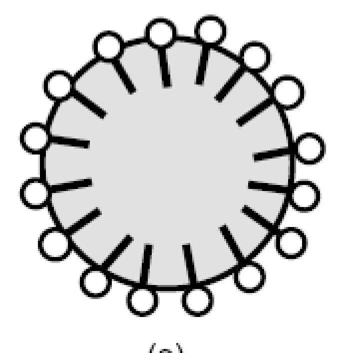
- Solution

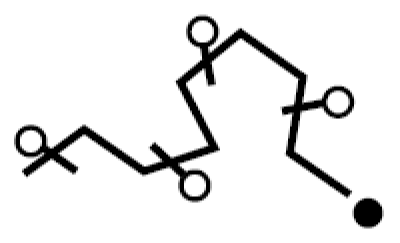
- “Bulk”

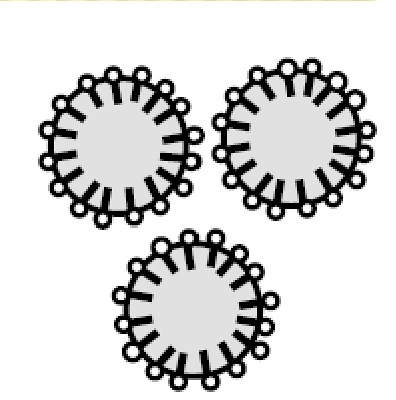
Poly(methylmethacrylate)

Emulsion

- Virtualy occurs in nanoreactors (micelles)
  - Water (Non-polluting)
    - Good heat dissipater
  - Water Soluble Initiator
  - Slightly water soluble Monomers
  - Emulsificant
- A colloidal dispersion of water polymer is produced.
- There is not precipitation

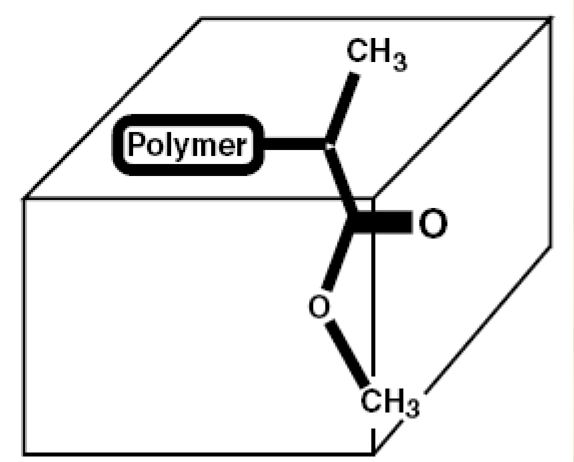

(a)

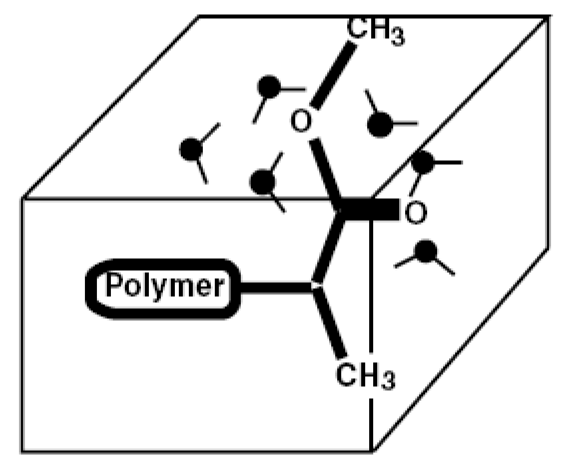

(b)


(c)

Solution

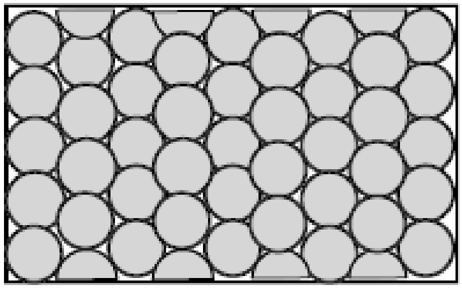
- Low viscosity obtained solutions
- Avoids interweaving
- Low reaction rate and low molecular weight
- The solvent acts as chain transfer agent
- Easy polymer extraction
- Precipitation may occur

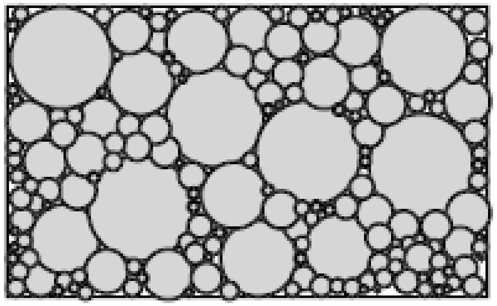




Suspension

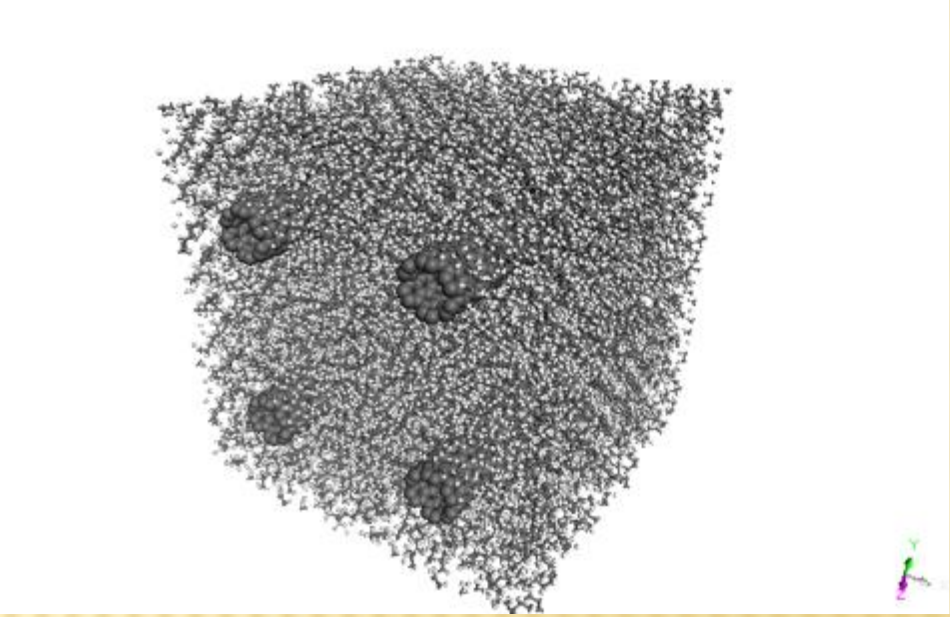
- Dispersed monomers by strong agitation
- Both monomer and polymer are insoluble in dispersing medium
- Polymerization occurs while dispersion
- Soluble initiator (peroxides generally)
- Aqueous phase
    - Heat exchange


(a)


(b)

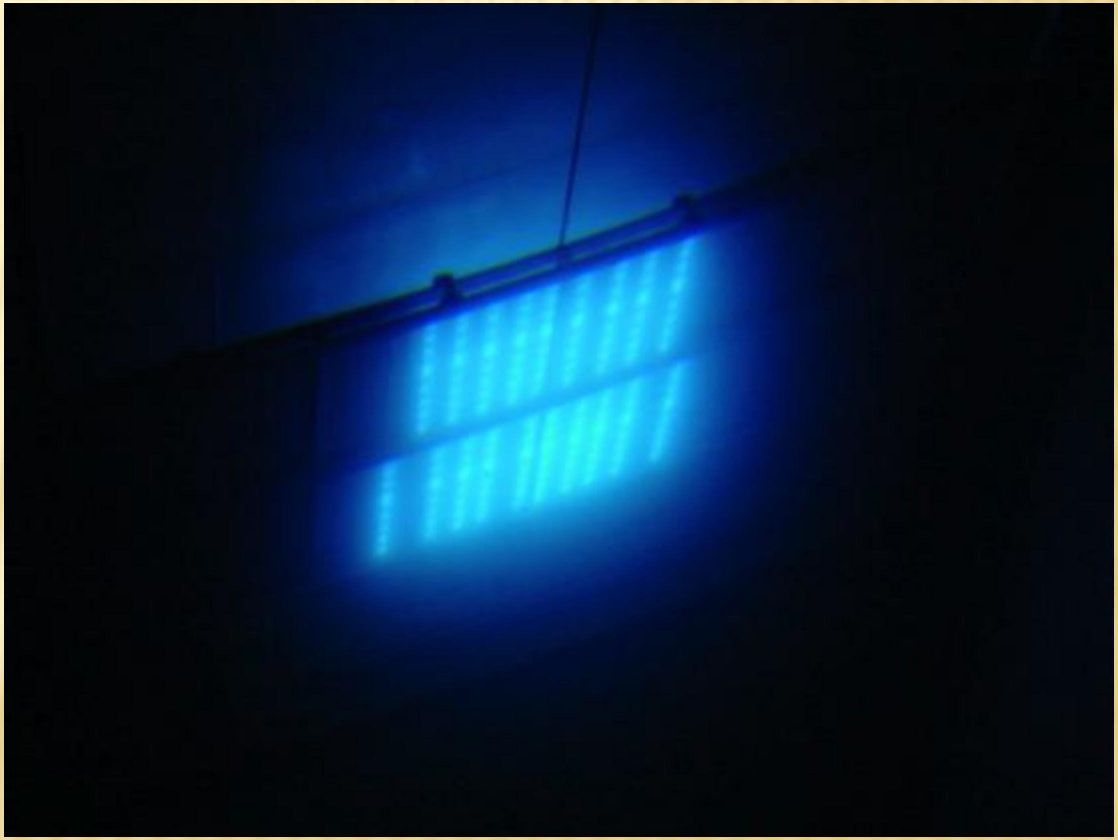
“Bulk”

- Conversion of monomers in polymers by heat or radiation
- Monomers: liquid, solid or gas
- Do not use solvents or dispersing medium
- It is not industrially important (small-scale)



Radiopolymerization

- Uses an ionizing radiation source
- Induces free radicals when initiating polymerization



Gamma radiation source ^{60}Co

Photopolymerization

- Used in dental medicine
- Camphoroquinone (photoinitiator agent)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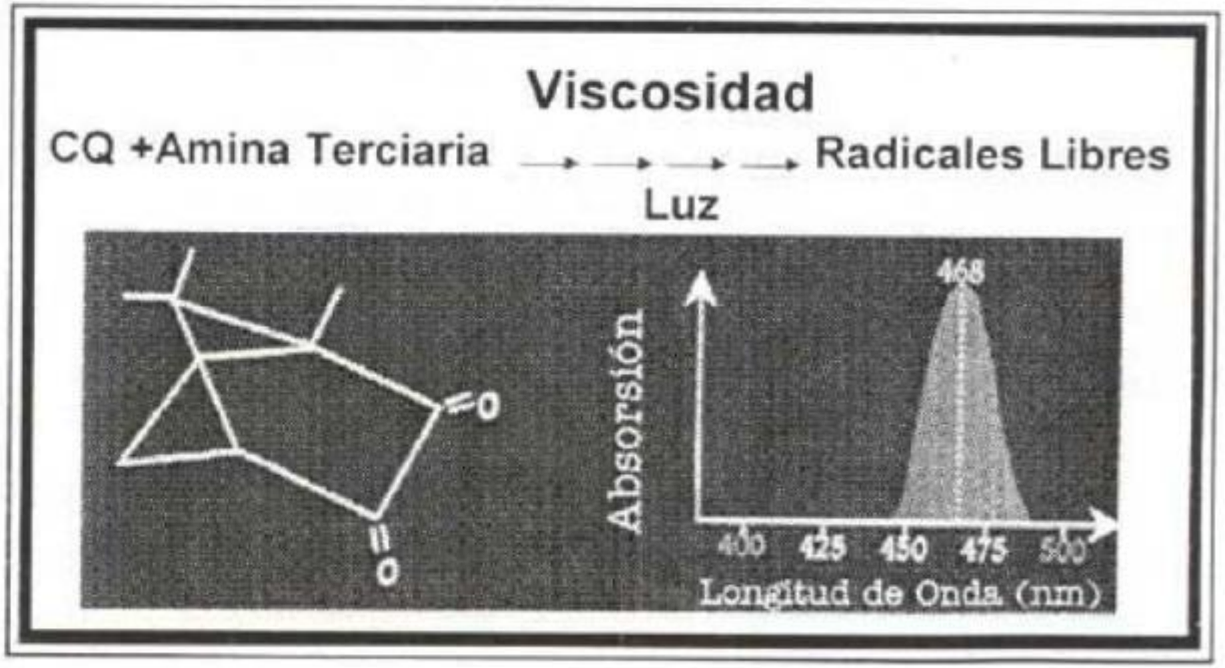


Vulcanization

- Treatment applied to rubber (natural and synthetic)
- Generally with S, compounds with S or peroxides among others (based on its final usage)
- Crosslinking creation

→

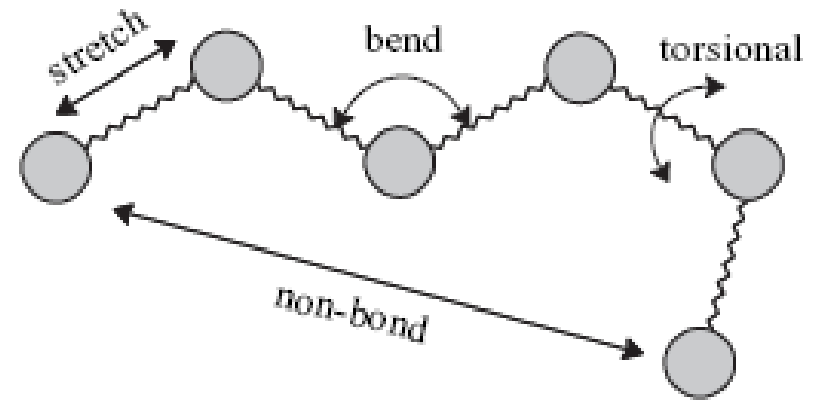
Vulcanización

- Computational Methods
  - Force Field
  - Semi-Empirical Methods
    - MNDO
    - AM1
    - PM3

Force Field Energy

- The electron energy is a parametric function of nuclear coordinates
- Dynamic treatment is relized with classic mechanic tools.
- Minimum energy in surface potential is sought translated in a more stable geometry.

$$E_{\mathrm{FF}} = E_{\mathrm{str}} + E_{\mathrm{bend}} + E_{\mathrm{tors}} + E_{\mathrm{vdw}} + E_{\mathrm{el}} + E_{\mathrm{cross}}$$



Semi-empirical methods

- Decrease of computational cost
- Use data obtained experimantally
- It has into account only valence electrons
- They are parameterized
  - MNDO (*Modiffed Neglect of Diatomic Overlap*) (*s, p(px, py, pz))*
    - First model (aproximation of two integral electrons)
    - Problems with predictions
      - Hydrogen bridges
      - Low ΔH_f reliability
  - AM1 (Austin Model 1) (S, P(px, py, pz))
    - Uses a modification of nuclear expresion
    - Description of hydrogene bridges
    - Aproximations overexploitation
    - Adds repulsion function
  - PM3 (Parametric Model 3) (*s, p(px, py, pz),/d)*
    - Similar to AM1, but different parametrization
    - Better thermochemical properties prediction
    - Problems with
- Studied molecule ≈ parametrized molecules, reliable results

METHODOLOGY

PHASE ONE
- LITERATURE REVIEW
- EXPERIMENTAL EXPLORATION

PHASE TWO
- TECHNICAL STUDY OF POSSIBLE SYNTHESIS ROUTES
- DESIGN OF POSSIBLE SYNTHESIS ROUTES

PHASE THREE
- EXPERIMENTAL TESTING OF SYNTHESIS ROUTES

PHASE FOUR
- FINAL REPORT

RESULTS AND ANALYSIS

PHASE ONE

- Obtainment of n-butene

H_2SO_4 (98%)

Heat

175° C-180° C

Dropwise add

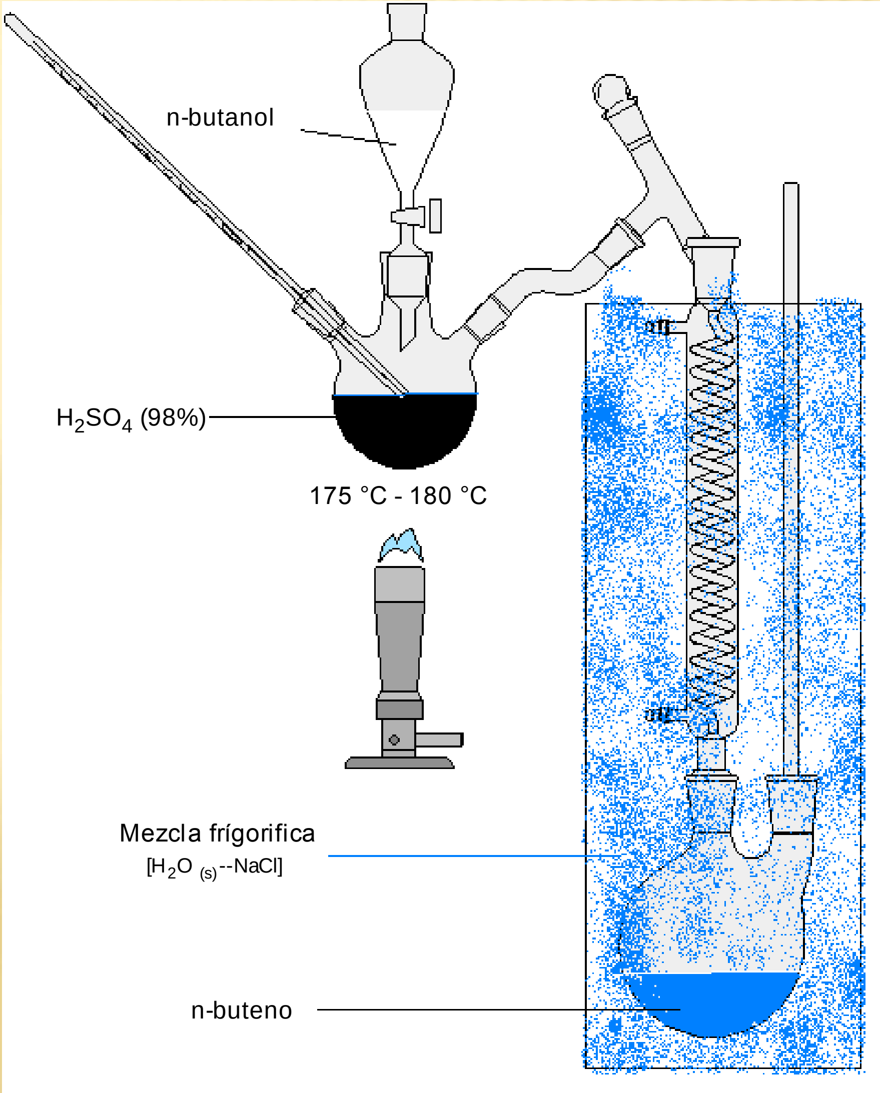
n-butanol

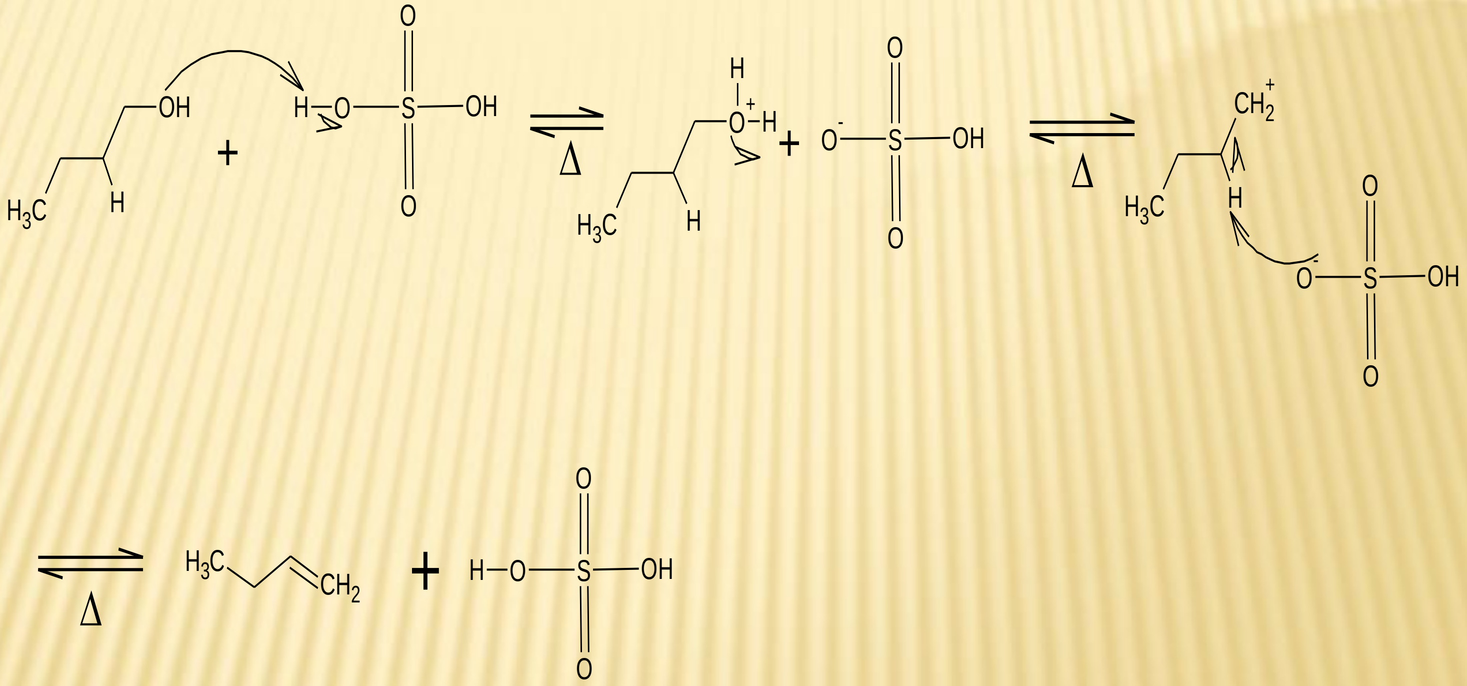
Collect in

Frigorífic mixture

According to

Diagram





Rection mechanism to dehidrate n-butanol

PHASE TWO

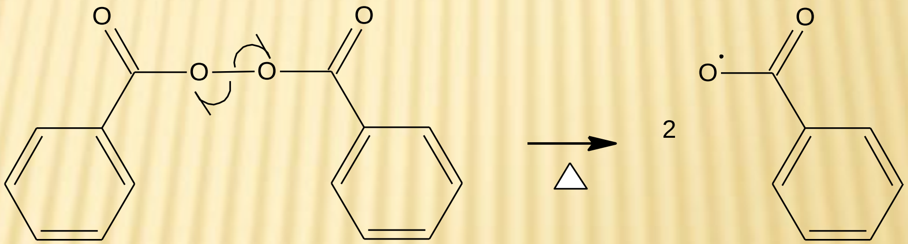
- Theoretical study of possible synthesis routes by semiempirical methods.

  Condensation.

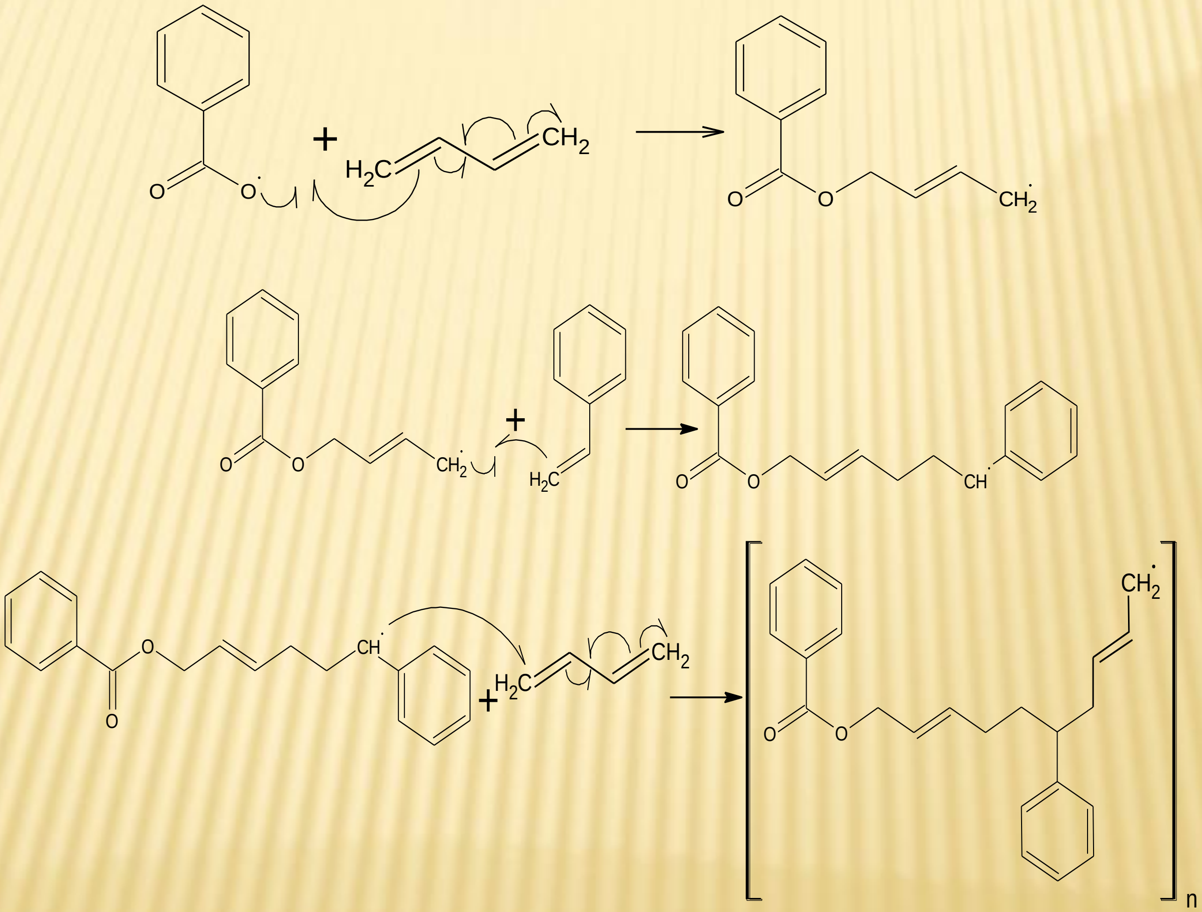
  - Ionic
    - Cationic
    - Anionic
  - Free Radicals

Polimerization by free radicals

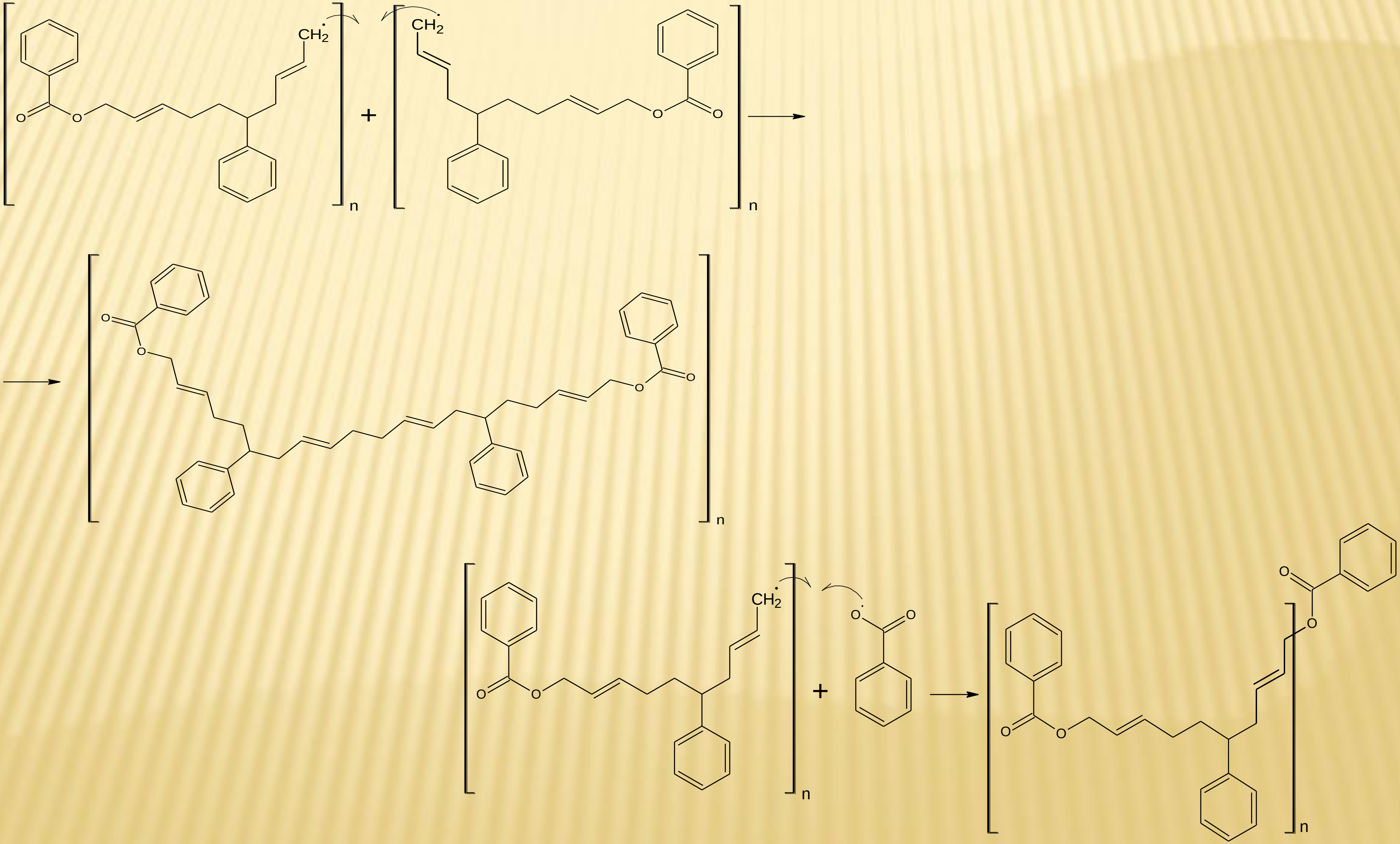
- Iniciation



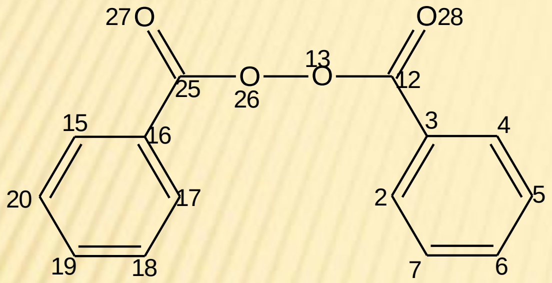
- Propagation



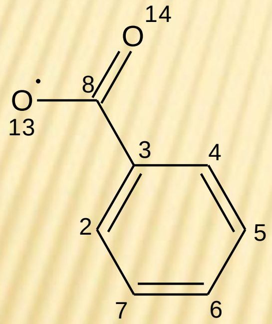
- Finalization



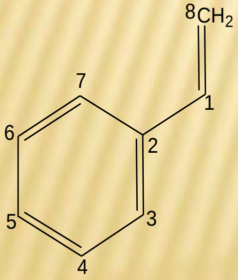
Values of HOMO and LUMO orbitals



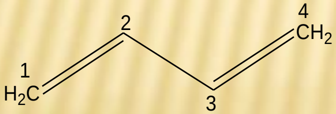
peroxido de benxoilo		Orbitales	
N° atomo	Atomo	HOMO	LUMO
12	C	-0.00108	0.31809
13	O	-0.01689	-0.10687
25	C	0.00037	0.08477
26	O	0.01835	-0.00781
27	O	0.06258	-0.07301
28	O	0.00466	-0.28112



radical oxidanilo (fenilcarbonil)		Orbitales	
N° atomo	Atomo	HOMO	LUMO
3	C	-0.00012	-0.32957
8	C	-0.00298	-0.59240
13	O	0.00258	0.27140
14	O	-0.00389	0.42479



estireno



1,3-butadieno

estireno		Orbitales	
N° atomo	Atomo	HOMO	LUMO
1	C	-0.32554	-0.29831
2	C	0.45588	-0.46489
3	C	0.29950	0.30725
4	C	-0.19624	0.20270
5	C	-0.45539	-0.47282
6	C	-0.18323	0.19400
7	C	0.30632	0.31038
8	C	-0.47244	0.44930

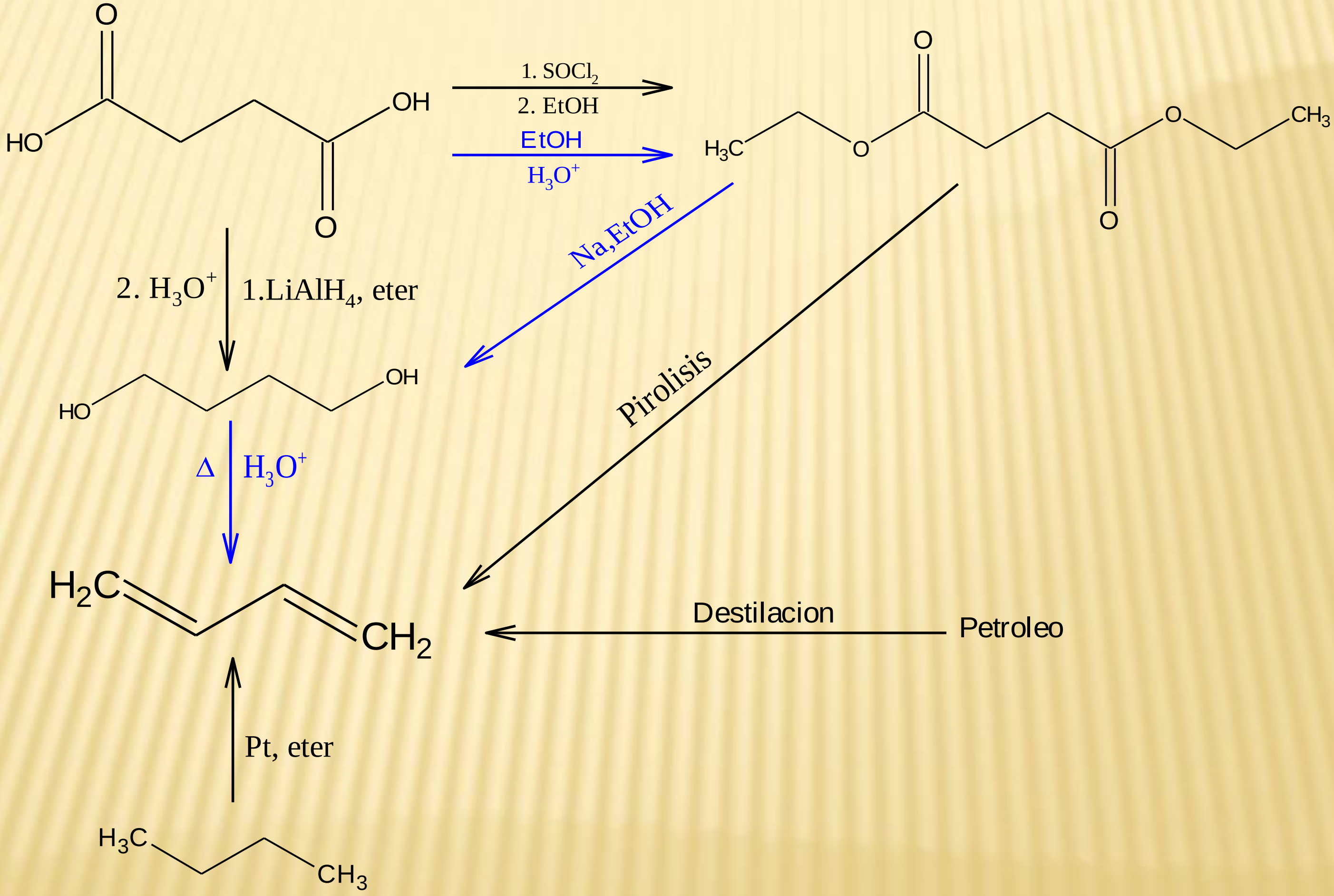
1,3-butadieno		Orbitales	
N° atomo	Atomo	HOMO	LUMO
1	C	0.55776	0.56016
2	C	0.42639	-0.42306
3	C	-0.42713	-0.42420
4	C	-0.55961	0.56195

Theoretical study of possible synthesis routes by groups theory

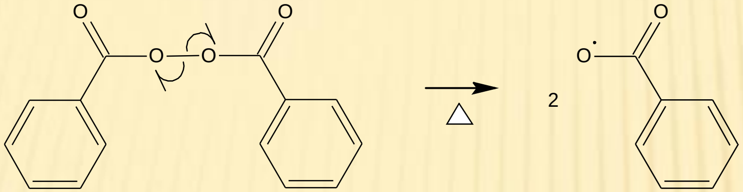
- Polyestirene obtainment
  - Phenylcarbonyl radical obtainment from a thermical decomposition of benzoyl peroxide.
  - Radical 1-phenyl-2-oxi(phenylcarbonyl)]etilo obtainment from phenylcarbonyl radical and styrene. *[Chain propagation].*
  - Polystyrene obtainment from two growing chains and, a growing chain and the phenylcarbonyl radical. *[ending]*

SBR obtainment

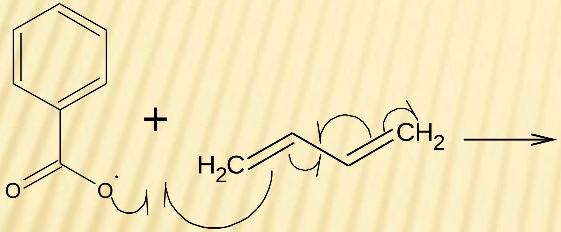
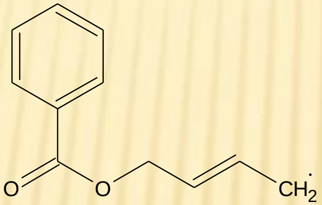
1,3-butadiene obtainment



Reaction mechanism to obtain SBR

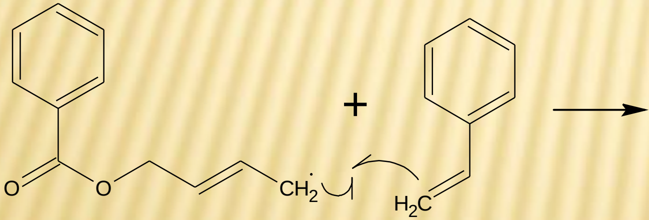
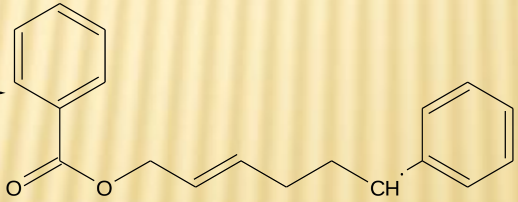


INICIATION

radical (2E)-4-[oxy(phenylcarbonyl)]-2-buten-1-ilo

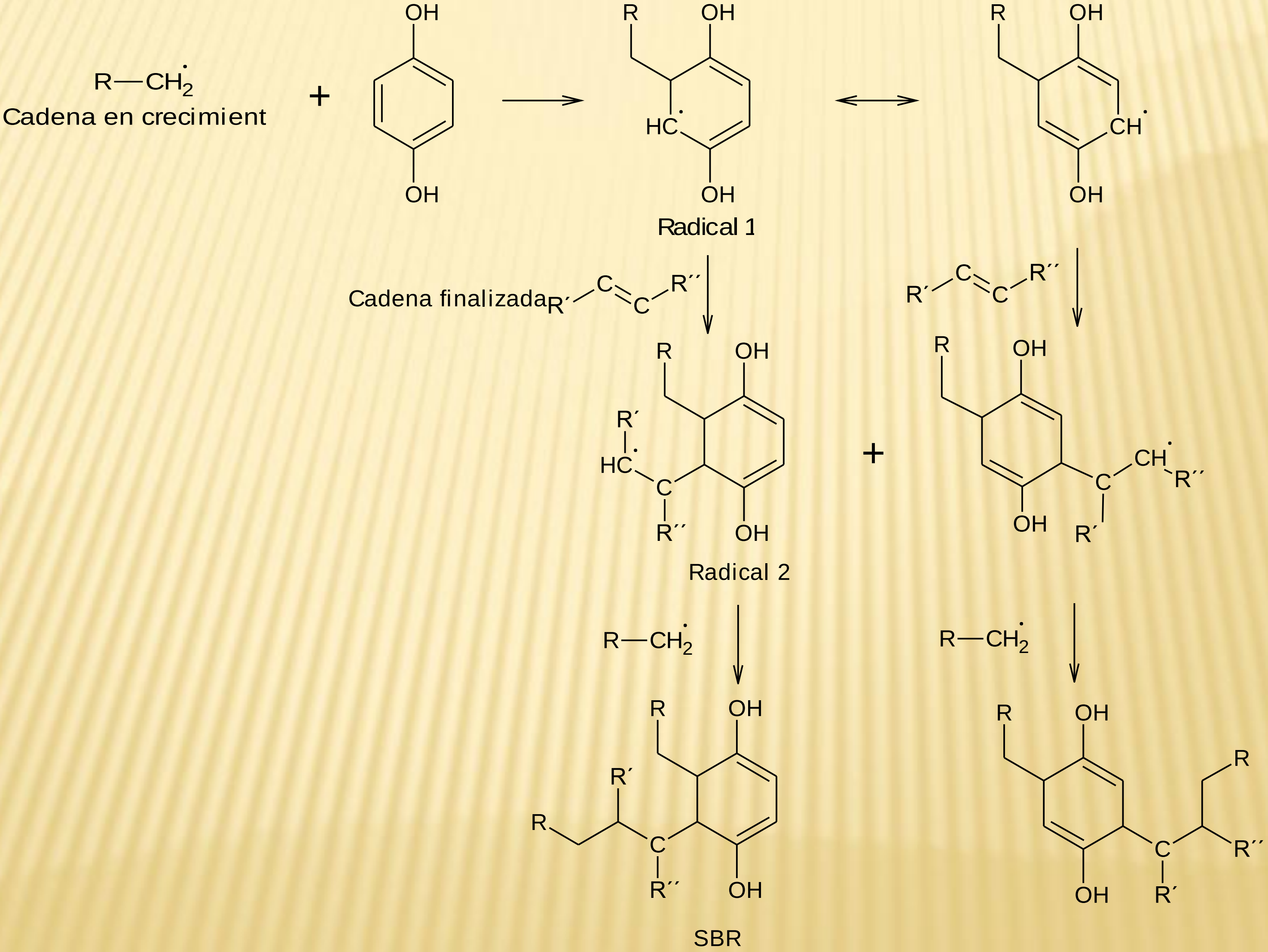
PROPAGATION

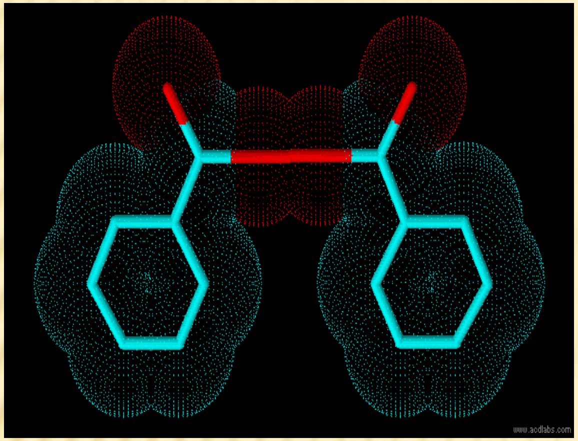
radical (2E)-6-fenil-1-[oxi(phenylcarbonyl)]-2-hexen-6-ilo

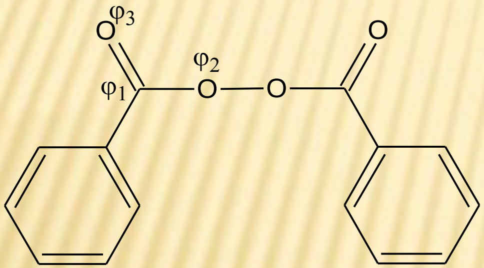
Growing chain

FINALIZATION AND CROSSLINKING



Benzoyl peroxide





Cs	E	δ_h
A`	1	1
A``	1	-1

Reduced Group

Cs	E	δ_h
Γ_{tota}	3	-3

A`: ½ {(1*1*1*3) + (1*-1*1*-3)} = 0
A``: ½ {(1*1*1*3) + (1*-1*1*-3) = 3

Projection operators

$$PA``\varphi_1 = (1)\,E\,\varphi_1 + (-1)\,\delta_h\,\varphi_1$$
$$= \varphi_1 + \varphi_1 = 2\varphi_1 \approx \varphi_1$$

$$PA``\varphi_2 = (1)\,E\,\varphi_2 + (-1)\,\delta_h\,\varphi_2$$
$$= \varphi_2 + \varphi_2 = 2\varphi_2 \approx \varphi_2$$

$$PA``\varphi_3 = (1)\,E\,\varphi_3 + (-1)\,\delta_h\,\varphi_3$$
$$= \varphi_3 + \varphi_3 = 2\varphi_3 \approx \varphi_3$$

Secular equation

$$A`` = \int \phi 1\,(H-E)\,\phi 1\,d_\Gamma + \int \phi 1\,(H-E)\,\phi 2\,d_\Gamma + \int \phi 1\,(H-E)\,\phi 3\,d_\Gamma$$
$$= H_{11} - E + H_{12} - ES_{12} + H_{13} - ES_{13}$$

$$A`` = \int \phi 2\,(H-E)\,\phi 1\,d_\Gamma + \int \phi 2\,(H-E)\,\phi 2\,d_\Gamma + \int \phi 2\,(H-E)\,\phi 3\,d_\Gamma$$
$$= H_{21} - ES_{21} + H_{22} - E + H_{23} - ES_{23}$$

$$A`` = \int \phi 3\,(H-E)\,\phi 1\,d_\Gamma + \int \phi 3\,(H-E)\,\phi 2\,d_\Gamma + \int \phi 3\,(H-E)\,\phi 3\,d_\Gamma$$
$$= H_{31} - ES_{31} + H_{32} - ES_{32} + H_{33} - E$$

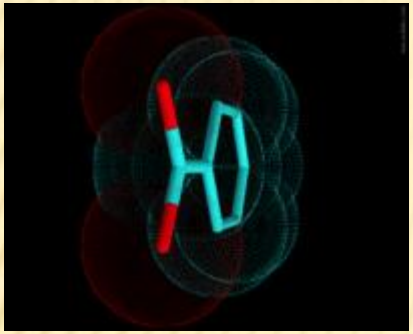
$$A`` = \begin{vmatrix} H_{11}-E & H_{12}-ES_{12} & H_{13}-ES_{13} \\ H_{21}-ES_{21} & H_{22}-E & H_{23}-ES_{23} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-E \end{vmatrix} = \begin{vmatrix} \overset{\alpha}{H_{11}-E} & \overset{\beta}{H_{12}} & \overset{\beta}{H_{13}} \\ \overset{\beta}{H_{21}} & \overset{\alpha}{H_{22}-E} & \overset{0}{H_{23}} \\ \overset{\beta}{H_{31}} & \overset{0}{H_{32}} & \overset{\alpha}{H_{33}-E} \end{vmatrix} = 0$$

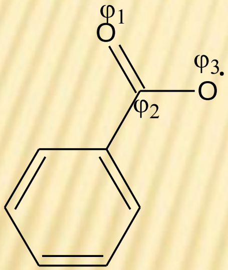
Replacing according Hûckel aproximation and solving matrix

$$A`` = \begin{vmatrix} -E & 1 & 1 \\ 1 & -E & 0 \\ 1 & 0 & -E \end{vmatrix} = 0 \Rightarrow -E^3 + 2E = 0$$

$E_1 = 0$; $E_2 = 1.44$; $E_3 = -1.44$

Phenylcarbonyl radical





C_2v	δyz	δxz	C_2	E
A_1	1	1	1	1
A_2	-1	-1	1	1
B_1	-1	1	-1	1
B_2	1	-1	-1	1

Reduced Groups

C_2v	δyz	δxz	C_2	E
Γ_{tota}	1	-3	-1	3

A_1: ¼ {(1*1*1*1) + (1*-3*1*1) + (1*-1*1*1) + (1*3*1*1)} = 0
A_2: ¼ {(1*1*1*-1) + (1*-3*1*-1) + (1*-1*1*1) + (1*3*1*1)} = 1
B_1: ¼ {(1*1*1*-1) + (1*-3*1*1) + (1*-1*1*-1) + (1*3*1*1)} = 0
B_2: ¼ {(1*1*1*1) + (1*-3*1*-1) + (1*-1*1*-1) + (1*3*1*1)} = 2
$\Gamma = 1\ A_2 + 2\ B_2 \approx A_2 + B_2$

Projection Operators

$PA_2\varphi_1 = (-1)\ \delta yz\ \varphi_1 + (-1)\ \delta xz\ \varphi_1 + (1)\ C_2\ \varphi_1 + (1)\ E\ \varphi_1$
$= -\ \varphi_3 + \varphi_1 - \varphi_3 + \varphi_1 = 2\varphi_1 - 2\varphi_3 \approx \varphi_1 - \varphi_3 = \psi_1$

$PB_2\varphi_1 = (1)\ \delta yz\ \varphi_1 + (-1)\ \delta xz\ \varphi_1 + (-1)\ C_2\ \varphi_1 + (1)\ E\ \varphi_1$
$= \varphi_3 + \varphi_1 + \varphi_3 + \varphi_1 = 2\varphi_1 + 2\varphi_3 \approx \varphi_1 + \varphi_3 = \psi_2$

$PA_2\varphi_2 = (-1)\ \delta yz\ \varphi_2 + (-1)\ \delta xz\ \varphi_2 + (1)\ C_2\ \varphi_2 + (1)\ E\ \varphi_2$
$= -\ \varphi_2 + \varphi_2 - \varphi_2 + \varphi_2 = 0$

$PB_2\varphi_2 = (1)\ \delta yz\ \varphi_2 + (-1)\ \delta xz\ \varphi_2 + (-1)\ C_2\ \varphi_2 + (1)\ E\ \varphi_2$
$= \varphi_2 + \varphi_2 + \varphi_2 + \varphi_2 = 4\varphi_2 \approx \varphi_2 = \psi_3$

$PA_2\varphi_3 = (-1)\ \delta yz\ \varphi_2 + (-1)\ \delta xz\ \varphi_2 + (1)\ C_2\ \varphi_2 + (1)\ E\ \varphi_2$
$= -\ \varphi_1 + \varphi_3 - \varphi_1 + \varphi_3 = \varphi_3 - \varphi_1 = \psi_4$

$PB_2\varphi_3 = (1)\ \delta yz\ \varphi_2 + (-1)\ \delta xz\ \varphi_2 + (-1)\ C_2\ \varphi_2 + (1)\ E\ \varphi_2$
$= \varphi_1 + \varphi_3 + \varphi_1 + \varphi_3 = 2\varphi_1 + 2\varphi_3 \approx \varphi_1 + \varphi_3 = \psi_5$

Secular equation

$$\int \psi 1 (H-E) \psi 1 \, d_{\Gamma} \quad + \quad \int \psi 1 (H-E) \psi 4 \, d_{\Gamma} \quad = \quad H_{11} - E \quad + \quad H_{14} - ES_{14}$$

A_2:

B_2:

Normalization

Replacing φ in ψ of Hamiltonian *(beign α = 0 y β = 1)*

$$H_{11} = \int \psi 1 H \psi 1 = \int \left[\frac{1}{\sqrt{2}} (\phi 1 - \phi 3) \right] H \left[\frac{1}{\sqrt{2}} (\phi 1 - \phi 3) \right] d_\Gamma = \frac{1}{2} \int (\phi 1 - \phi 3)\ H\ (\phi 1 - \phi 3)\ d_\Gamma$$

$$H_{11} = \frac{1}{2} \left[\overbrace{\int \phi 1 H \phi 1 d_\Gamma}^{\alpha} - \overbrace{\int \phi 1 H \phi 3 d_\Gamma}^{0} - \overbrace{\int \phi 3 H \phi 1 d_\Gamma}^{0} + \overbrace{\int \phi 1 H \phi 1 d_\Gamma}^{\alpha} \right] = 0$$

$$H_{14} = \int \psi 1 H \psi 4 = \int \left[\frac{1}{\sqrt{2}} (\phi 1 - \phi 3) \right] H \left[\frac{1}{\sqrt{2}} (\phi 3 - \phi 1) \right] d_\Gamma = \frac{1}{2} \int (\phi 1 - \phi 3)\ H\ (\phi 3 - \phi 1)\ d_\Gamma$$

$$H_{14} = \frac{1}{2} \left[\overbrace{\int \phi 1 H \phi 3 d_\Gamma}^{0} - \overbrace{\int \phi 1 H \phi 1 d_\Gamma}^{\alpha} - \overbrace{\int \phi 3 H \phi 3 d_\Gamma}^{\alpha} + \overbrace{\int \phi 3 H \phi 1 d_\Gamma}^{0} \right] = 0$$

$$H_{44} = \int \psi 4 H \psi 4 = \int \left[\frac{1}{\sqrt{2}} (\phi 3 - \phi 1) \right] H \left[\frac{1}{\sqrt{2}} (\phi 3 - \phi 1) \right] d_\Gamma = \frac{1}{2} \int (\phi 3 - \phi 1)\ H\ (\phi 3 - \phi 1)\ d_\Gamma$$

$$H_{44} = \frac{1}{2} \left[\overbrace{\int \phi 3 H \phi 3 d_\Gamma}^{\alpha} - \overbrace{\int \phi 3 H \phi 1 d_\Gamma}^{0} - \overbrace{\int \phi 1 H \phi 3 d_\Gamma}^{0} + \overbrace{\int \phi 1 H \phi 1 d_\Gamma}^{\alpha} \right] = 0$$

$$H_{41} = \int \psi 4 H \psi 1 = \int \left[\frac{1}{\sqrt{2}} (\phi 3 - \phi 1) \right] H \left[\frac{1}{\sqrt{2}} (\phi 1 - \phi 3) \right] d_\Gamma = \frac{1}{2} \int (\phi 3 - \phi 1)\ H\ (\phi 1 - \phi 3)\ d_\Gamma$$

$$H_{41} = \frac{1}{2} \left[\overbrace{\int \phi 3 H \phi 1 d_\Gamma}^{0} - \overbrace{\int \phi 3 H \phi 3 d_\Gamma}^{\alpha} - \overbrace{\int \phi 1 H \phi 1 d_\Gamma}^{\alpha} + \overbrace{\int \phi 1 H \phi 3 d_\Gamma}^{0} \right] = 0$$

$$H_{22} = \int \psi 2\, H\, \psi 2 = \int \left[\frac{1}{\sqrt{2}} (\phi 1 + \phi 3) \right] H \left[\frac{1}{\sqrt{2}} (\phi 1 + \phi 3) \right] d_{\Gamma} = \frac{1}{2} \int (\phi 1 + \phi 3)\; H\; (\phi 1 + \phi 3)\; d_{\Gamma}$$

$$H_{22} = \frac{1}{2} \left[\overbrace{\int \phi 1\, H\, \phi 1\, d_{\Gamma}}^{\alpha} + \overbrace{\int \phi 1\, H\, \phi 0\, d_{\Gamma}}^{0} + \overbrace{\int \phi 3\, H\, \phi 1\, d_{\Gamma}}^{0} + \overbrace{\int \phi 3\, H\, \phi 3\, d_{\Gamma}}^{\alpha} \right] = 0$$

$$H_{23} = \int \psi 2\, H\, \psi 3 = \int \left[\frac{1}{\sqrt{2}} (\phi 1 + \phi 3) \right] H\, [\phi 2]\, d_{\Gamma} = \frac{1}{\sqrt{2}} \int (\phi 1 + \phi 3)\; H\; (\phi 2)\; d_{\Gamma}$$

$$H_{23} = \frac{1}{\sqrt{2}} \left[\overbrace{\int \phi 1\, H\, \phi 2\, d_{\Gamma}}^{\beta} + \overbrace{\int \phi 3\, H\, \phi 2\, d_{\Gamma}}^{\beta} \right] = \frac{2}{\sqrt{2}}$$

$$H_{25} = \int \psi 2\, H\, \psi 5 = \int \left[\frac{1}{\sqrt{2}} (\phi 1 + \phi 3) \right] H \left[\frac{1}{\sqrt{2}} (\phi 1 + \phi 3) \right] d_{\Gamma} = \frac{1}{2} \int (\phi 1 + \phi 3)\; H\; (\phi 1 + \phi 3)\; d_{\Gamma}$$

$$H_{25} = \frac{1}{2} \left[\overbrace{\int \phi 1\, H\, \phi 1\, d_{\Gamma}}^{\alpha} + \overbrace{\int \phi 1\, H\, \phi 3\, d_{\Gamma}}^{0} + \overbrace{\int \phi 3\, H\, \phi 1\, d_{\Gamma}}^{0} + \overbrace{\int \phi 3\, H\, \phi 3\, d_{\Gamma}}^{\alpha} \right] = 0$$

$$H_{32} = \int \psi 3\, H\, \psi 2 = \int [\phi 2]\, H \left[\frac{1}{\sqrt{2}} (\phi 1 + \phi 3) \right] d_{\Gamma} = \frac{1}{\sqrt{2}} \int (\phi 2)\; H\; (\phi 1 + \phi 3)\; d_{\Gamma}$$

$$H_{32} = \frac{1}{\sqrt{2}} \left[\overbrace{\int \phi 2\, H\, \phi 1\, d_{\Gamma}}^{\beta} + \overbrace{\int \phi 2\, H\, \phi 3\, d_{\Gamma}}^{\beta} \right] = \frac{2}{\sqrt{2}}$$

$$H_{33} = \int \psi 3\, H\, \psi 3 = \int [\phi 2]\, H\, [\phi 2]\, d_{\Gamma} = \int (\phi 2)\; H\; (\phi 2)\; d_{\Gamma}$$

$$H_{33} = \left[\overbrace{\int \phi 2\, H\, \phi 2 d_{\Gamma}}^{\alpha} + \right] = 0$$

$$H_{35}=\int\psi 3\,H\,\psi 5=\int[\phi 2]\,H\left[\frac{1}{\sqrt{2}}(\phi 1+\phi 3)\right]d_{\Gamma}=\frac{1}{\sqrt{2}}\int(\phi 2)\;H\;(\phi 1+\phi 3)\;d_{\Gamma}$$

$$H_{35}=\frac{1}{\sqrt{2}}\left[\overbrace{\int\phi 2\,H\,\phi 1 d_{\Gamma}}^{\beta}+\overbrace{\int\phi 2\,H\,\phi 3 d_{\Gamma}}^{\beta}\right]=\frac{2}{\sqrt{2}}$$

$$H_{52}=\int\psi 5\,H\,\psi 2=\int\left[\frac{1}{\sqrt{2}}(\phi 1+\phi 3)\right]H\left[\frac{1}{\sqrt{2}}(\phi 1+\phi 3)\right]d_{\Gamma}=\frac{1}{2}\int(\phi 1+\phi 3)\;H\;(\phi 1+\phi 3)\;d_{\Gamma}$$

$$H_{52}=\frac{1}{2}\left[\overbrace{\int\phi 1 H\,\phi 1 d_{\Gamma}}^{\alpha}+\overbrace{\int\phi 1 H\,\phi 3 d_{\Gamma}}^{0}+\overbrace{\int\phi 3 H\,\phi 1 d_{\Gamma}}^{0}+\overbrace{\int\phi 3 H\,\phi 3 d_{\Gamma}}^{\alpha}\right]=0$$

$$H_{53}=\int\psi 5 H\,\psi 3=\int\left[\frac{1}{\sqrt{2}}(\phi 1+\phi 3)\right]H\;[\phi 2]\;d_{\Gamma}=\frac{1}{\sqrt{2}}\int(\phi 1+\phi 3)\;H\;(\phi 2)\;d_{\Gamma}$$

$$H_{53}=\frac{1}{\sqrt{2}}\left[\overbrace{\int\phi 1 H\,\phi 2\,d_{\Gamma}}^{\beta}+\overbrace{\int\phi 3 H\,\phi 2\,d_{\Gamma}}^{\beta}\right]=\frac{2}{\sqrt{2}}$$

$$H_{55}=\int\psi 5\,H\,\psi 5=\int\left[\frac{1}{\sqrt{2}}(\phi 1+\phi 3)\right]H\left[\frac{1}{\sqrt{2}}(\phi 1+\phi 3)\right]d_{\Gamma}=\frac{1}{2}\int(\phi 1+\phi 3)\;H\;(\phi 1+\phi 3)\;d_{\Gamma}$$

$$H_{55}=\frac{1}{2}\left[\overbrace{\int\phi 1 H\,\phi 1 d_{\Gamma}}^{\alpha}+\overbrace{\int\phi 1 H\,\phi 0\,d_{\Gamma}}^{0}+\overbrace{\int\phi 3 H\,\phi 1 d_{\Gamma}}^{0}+\overbrace{\int\phi 3 H\,\phi 3 d_{\Gamma}}^{\alpha}\right]=0$$

Replacing according to Hûckel approximation and solving the matrix

$$A_2 = \begin{vmatrix} -E & 0 \\ 0 & -E \end{vmatrix} = 0 \Rightarrow E^2 = 0$$ $E_1 = 0$

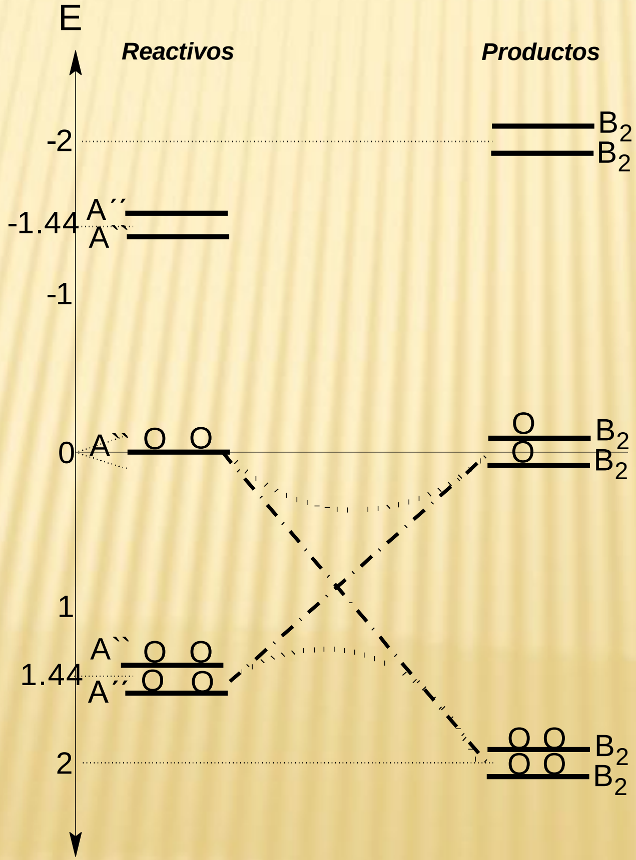
$$B_2 = \begin{vmatrix} -E & \frac{2}{\sqrt{2}} & 0 \\ \frac{2}{\sqrt{2}} & -E & \frac{2}{\sqrt{2}} \\ 0 & \frac{2}{\sqrt{2}} & -E \end{vmatrix} = 0 \Rightarrow -E^3 + 4E = 0$$

$E_2 = 0$

$E_3 = 2$

$E_4 = -2$

Correlation diagram to create two oxidanilo radicals (phenylcarbonyl)

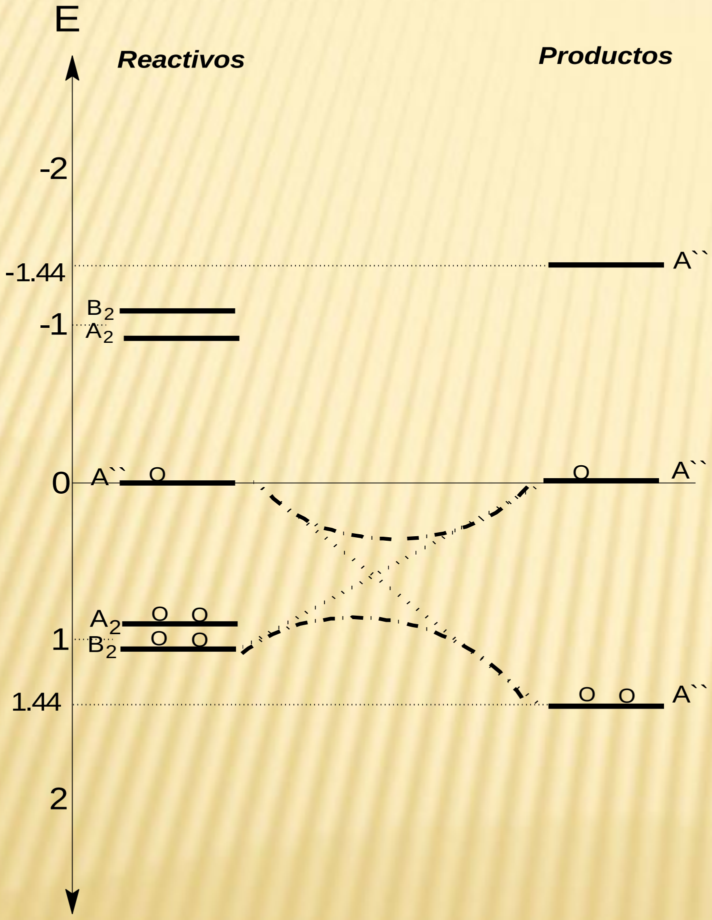


Valores de energias seculares en las moleculas involucradas en la obntencion de SBR

Moleculas estudiadas	Grupo puntual de simetria	Energias seculares (β)
Peroxido de benzoilo	C_{2v}	$E_1=1$; $E_2=-1$
Radical oxidanilo(fenilcarbonil)	C_{2v}	$E_1=0$; $E_2=2$; $E_3=-2$
Estireno	C_{2v}	$E_1=1$; $E_2=-1$
1,3-butadieno	C_{2v}	$E_1=0{,}62$; $E_2=1{,}62$; $E_3=-0{,}62$; $E_4=-1{,}62$
radical (2E)-4-[oxy(fenilcarbonil)]-2-buten-1-ilo	Cs	$E_1=0$; $E_2=1{,}44$; $E_3=-1{,}44$
radical (2E)-6-fenil-1-[oxi(fenilcarbonil)]-2-hexen-6-ilo	Cs	$E_1=0$; $E_2=1{,}44$; $E_3=-1{,}44$
Hidroquinona	C_{2v}	$E_1=1$; $E_2=-1$; $E_3=1$; $E_4=-1$
Radical 1	Cs	$E_1=0$; $E_2=1{,}44$; $E_3=-1{,}44$
Radical 2	Cs	$E_1=0$; $E_2=1{,}44$; $E_3=-1{,}44$
Cadena finalizada	C_{2v}	$E_1=1$; $E_2=-1$
SBR	C_1	$E_1=1$; $E_2=-1$

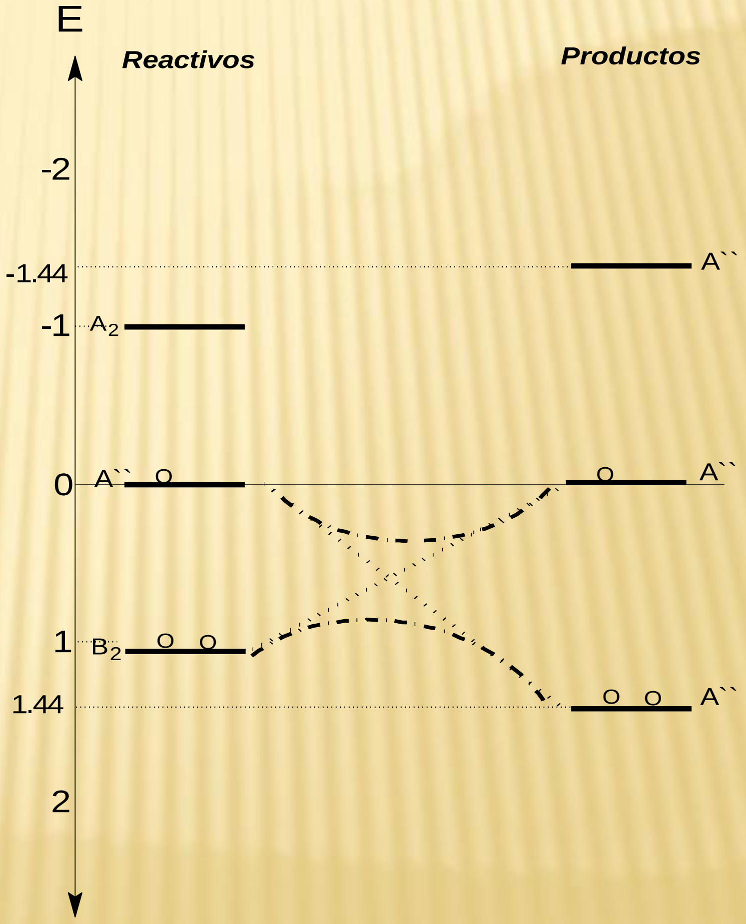
Correlation diagrams

Radical 1



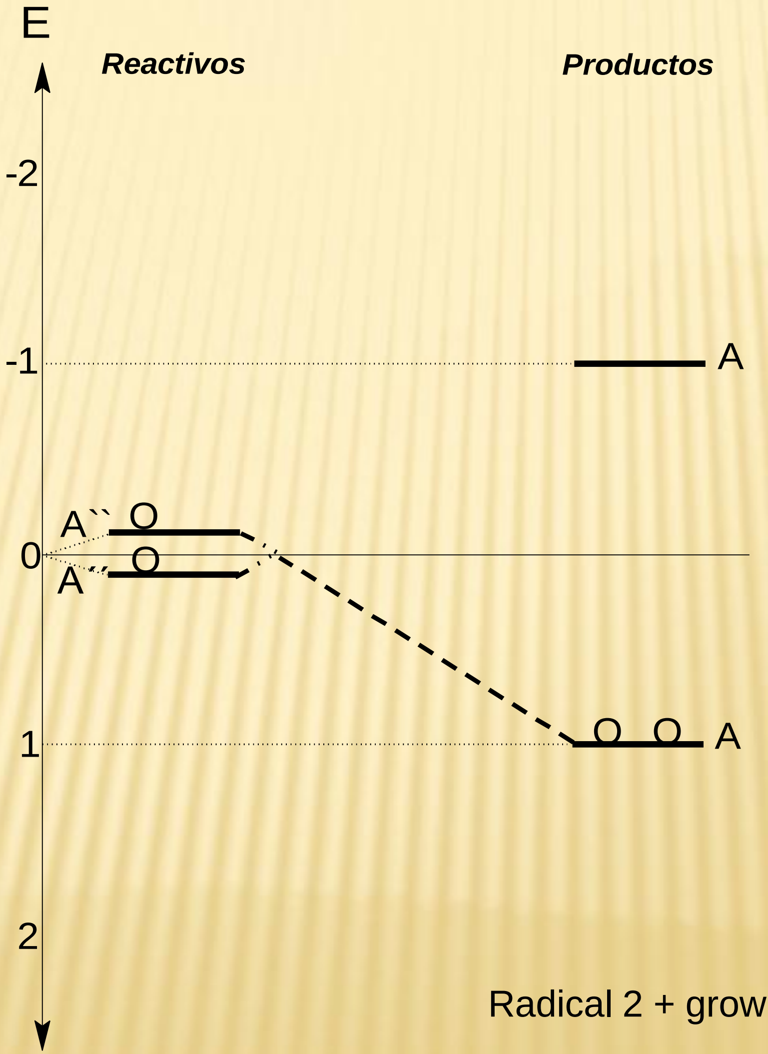
Growing chain + hydroquinone

Radical 2



Radical 1 + ending chain

SBR

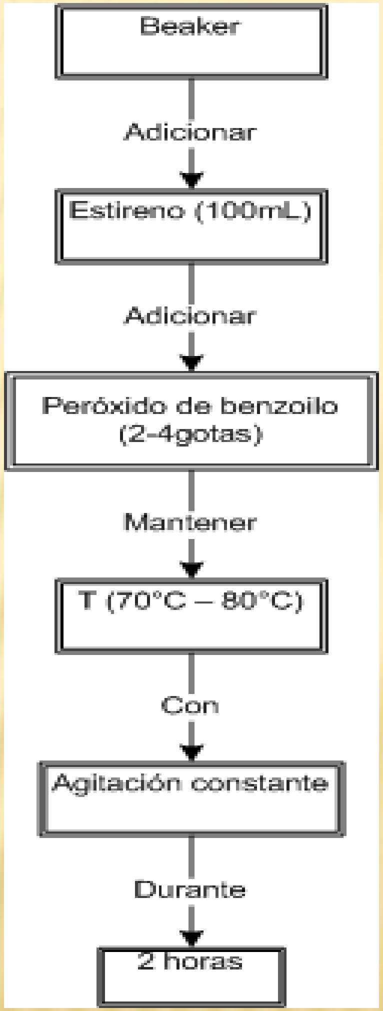


Radical 2 + growing chain

Design of possible synthesis routes

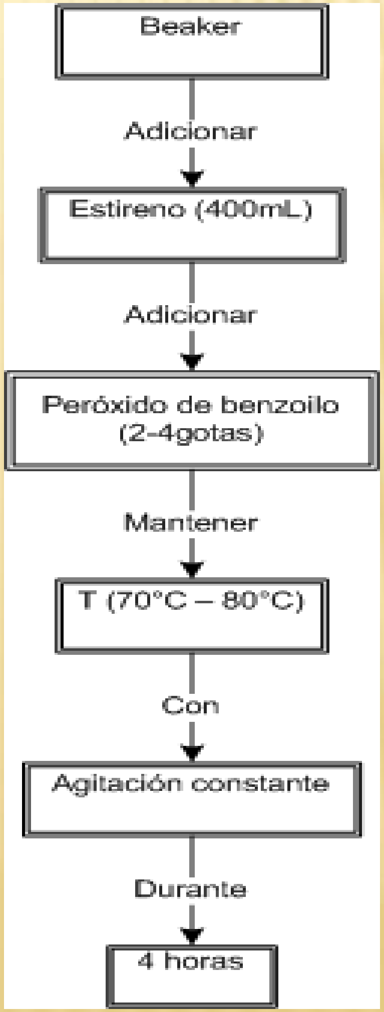
- Polystyrene synthesis route

A.



Beaker
Adicionar
Estireno (100mL)
Adicionar
Peróxido de benzoilo (2-4gotas)
Mantener
T (70°C – 80°C)
Con
Agitación constante
Durante
2 horas

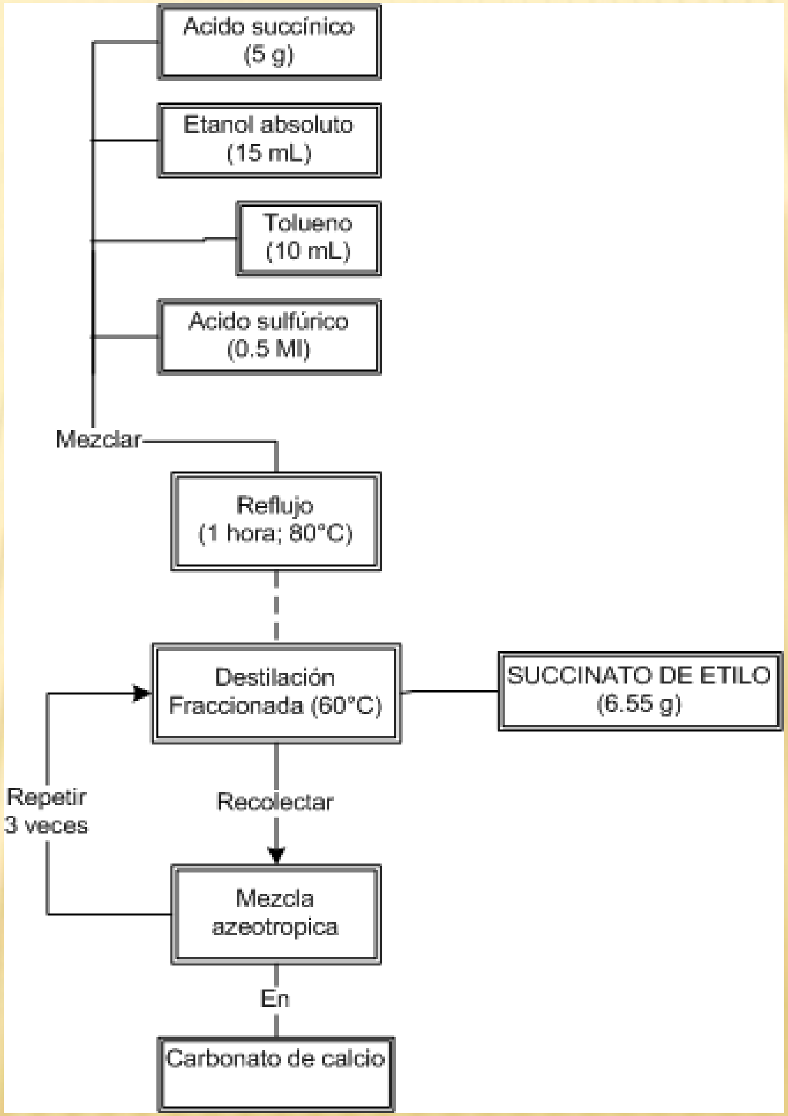
B.



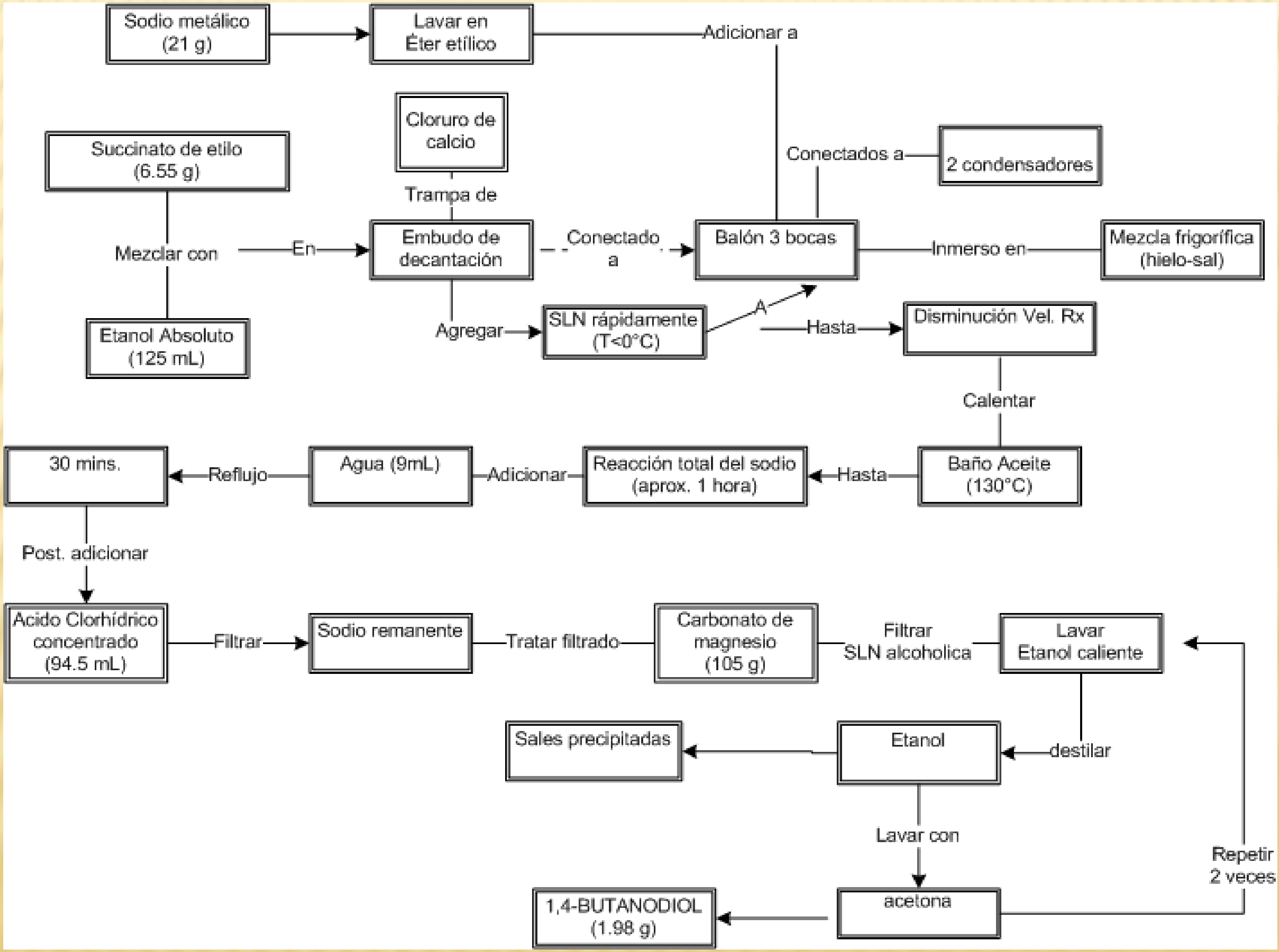
Beaker
Adicionar
Estireno (400mL)
Adicionar
Peróxido de benzoilo (2-4gotas)
Mantener
T (70°C – 80°C)
Con
Agitación constante
Durante
4 horas

Synthesis routes for 1,3-butadiene

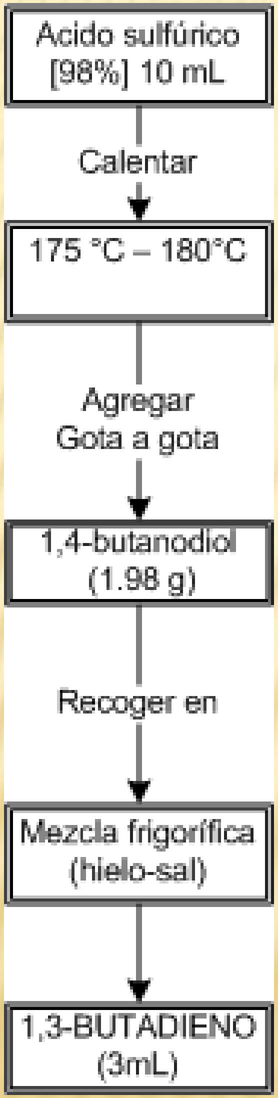
1. Ethyl succinate obtainment



2. 1,4-butannodiol obtainment



3. 1,3-butadieno obtainment



Acido sulfúrico [98%] 10 mL

Calentar

175 °C – 180°C

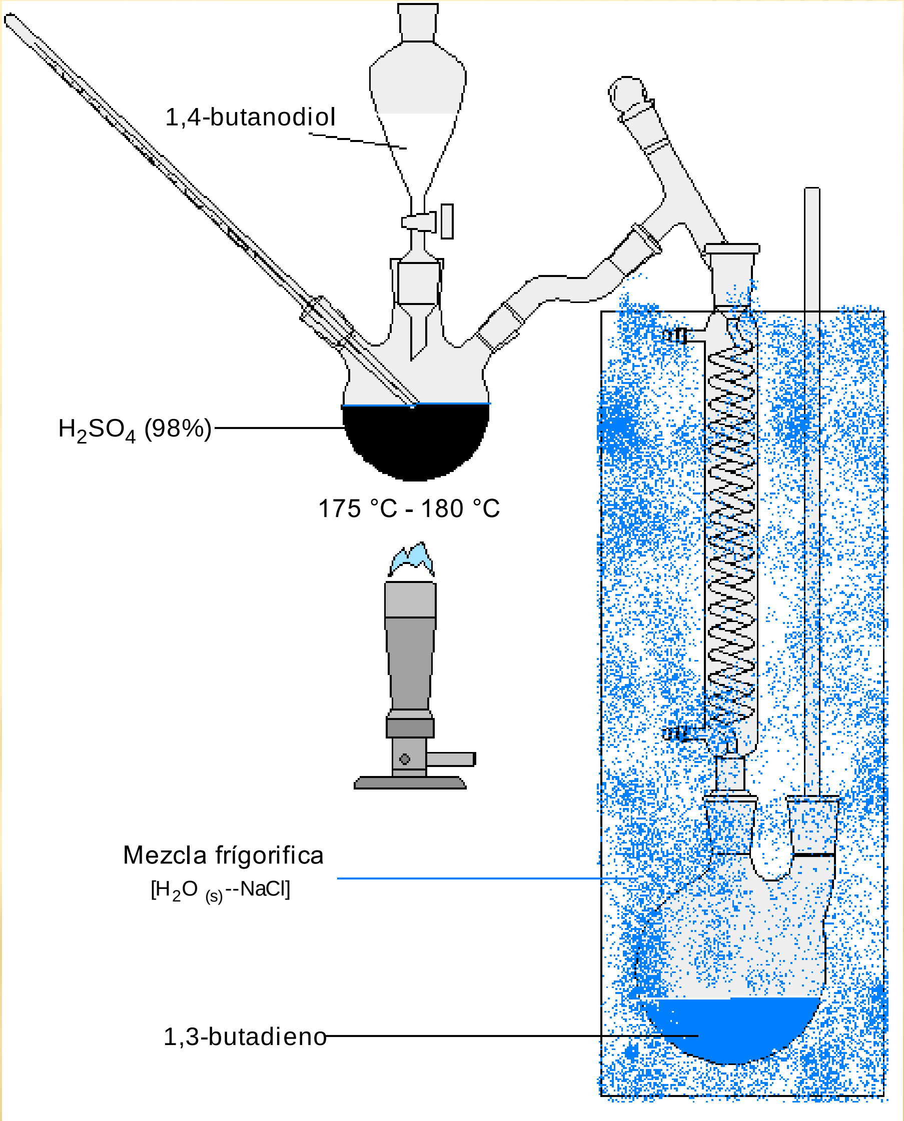
Agregar Gota a gota

1,4-butanodiol (1.98 g)

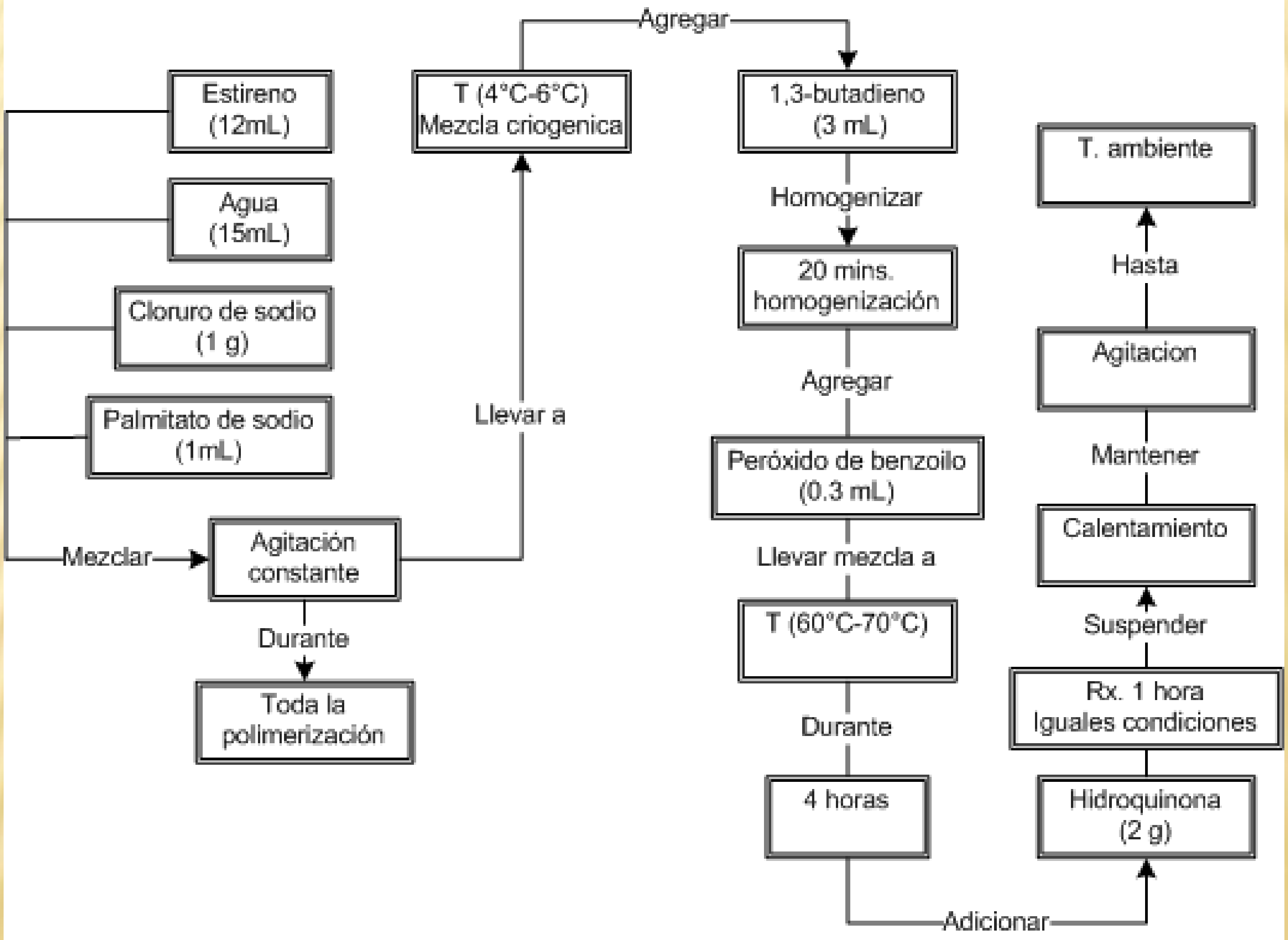
Recoger en

Mezcla frigorífica (hielo-sal)

1,3-BUTADIENO (3mL)

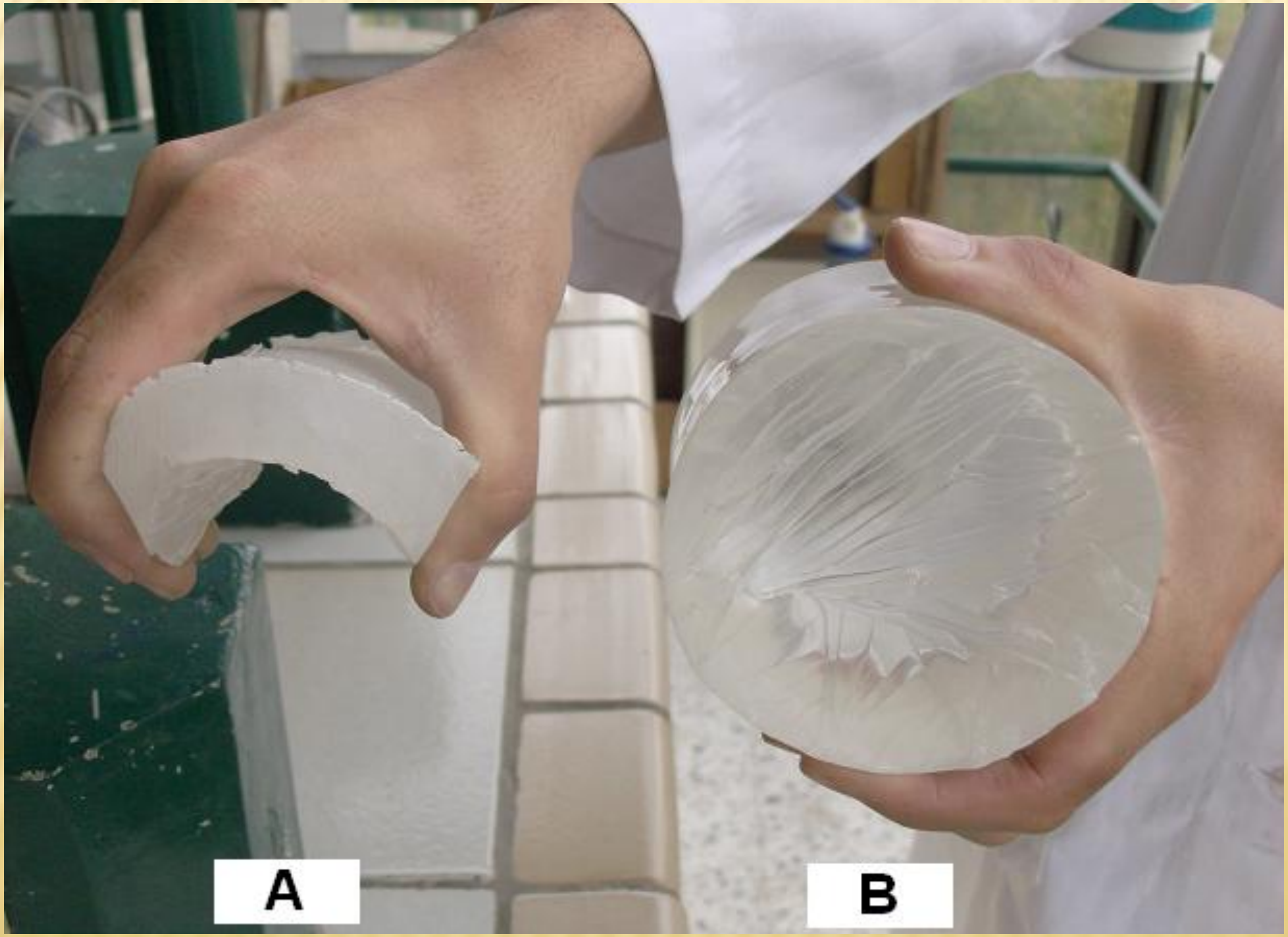


Synthesis route for SBR



PHASE THREE

- Experimental testing of synthesis routes



A. Semirigid polystyrene
B. Rigid Polystyrene

SBR films and elasticity demonstration

SBR

CONCLUSIONS

- Four possible synthetic routes similar to natural rubber using the semi-empirical AM1 method were studied. The results show that the highest electronic densities are found on the active atom in the radical compared to the electronic densities of ions and atoms of interest in a possible condensation.
- It was determined that the free radical synthesis does not show symmetry restrictions by the study group theory, and it is possible to perform by thermal power with low activation energy thresholds.
- Two synthetic routes were designed. The first one for obtaining polystyrene, the second one for obtaining SBR. These were selected for experimental corroboration of results, which yields of 90% for polystyrene and 75% for the SBR were obtained. To these synthesis routes modifications were made regarding the reported in literature to study them with theoretical tools and determine their predictive capacity to design polymer synthesis similar to natural rubber. In a future, it is expected that others can explore unknown synthesis routes are not known since this investigation showed that the used methods are reliable.

RECOMMENDATIONS

- Quantitative technique tests are recommended according to the Colombian Technical Standards and American Society for Testing Materials of the synthesized polymers. For this, proper amounts to make the test tubes must be taken.
- Furthermore, from this study, the searching of another crosslinking and ending agents, emulsifiers, among other additives to compare results and optimize the process are recommended.
- In the same way, it must promote and deepening the usage of resources the Universidad Distrital Francisco José de Caldas regarding theoretical and computational chemistry to study manifold chemistry systems.

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