

**PHOTO- RADIORACEMIZATION OF
CHIRAL MOLECULES
AND
THE RADIATION-INDUCED
AMPLIFICATION OF CHIRALITY**

Dr. Franco Cataldo

Soc. Lupi Chemical Research Institute, Via Casilina
1626/A, 00133 Rome, Italy

-----000000000000-----

University of Tor Vergata, Dept. of Materials Science,
Rome, Italy

CHIRALITY IN MOLECULAR WORLD

- Chirality phenomenon is present in all molecules which present at least a center of asymmetry.
- One center of asymmetry makes possible that a given molecule can have an exact isomer which is its mirror image. The two isomers cannot be overlapped.

ENANTIOMERS

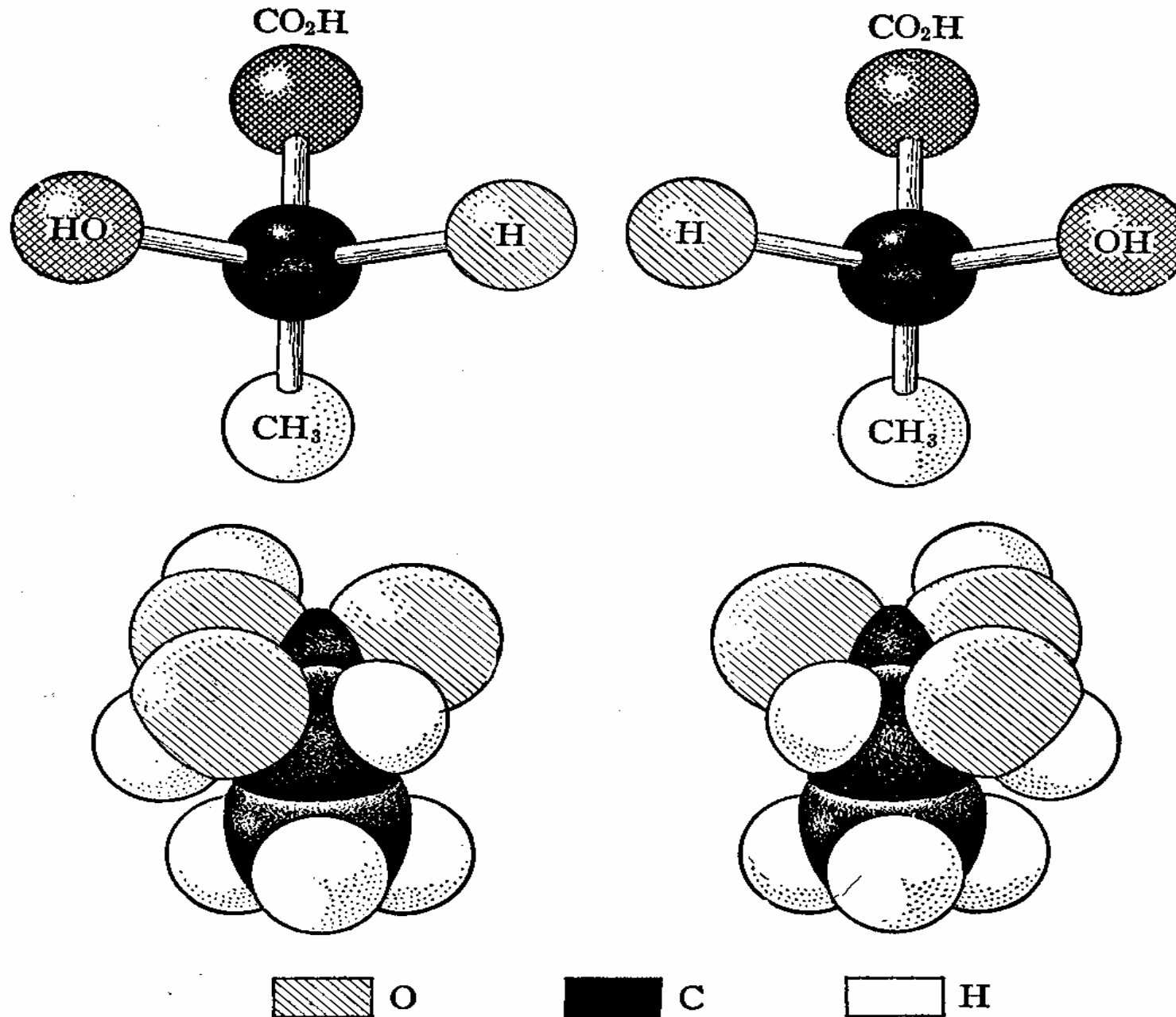


FIG. 3.3. — Enantiomeric Lactic Acids

WHY CHIRALITY IS SO IMPORTANT IN AN ASTROBIOLOGICAL CONTEXT?

- Life is impossible without chirality.
- All the biochemical processes in the living organisms, which ensure reproduction, assimilation, energy production, movement, growth..... employ chiral molecules and macromolecules.
- In general all amino acids employed in proteins by all organisms are essentially in the “levo” form while the sugars present in DNA and RNA which are the unique chiral units of these macromolecules are in the “dextro” form.
- Finding a chiral excess in a certain matrix can be considered a condition necessary but not sufficient to demonstrate that life is there.
- Not sufficient because also certain physical fields can cause a chiral excess abiotically because they can induce some selectivity in chemical reactions.

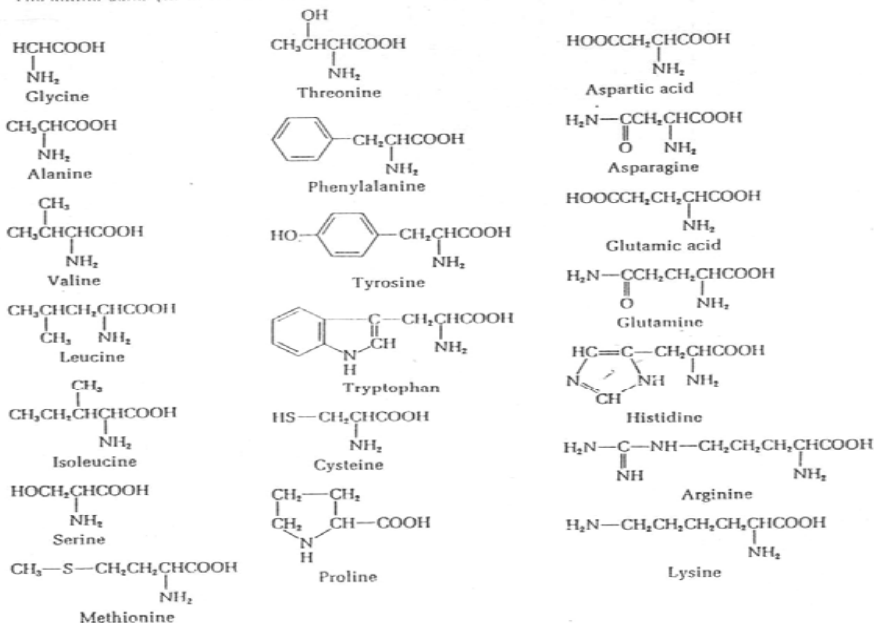
Aminoacids found in meteorites

TABLE VI
Comparison of Amino Acids in Murchison Meteorite and in Electric Discharge Synthesis, Normalized to Glycine

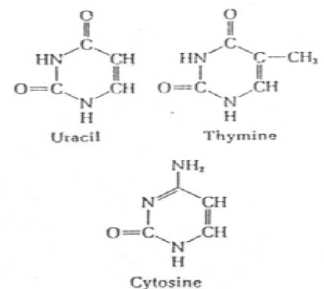
Amino acid	Murchison meteorite	Electric discharge
Glycine	100	100
Alanine	>50	>50
α -Amino- <i>n</i> -butyric acid	>50	>50
α -Aminoisobutyric acid	10	>50
Valine	10	1
Norvaline	10	10
Isovaline	1	1
Proline	10	0.1
Pipecolic acid	0.1	<1
Aspartic acid	10	10
Glutamic acid	10	1
β -Alanine	1	1
β -Amino- <i>n</i> -butyric acid	0.1	0.1
δ -Aminoisobutyric acid	0.1	0.1
γ -Aminobutyric acid	0.1	1
Sarcosine	1	10
<i>N</i> -Ethylglycine	1	10
<i>N</i> -Methylalanine	1	1

The Primordial Biomolecules

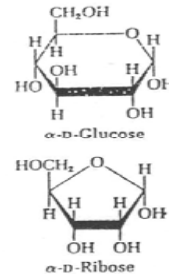
The amino acids (in un-ionized form)



The pyrimidines



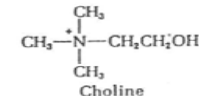
The sugars



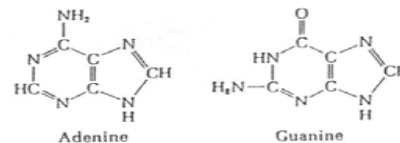
A sugar alcohol



A nitrogenous alcohol



The purines



A fatty acid

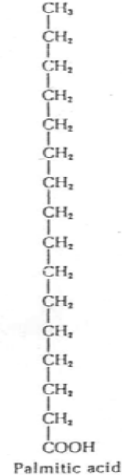


FIGURE 1 The basic molecules of life. (From Lehninger, 1975.)

The aminoacids in meteorites present a levo excess

EXTRATERRESTRIAL AMINO ACIDS AND ORIGIN OF LIFE

TABLE 2-4 Recent enantiomeric analyses of amino acids from the Murchison and Murray meteorites by Cronin and Pizzarello

Amino acid	Murchison % L-ee (corr.)	Murray % L-ee (corr.)
2-amino-2,3-dimethylpentanoic acid		
2S,3S/2R,3R	7.0	1.0
2S,3R/2R,3S	9.1	2.2
2-amino-2-methylpentanoic acid	2.8	1.4
2-amino-2-methylbutanoic acid (isovaline)	8.4	6.0
2-amino-2,3-dimethylbutanoic acid	2.8	1.0
2-amino-2-methylhexanoic acid	4.4	1.8
2-amino pentanoic acid (norvaline)	0.4 ^a	0.8 ^a
2-amino butanoic acid (butyrine)	0.4 ^a	-0.4 ^a
2-amino propanoic acid (alanine)	1.2	0.4
2-amino-3-methylbutanoic acid (valine)	2.2	-0.4 ^a

^aNot significant.

HYPOTHESIS ON CHIRAL MOLECULES FORMATION

LINEARLY POLARIZED LIGHT FROM NEUTRON STARS

CIRCULARLY POLARIZED LIGHT FROM FAINT STARS

CIRCULARLY POLARIZED LIGHT ON PLANET SURFACE

INCLUSION POLYMERIZATION IN CHIRAL CLAYS

VESTER-ULBRICHT HYPOTHESIS (Parity violation in weak
interactions)

ACTION OF VERY HIGH PRESSURE ON RACEMIC
MIXTURES

ASYMMETRIC INORGANIC SURFACES (acting as catalysts)

PROTECTION AND AMPLIFICATION OF CHIRALITY

ADSORPTION AND INCLUSION

SELECTIVE ADSORPTION ON CHIRAL SURFACES

SPONTANEOUS SYMMETRY BREAKING OF RACEMIC
MIXTURES

FAR-FROM EQUILIBRIUM THERMODYNAMICS (PRIGOGINE *et*
al.)

POLYMER CHAINS WITH PREFERENTIAL HELICITY

SMALL MOLECULES WITH ASYMMETRIC CARBON ATOMS

MAIN PHENOMENA CAUSING RACEMIZATION

ACTION OF HEAT ON SCALEMIC MIXTURES

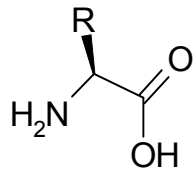
ACTION OF METAL IONS ON SCALEMIC
MIXTURES

ACTION OF LIGHT (PHOTORACEMIZATION)

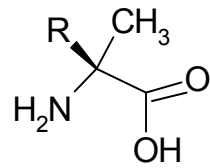
ACTION OF HIGH ENERGY RADIATION
(RADIORACEMIZATION)

RACEMIZATION EXAMPLE: THE CASE OF AMINOACIDS

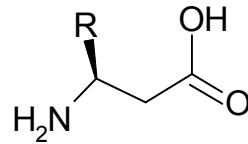
SCHEME 1



alpha aminoacids

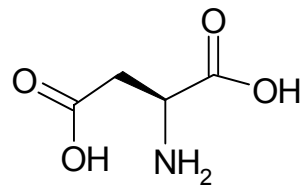


methyl aminoacids

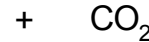
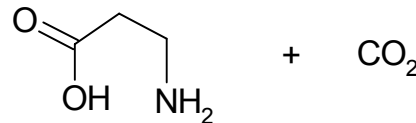
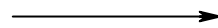


beta aminoacids

Alpha aminoacids are formed in abiotic syntheses together with methylaminoacids. In meteorites the enantiomeric excess is due to methylaminoacids which are not racemizable. The alpha aminoacids racemize.

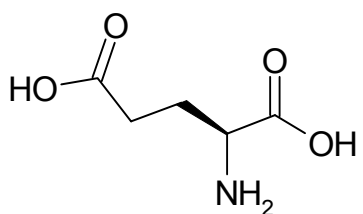


aspartic acid

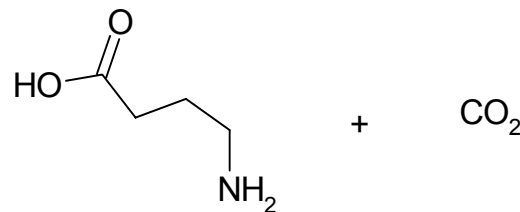
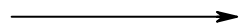


beta-alanine

Racemization involves either the conversion of alpha aminoacids to alpha-omega aminoacids which are not chiral or a more simple inversion reaction at the chiral center (see next slide).



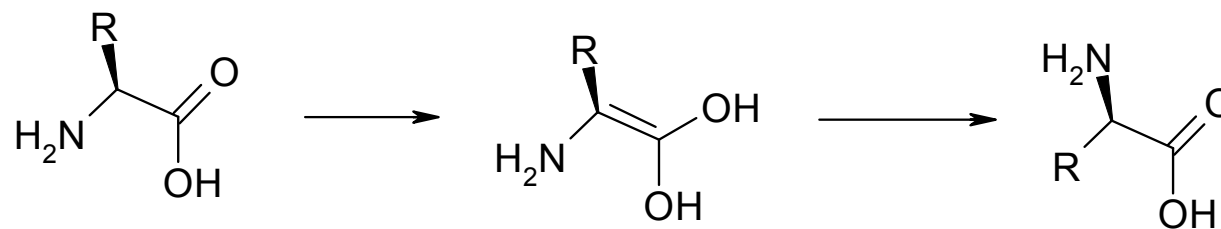
glutamic acid



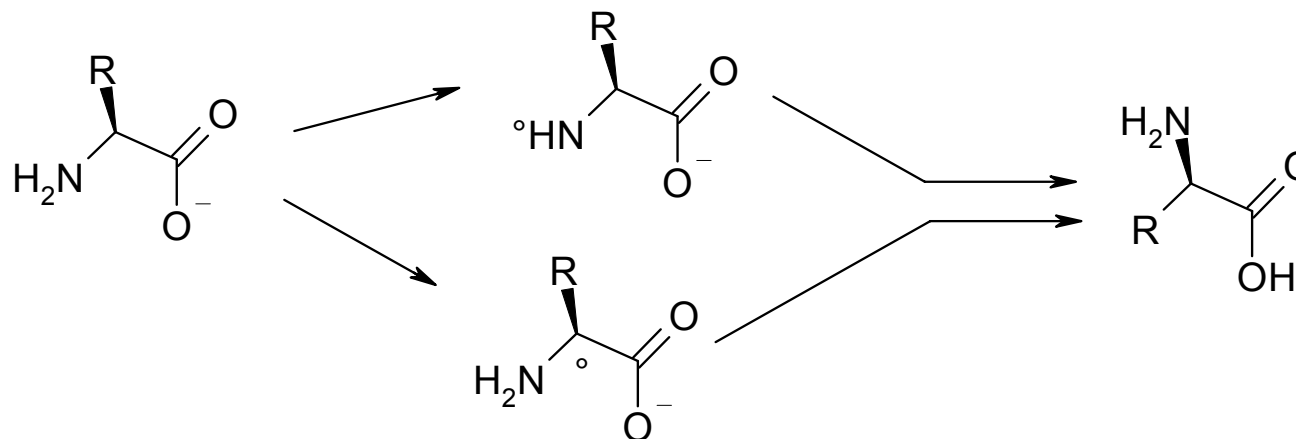
gamma-aminobutyric acid

The racemization mechanism of alpha-aminoacids

SCHEME 2



Racemization through keto-enol mechanism



Racemization through a radical-anion mechanism during radiolysis

A series of studies on radioracemization of terpenes

F. Cataldo et al. J. Radioanal. Nuclear Chem. **262** (2004) 423

TABLE 1 - SUMMARY RESULTS OF RADIOLYSIS OF TERPENES

	R(+)-Limonene	S(-)-Limonene	R(-)-alpha-phellandrene
Assay (GC) from supplier FLUKA	>98%	>97%	50%
S.O.R. pure sample ref.	+123.8°	-101.3°	-217°
S.O.R. supplier specification	+109° : +115°	-85° : -95°	-125 : -135
S.O.R. measured on pristine samples	+109.9°	-89.9°	-135.5
S.O.R. measured after radiolysis (317KGy)	+107.1°	-84,2°	-124.7
% of changes after radiolysis	2.6	6.3	8.0
% Optical purity before radiolysis	88,8	88,7	62,4
% Optical purity after radiolysis	86,5	83,1	57,5

Notes: S.O.R. = Specific Optical Activity (degrees)

GC = Gas Chromatography

Example of radioracemization: S(-)limonene

TABLE 2 - SELECTED RADIOLYSIS PRODUCTS VS INITIAL COMPOSITION

S(-) Limonene	Before radiolysis	After Radiolysis
Retention time (min)	Area %	Area%
1.177	-	1.0
1.292	-	1.0
1.381	-	1.8
1.543	-	5.4
1.695	-	3.6
1.813	-	0.2
2.721	3.4	4.7
3.714	96.6	82.3

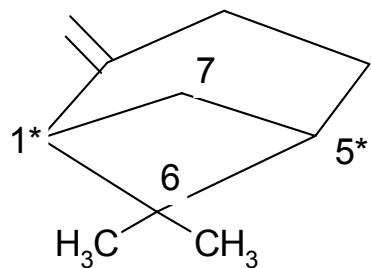
- **True and false radioracemization**
- **True:** the racemization acts exclusively on a sensitive chiral center, the molecule is preserved; this is more probable with UV radiation rather than with γ radiation
- **False or apparent:** the macroscopic racemization can be measured but is due to the complete degradation of the molecule including its chiral centers

α -pinene radioracemization and the anomalous behaviour of β -pinene

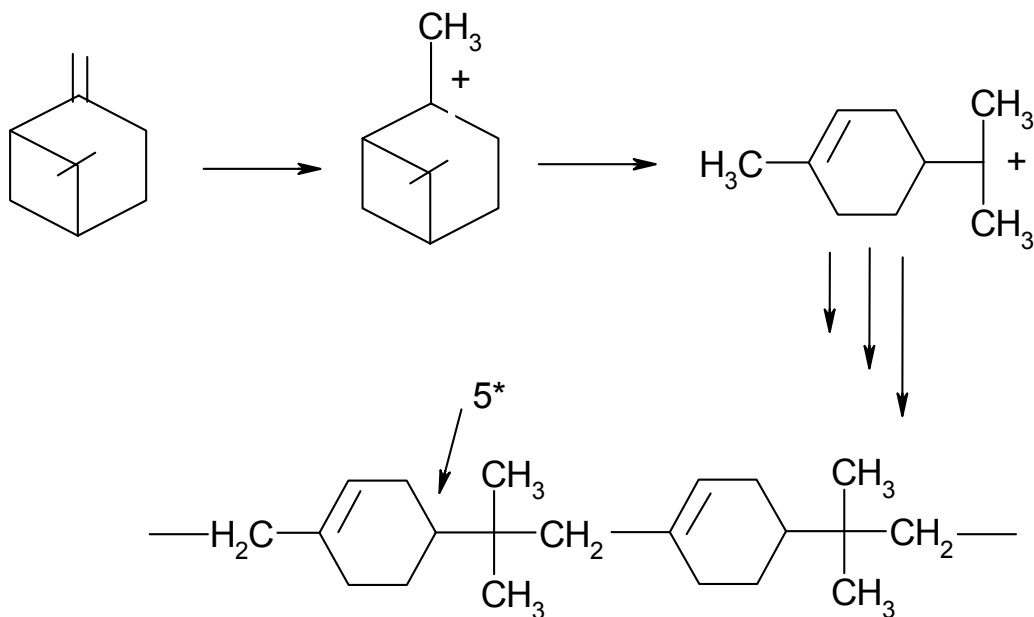
TABLE 1 - EFFECT OF RADIOLYSIS ON OPTICAL ACTIVITY -CRUDE MIXTURE-

	alpha(-)pinene	alpha (+)pinene	beta (-) pinene
Initial purity by GC	> 98%	>97%	>99%
[α] _D Literature	-51.3(*); -52.4(**)	+51.1(*); +52.4(**)	-23.4(***)
[α] _D Before radiolysis	-41.9	+49.2	-23.1
[α] _D 150kGy radiolysis	-41.5	+48.7	-22.3
[α] _D 300kGy radiolysis	-41.2	+48.2	-23.4
[α] _D 600kGy radiolysis	-40.3	+47.9	-25.0

The radiation-induced polymerization of B(-)pinene: a case of chiral amplification



(1S,5S)(-)-β-Pinene



Poly(β(-)-Pinene)

- See:

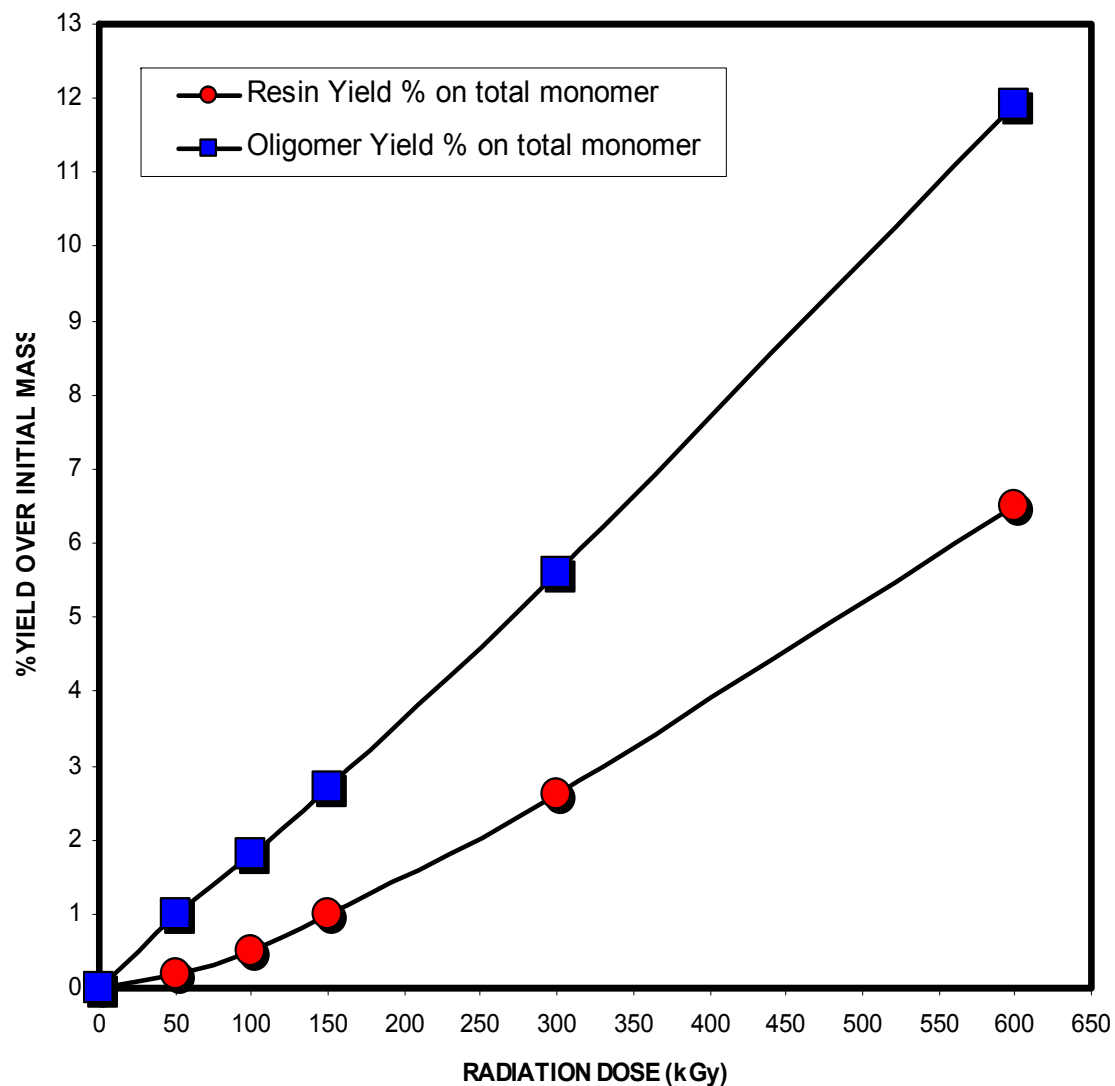
F.Cataldo et al. Radiation Phys. Chem. 75 (2006) 572;

- See also:

F. Cataldo et al. Origin of Life Evol. Biosph., *in press.*

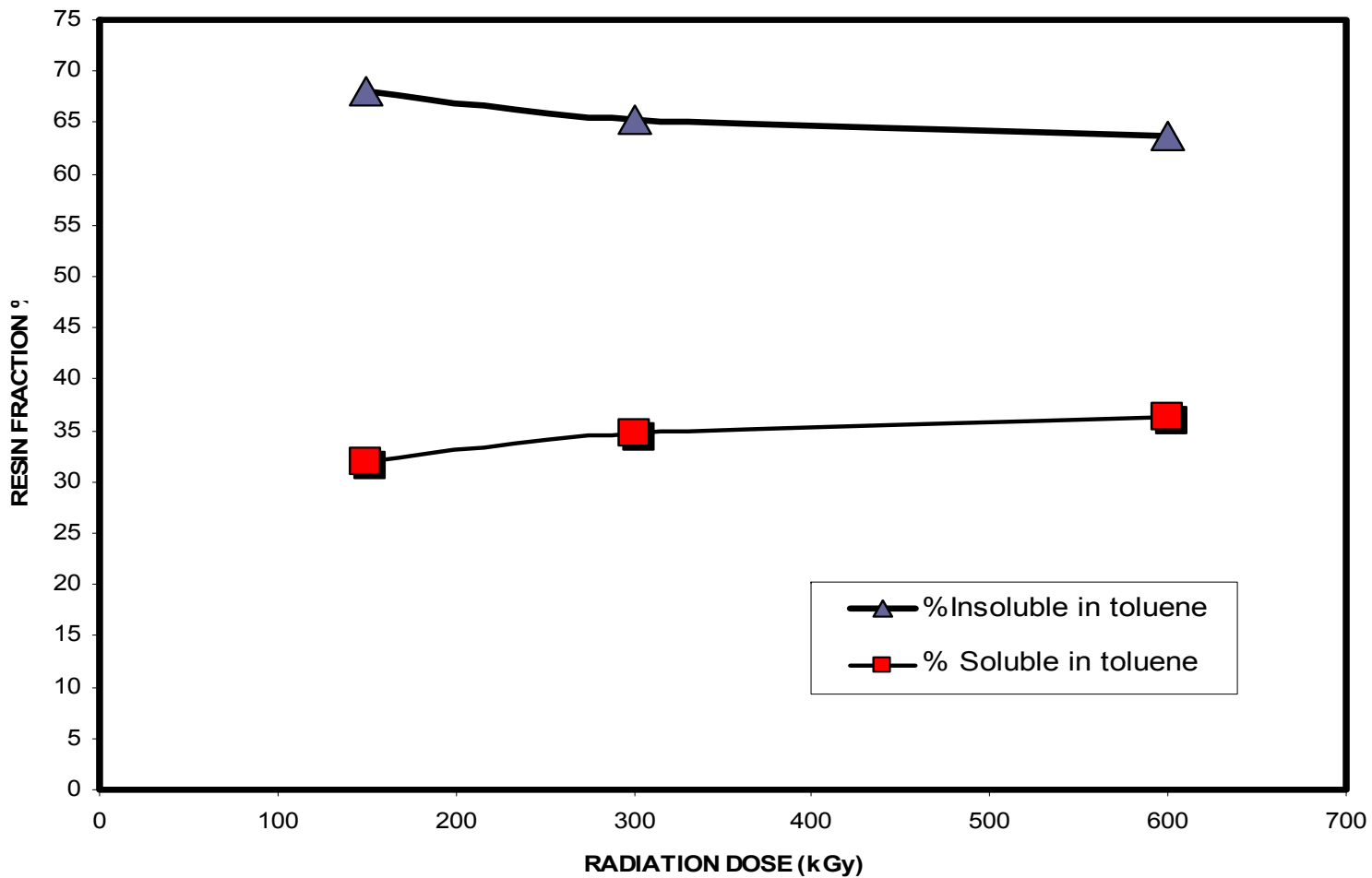
F.Cataldo et al. J. Radioanal. Nucl. Chem., *in press.*

Effect of radiation dose on the yield of $\beta(-)$ pinene solid radiopolymer and radiodimer (oligomer)



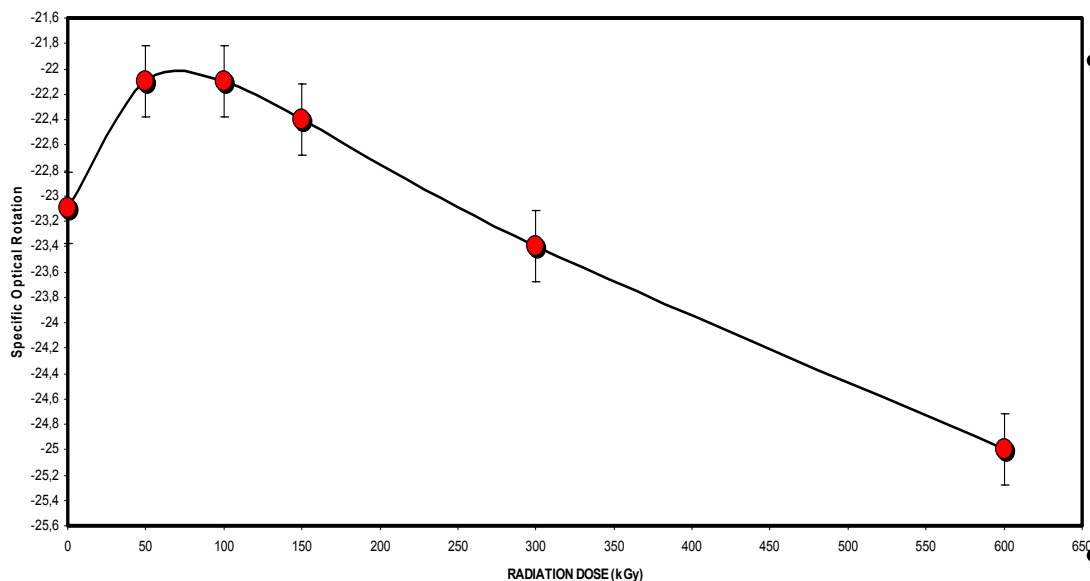
- Yield of white, solid, insoluble poly(β -pinene) resin compared with the yield of dimer/trimer mixture of oligomers of β -pinene (measured as acetonitrile insolubles).
- There is a linear dependence of the yield of these products with the radiation dose administered to β -pinene. Earlier results are confirmed.

Toluene soluble and insoluble fraction of $\beta(-)$ pinene solid radiopolymer as function of the radiation dose.



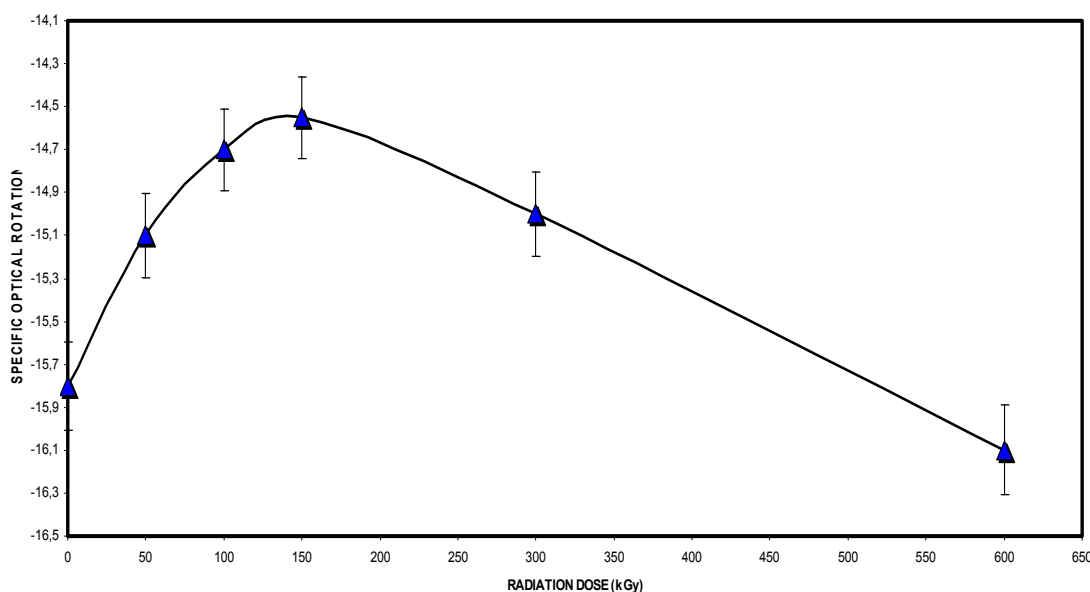
Optical activity of radiolyzed β -(-)pinene

EFFECT OF RADIATION DOSE ON BETA PINENE OPTICAL ACTIVITY



Effect of radiation dose on the specific optical rotation of crude unfractionated β -pinene. At low radiation dose the radoracemization phenomenon appears prevalent but at higher doses there is a linear increase in the optical activity.

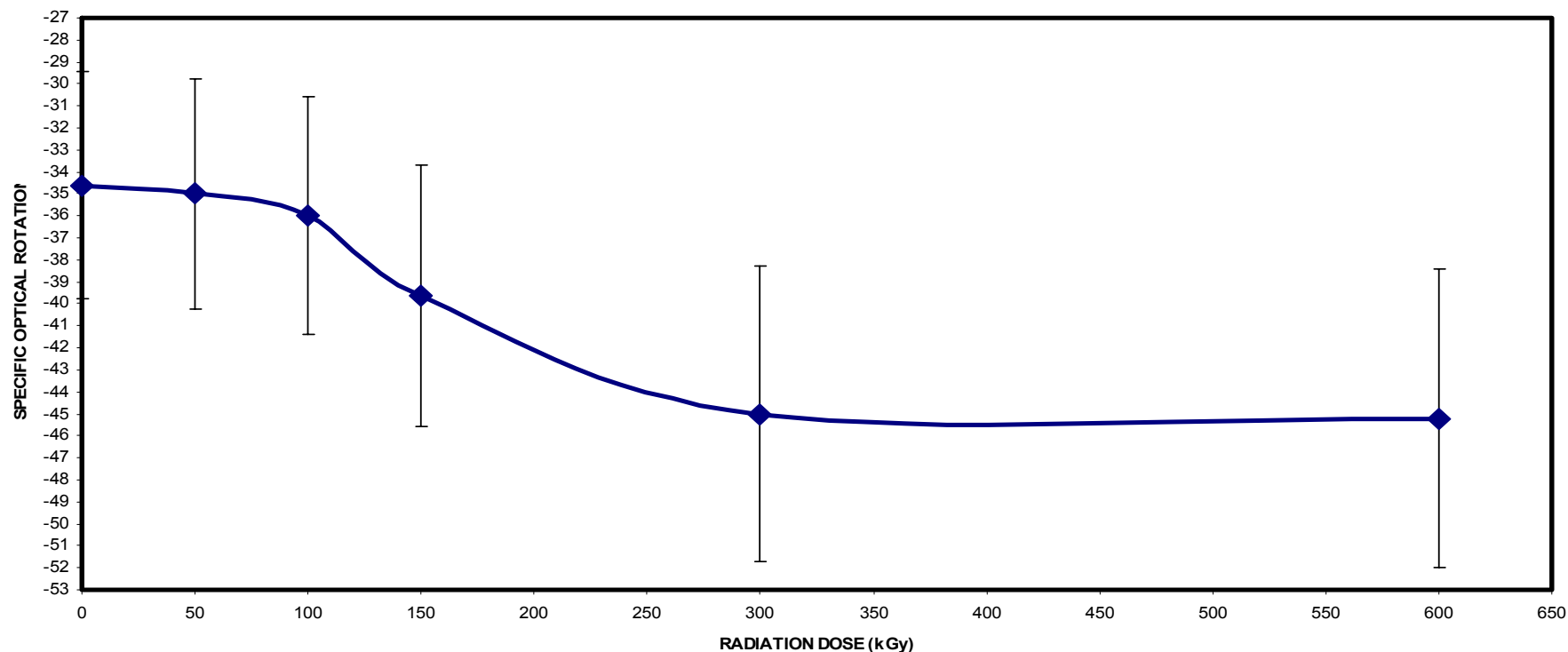
BETA PINENE SOLUBLES IN ACETONITRILE



Effect of radiation dose on the specific optical rotation of the acetonitrile soluble fraction of radiolyzed β -pinene. The value at 0 kGy has been measured on pure β -pinene dissolved in acetonitrile. In this graph, the same trends of Fig.1 can be observed. At low doses a trend to radoracemization followed by a linear increment of the optical activity at higher doses. Evidently, a minimum dimer/trimer fraction remains dissolved in acetonitrile and contribute to the optical activity enhancement at high radiation dose.

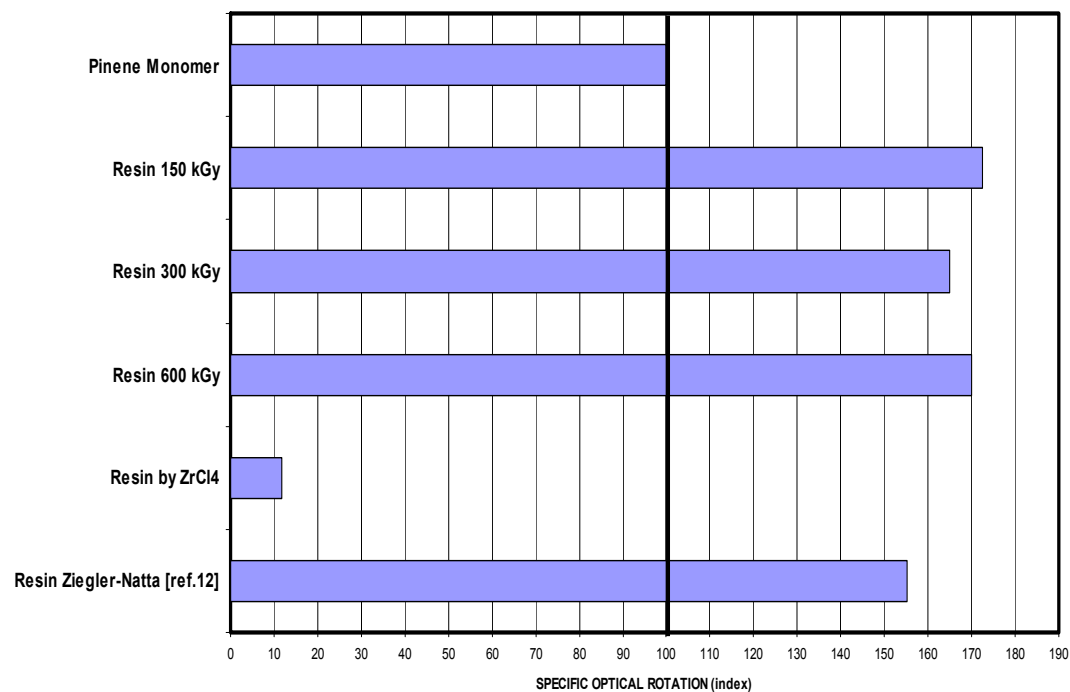
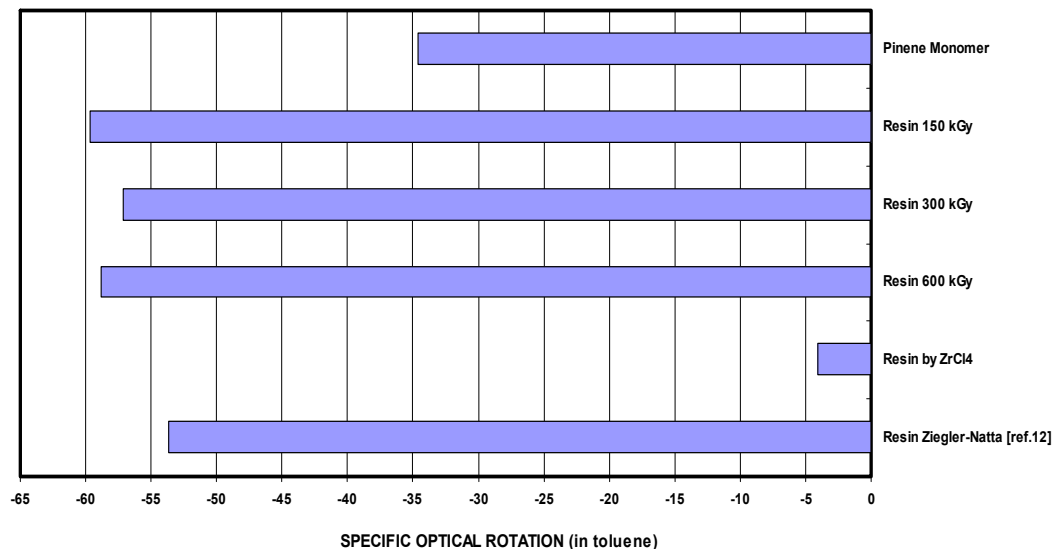
Optical activity of $\beta(-)$ pinene oligomers

BETA PINENE INSOLUBLES IN ACETONITRILE SOLUBLES IN TOLUENE



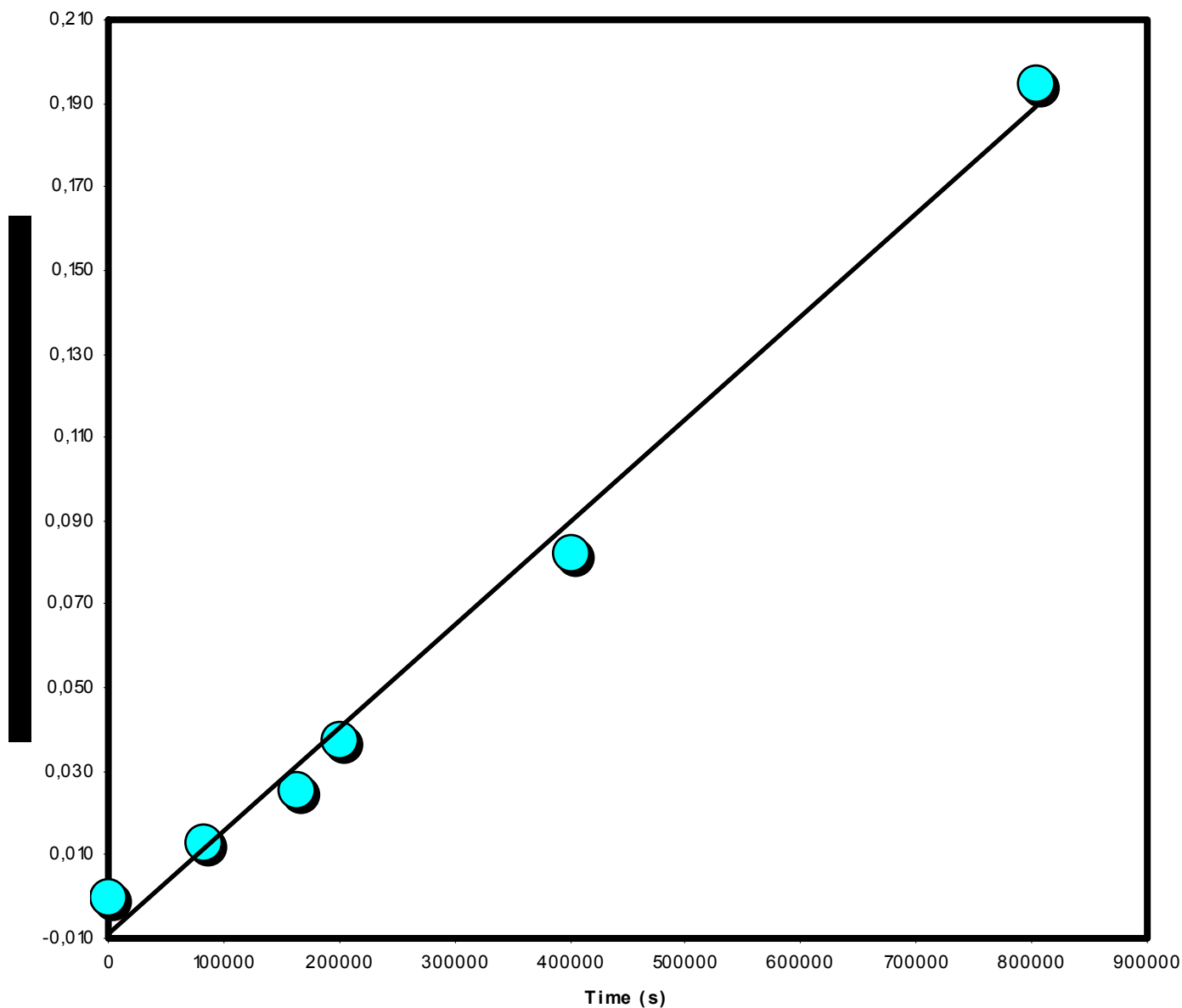
- Measurements of the specific optical rotation of the acetonitrile insoluble fraction obtained from radiolyzed β -pinene. The acetonitrile insolubles were dissolved in toluene and the optical activity was measured in this solvent. The **acetonitrile insoluble fraction has been assigned to β -pinene dimer and trimer.**
- The value at 0 kGy refers to pure, not radiolyzed β -pinene dissolved in toluene. Note that above 50 kGy the β -pinene dimer and trimer show an enhanced optical activity in comparison to the reference value at 0 kGy. They contribute to the enhancement of the optical rotation of the graphs of the previous slide.

Optical activity of poly(β -(-)pinene) resin



- Specific optical rotation of poly(β -pinene) resins (dissolved in toluene) compared with the specific optical rotation of pure β -pinene monomer in toluene.
- The specific optical rotation of the poly(β -pinene) resins produced at 150, 300 and 600 kGy appear comparable to the $[\alpha]_D$ value of the poly(β -pinene) resin obtained on a stereospecific Ziegler-Natta catalyst and show an $[\alpha]_D$ value which is double of the starting monomer in the same solvent.
- Instead the poly(β -pinene) resin prepared by cationic polymerization (ZrCl₄) offers a very low optical activity.

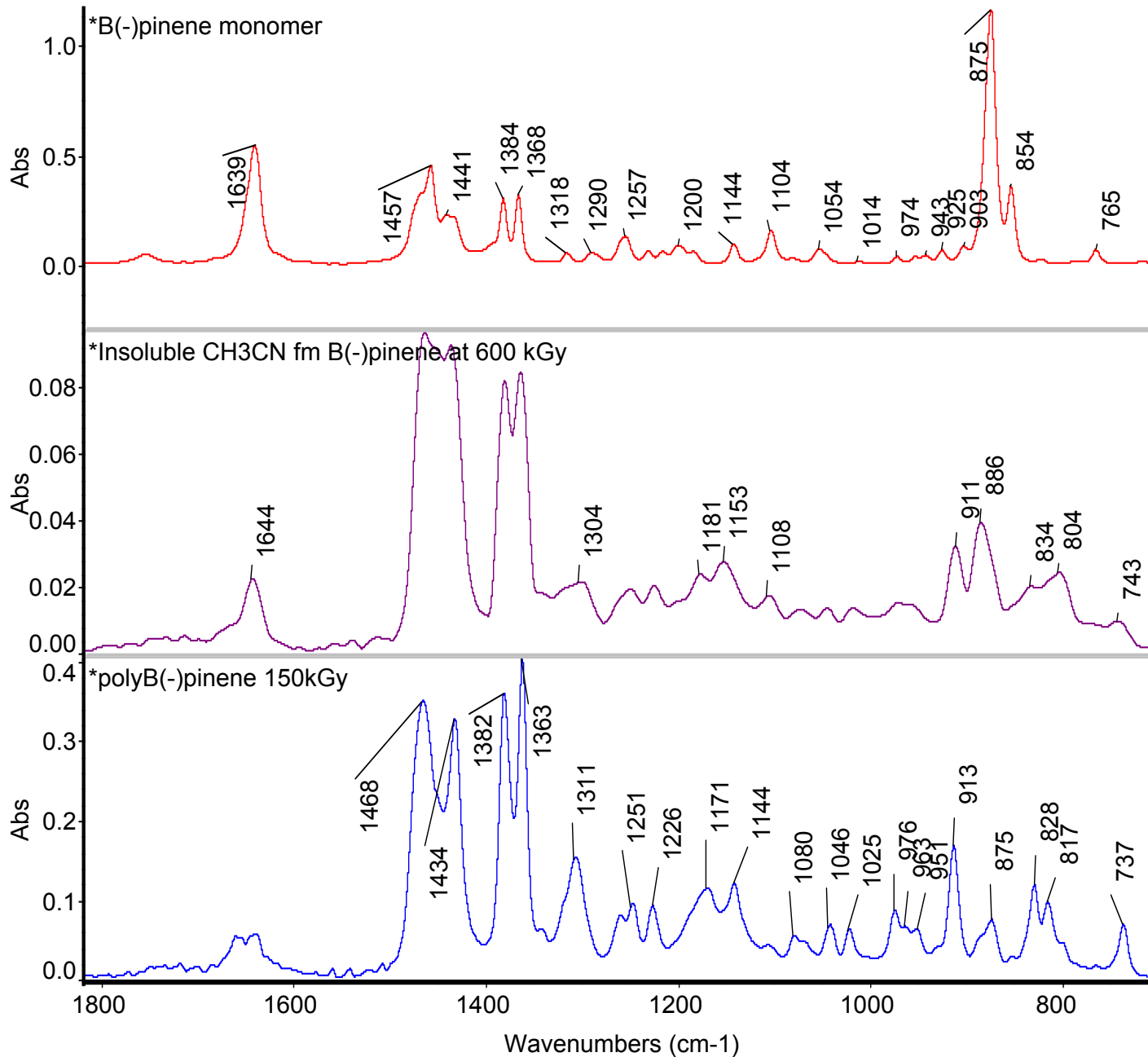
Kinetics of β -pinene consumption during radiolysis assuming total conversion to dimer & resin



Pseudofirst order kinetic rate constant in the radiation-induced polymerisation of β -pinene. The k value found is $1.90 \times 10^{-7} \text{ s}^{-1}$.

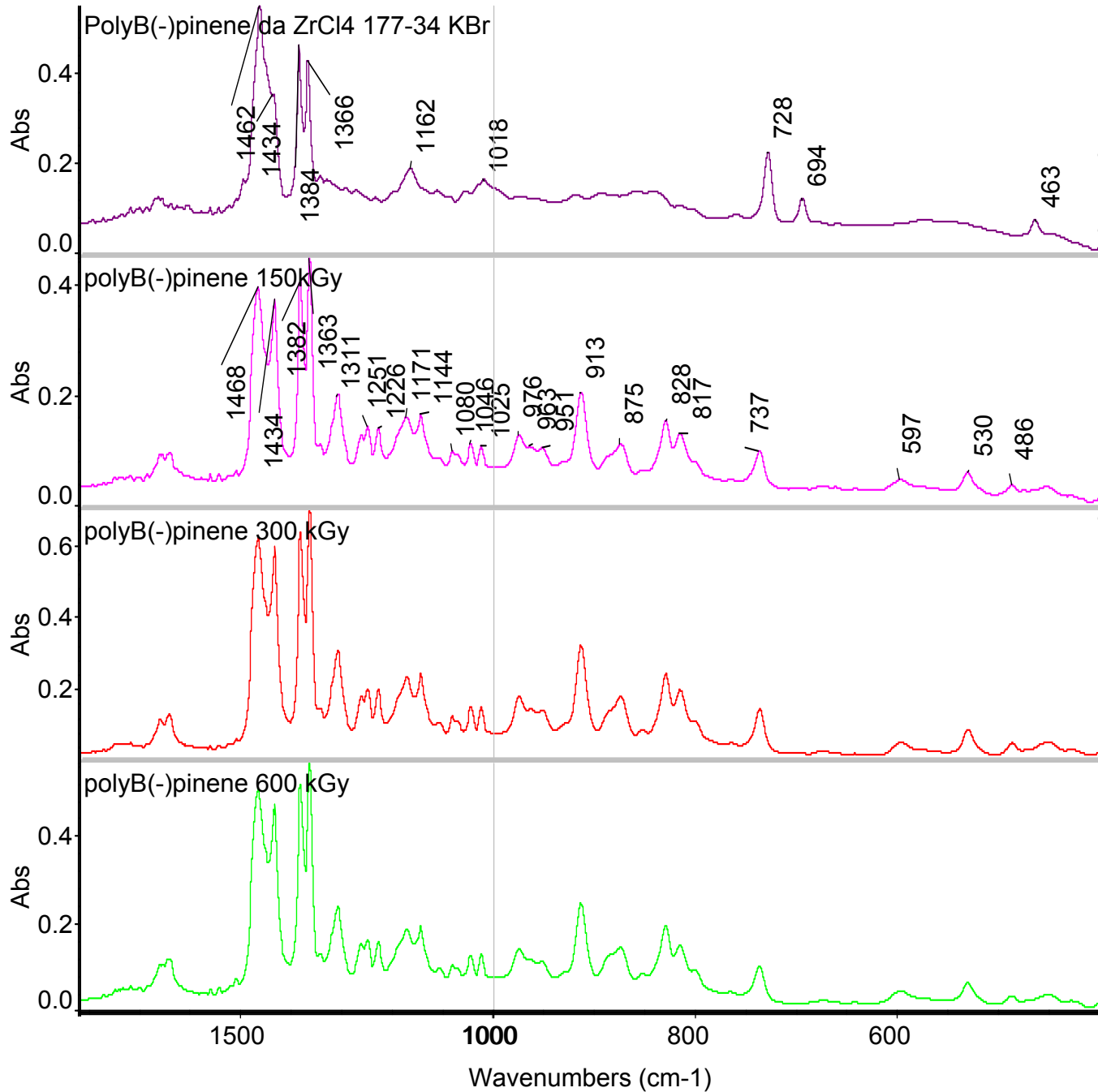
The radiation chemical yield $G = 1.93 \times 10^{-6} \text{ s}^{-1}$.

FT-IR spectra of poly $\beta(-)$ pinenes 1



- FT-IR spectra. **(Top):** $\beta(-)$ pinene monomer before radiolysis.
- **(Middle):** $\beta(-)$ pinene dimer recovered as insoluble fraction in acetonitrile.
- **(Bottom):** $\beta(-)$ pinene radiopolymer solid white resin obtained after 150 kGy radiation dose.

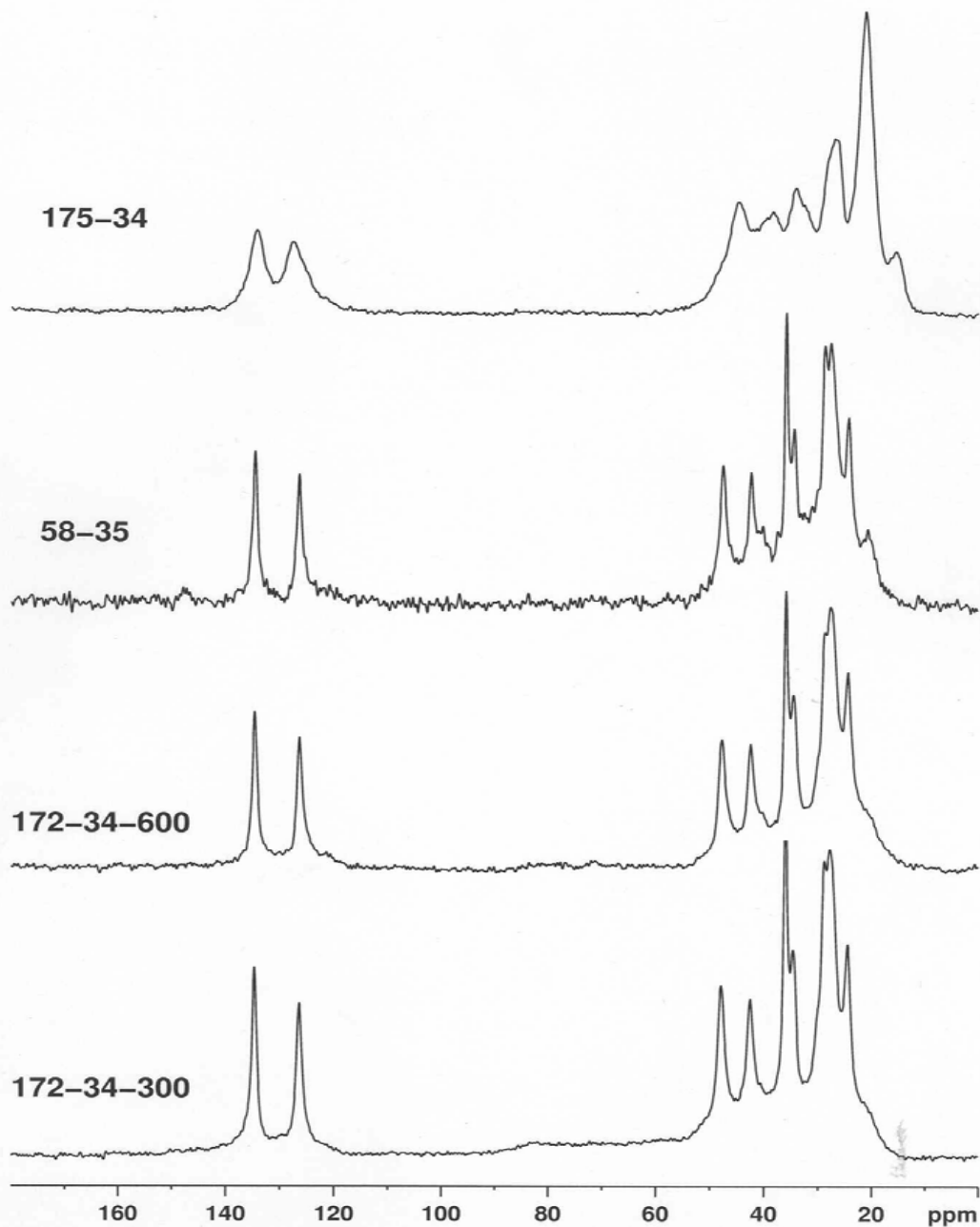
FT-IR spectra of poly $\beta(-)$ pinenes 2



- FT-IR spectra.
- **(Top spectrum):**
 $\beta(-)$ pinene resin from cationic polymeriz.
- Poly($\beta(-)$ pinene) solid resins recovered after radiolysis at 150, 300 and 600 kGy and resin separation).

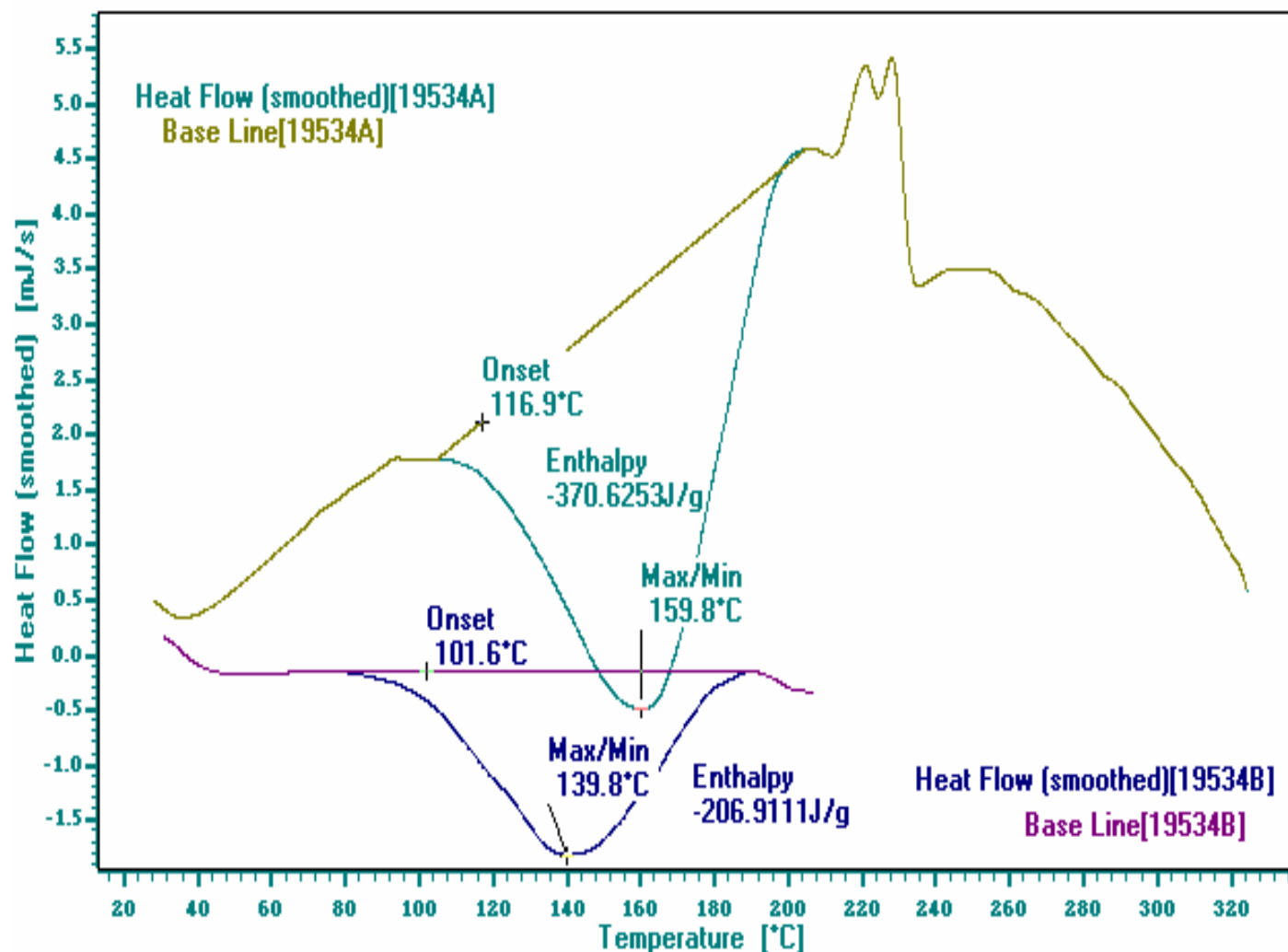
SOLID STATE C¹³-NMR OF POLY(β(-)PINENE)

RESINS



- The top spectrum is the less defined and is due to cationic polymerization $[\alpha]_D \rightarrow 0$
- The second from top is produced by free radical initiator
- The last two are from radiation-induced polymerization

DSC on polyB(-)pinene polymers



- The trace at the top with onset softening point of 117°C and peak melting point of 160°C refers to poly(β(-)pinene) radiopolymer.
- The trace at the bottom of the figure with onset at 102°C and peak at 140°C is due to poly(β(-)pinene) obtained by cationic polymerization.

Optical activity of fractions of radiolyzed B(-)pinene

TABLE corr - OPTICAL ACTIVITY OF BETA PINENE AND ITS PRODUCTS BEFORE AND AFTER RADIOLYSIS

	beta(-)pinene Crude oil	beta(-)pinene Solubles in acetonitrile	beta(-)pinene Solubles in toluene	beta(-)pinene Resin in Toluene
[a] _D Before radiolysis	-23,1 (neat)	-15,8 (c=8)	-34,6 (c=3) (*)	-34,6 (c=3) (*)
[a] _D 50kGy radiolysis	-22.1(neat)	-15,1 (c=12)	-31,3 (c=1)	
[a] _D 100kGy radiolysis	-22.2 (neat)	-14,7 (c=8)	-36.0 (c=6)	
[a] _D 150kGy radiolysis	-22.4 (neat)	-14.5 (c=8)	-39.6 (c=1)	-59.7 (c=0.2)
[a] _D 300kGy radiolysis	-23.4 (neat)	-15.0 (c=7)	-45.6 (c=2)	-57.1 (c=0.2)
[a] _D 600kGy radiolysis	-25.0 (neat)	-16.1 (c=6)	-45.2 (c=3)	-58.8 (c=0.4)

(*) pure beta pinene monomer in toluene

Optical activity of fractions of radiolyzed B(-)pinene (index values)

TABLE corr - OPTICAL ACTIVITY (index values) OF BETA PINENE AND ITS PRODUCTS BEFORE AND AFTER RADIOLYSIS

	beta(-)pinene Crude oil	beta(-)pinene Solubles in acetonitrile	beta(-)pinene Solubles in toluene	beta(-)pinene Resin in Toluene
[a] _D Before radiolysis	100	100	100	100
[a] _D 50kGy radiolysis	96	96	90	
[a] _D 100kGy radiolysis	96	93	104	
[a] _D 150kGy radiolysis	97	92	114	173
[a] _D 300kGy radiolysis	101	95	132	165
[a] _D 600kGy radiolysis	108	102	131	170

(*) pure beta pinene monomer in toluene