

## $\gamma$ -Radiation Induced Polymerization of a Chiral Monomer: A New Way to Produce Chiral Amplification

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**Abstract** The treatment of the terpene  $\beta(-)$ pinene with  $\gamma$  radiation (at dose level: 150, 300 and 600 kGy) causes its polymerization into a resin and into a dimer. The yield of the resin and of the dimer appears to be linearly dependent to the radiation dose. The structure of the products was studied by FT–IR spectroscopy also in comparison to a reference  $\beta(-)$ pinene resin prepared by cationic polymerization. A highly ordered structure was found in the case of the radiopolymer in comparison to the resin from cationic polymerization. Polarimetric measurements have shown astonishing enhancement in the optical activity of the radiopolymer and radiodimer in comparison to the starting optical activity of the  $\beta(-)$  pinene monomer. Also DSC (differential scanning calorimetry) data supports the unexpected highly ordered structure for the  $\beta(-)$ pinene radiopolymer in comparison to the resin prepared by cationic polymerization. The results have been discussed in terms of amplification of chirality caused by  $\gamma$  radiation and the implications of this fact on the mechanism of chiral amplification on prebiotic molecules.

**Keywords**  $\beta(-)$ pinene · terpene resin · radiopolymerization · optical activity · chirality · chiral amplification · origin of chirality · origin of life

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## Introduction

All theories which try to explain the origin of chiral homogeneity in the Earth can be classified under two main groups the biotic and the abiotic (Bonner 1988). Biotic theories sustain that prebiotic enantiomeric homogeneity is not a prerequisite for the origin of life. Thus, according to biotic theories, life originated at an advanced stage of chemical evolution employing initially racemic building blocks and only at a later stage of chemical evolution the early form of life gradually selected one enantiomer.

Observing the present biological world, the biochemistry which permits a so perfect and effective functioning of all living organisms, it appears quite impossible to conceive even the simplest living organism without the chirality of the key biological molecules and macromolecules (Brack 1998; Palyi et al. 1999; Podlech 2001; Palyi et al. 2004). Therefore, the abiotic theories sustain the thesis that life originated after the initial establishment of the enantiomeric excess. A chiral excess of the precursor molecules specialized in the life biochemistry should have formed before the appearance of any form of life. The experimental evidence of this possibility has been offered by the analysis of certain meteorites such as the carbonaceous chondrites which have already shown that the enantiomeric excess is already formed spontaneously, by a natural process under abiotic conditions (Cronin and Pizzarello 1999).

There are many hypothesis on how chirality appeared in a prebiotic world and some of these hypothesis are also supported by experimental facts; for reviews see Palyi et al. 1999, 2004; Cataldo et al. 2005. Among the most convincing mechanisms which lead to the enantiomeric excess, asymmetric photolysis of racemic substrates with circularly polarized light is a commonly accepted process which may have led to enantiomeric excess under prebiotic conditions (Inoue and Ramamurthy 2004; Griesbeck and Meierhenrich 2002; Jorissen and Cerf 2002). It is even thought that such process of asymmetric photolysis occurs in the circumstellar and interstellar medium due to the action of circularly polarized UV light emitted by stars (Bailey et al. 1998). The chiral molecules formed in such process in the interstellar medium are then incorporated in cometary bodies and delivered to planets and satellites where the conditions are more suitable for the development of life (Cronin and Pizzarello 1999).

However, the chirality can have had origin also from many other processes which have been reviewed recently (Cataldo et al. 2005); furthermore, a number of other photochemical events can generate the chirality (Matsuura and Koshima 2005; Inoue and Ramamurthy 2004).

Whatever the process considered as the source of homochirality in the biological world, the enantiomeric excess which can be reached is relatively low (Podlech 2001). Therefore, a number of other processes have been advocated as mechanism of chiral amplification (Podlech 2001; Palyi et al. 1999), ranging from the amplification of photochemical events (Ichimura 2003), to the asymmetric autocatalysis (Soai and Sato 2002) which involves the fact that the small amount of an enantiomer formed from an asymmetric reaction can inhibit the formation of its optical antipode.

The problem of chiral amplification and detection can be also faced in terms of helical polymers (Green and Jha 1997; Nakano and Okamoto 2001; Yashima et al. 2004). When chiral monomers are used to build the helical polymers, the optical activity of the corresponding polymer does not correspond to the contribution of the single monomers. Usually a very high excess of chirality is achieved due to the helical configuration assumed by the polymer chain, a configuration which is partially retained also in solution. This fact can be easily verified both in peptides, in proteins and in RNA and DNA macromolecules.

It is also possible to prepare helical polymers completely free from asymmetric carbon atoms in the backbone or in the substituents: the chirality arises simply from the screw

sense of the helix without the need of using chiral monomers (Nakano and Okamoto 2001; Cataldo and Keheyan 2003). In such case chiral auxiliaries or inclusion polymerization technique must be adopted. Alternatively, a non-racemic mixture of monomers can be polymerized and the helicity of the polymer will be dominated by the enantiomeric monomer which is present in excess. For instance in the case of polyisocyanates (Podlech 2001; Nakano and Okamoto 2001) with only 8% of enantiomeric excess (ee) the helicity in the polymer will be already 100% of the maximum helicity achievable by using exclusively one of the two optical antipodes as monomer. This effect is due to the so-called commander and soldier interaction (Yashima et al. 2004).

In our previous study on the radiolysis of chiral molecules we have verified the phenomenon of radoracemization (Cataldo et al. 2004) which may be distinguished into true and apparent racemization and simply consists in the fact that the optical activity of an enantiomer decays gradually to zero as function of the radiation dose administered either because it is radiolyzed to compounds free from asymmetric carbon atoms or because a true inversion in the chiral center occurs due to the action of the high energy radiation (a similar effect occurs with UV light and is called photoracemization). Here we report instead about the unusual and unexpected case of chirality enhancement during  $\gamma$  irradiation of a chiral terpene:  $\beta(-)$ pinene.

## Experimental

$\beta(-)$ Pinene >99.0% pure (by GC as sum of enantiomers) was obtained from Fluka. The specific optical rotation was checked before irradiation and found  $[\alpha]_D = -23.1^\circ$  (neat using  $d = 0.871$  g/ml) in line with literature data  $[\alpha]_D = -22.4^\circ$  (Budavari 1996). The polarimetric measurements were made on a Optika polarimeter model Pol 1 using the D sodium line at 589.3 nm.

The FT-IR spectra were recorded in KBr pellet on a Nicolet IR-300 from Thermo-Electron Corporation. A DSC (differential scanning calorimeter) from Linseis model L63 was used to measure the softening point of the resins. The samples were heated at  $5^\circ\text{C}/\text{min}$  in static air.

### Irradiation experiments

Three samples of 27 ml each were irradiated in three different glass vials fitted with screw cap.

Use was made of a  $^{60}\text{Co}$  gamma-cell from Atomic Energy of Canada as  $\gamma$  radiation source at a dose rate of 2.7 kGy/h. The total radiation dose administered to the three samples was 150, 300 and 600 kGy. After the irradiation the three samples showed the presence of a white resinous precipitate on the bottom and on the walls of the flask. The liquid  $\beta(-)$ pinene was separated from its solid resin by decantation.

The resins were quantitatively recovered from the respective flasks, washed with methanol and recovered by filtration on filter paper. After drying their mass was determined gravimetrically.

### Measurement of the optical activity on the irradiated $\beta(-)$ pinene

The optical activity of the irradiated samples was measured on neat undiluted liquid  $\beta(-)$  pinene using a density  $d = 0.871$  g/ml, the results are reported in Table I.

The irradiated samples of  $\beta(-)$ pinene were diluted with acetonitrile. Typically about 8.0 g of each irradiated  $\beta(-)$ pinene samples were diluted in 100 ml of acetonitrile. In this

**TABLE I** Specific optical rotation of  $\beta(-)$ pinene monomer, radiodimer and radiopolymer

Radiation dose (kGy)	$\beta(-)$ pinene monomer [ $\alpha$ ] <sub>D</sub> (neat)	$\beta(-)$ pinene monomer <sup>a</sup> [ $\alpha$ ] <sub>D</sub> (acetonitrile $c = 6.0$ )	$\beta(-)$ pinene dimer [ $\alpha$ ] <sub>D</sub> (toluene $c = 3.5$ )	$\beta(-)$ pinene resin [ $\alpha$ ] <sub>D</sub> (toluene $c = 0.3$ )
0	-23.1	-16.1 <sup>b</sup>	-34.6 <sup>b</sup>	-34.6 <sup>b</sup>
150	-22.3	-14.3	-39.6	-59.7
300	-23.4	-15.0	-45.6	-57.1
600	-25.0	-16.1	-45.2	-58.8

<sup>a</sup> After dimer separation<sup>b</sup> Pure pinene monomer in acetonitrile or in toluene

operation a fraction of insoluble  $\beta(-)$ pinene derivative remained on the walls and at the bottom of the flask under the form of sticky mass or droplets. It was hence possible to separate the acetonitrile solution from this oligomeric insoluble fraction by decantation. The optical activity of  $\beta(-)$ pinene solution in acetonitrile was determined. The mass of insoluble fraction in acetonitrile was determined gravimetrically. It was then dissolved completely in toluene and its optical activity was measured polarimetrically. A blank was made by dissolving 8.0 g of pure not irradiated  $\beta(-)$ pinene in 100 ml acetonitrile. The sample dissolved completely without the separation of any insoluble viscous precipitate.

#### Measurement of the optical activity on $\beta(-)$ pinene radiopolymer (resin)

About 200 mg of each resin sample purified and dried as described above were treated with 25 ml of toluene. Each resin sample showed limited solubility in toluene so that only 1/3 of the sample was soluble. The insoluble fraction was recovered by filtration, washed with acetone, dried and weighted to determine the soluble amount. The optical activity on the toluene soluble fraction was determined polarimetrically.

#### Preparation of a reference poly( $\beta(-)$ pinene) sample resin by cationic polymerization

The details of the cationic polymerization of  $\beta(-)$ pinene as reference resin have been reported previously (Cataldo and Keheyan 2006). The specific optical rotation of this resin in toluene ( $c = 2$ ) was found  $[\alpha]_D = -4.2^\circ \pm 0.6$ .

## Results and Discussion

### Yields of poly( $\beta(-)$ pinene) and pinene dimer

The radiolysis of  $\beta(-)$ pinene in bulk produced a white resin. This was quite unexpected since previous irradiation of other chiral terpenes like limonenes and phellandrene did not produce any solid resin. The resin was a  $\beta(-)$ pinene radiopolymer, as will be shown in the following sections. As described in the experimental section, the resin was easily separated from the residual monomer and it was washed and dried before determining the yield gravimetrically. A linear response between radiation dose and resin yield was observed (Cataldo and Keheyan 2006); the maximum yield of 6.5% of solid resin over the initial mass of the monomer was achieved after 600 kGy.

Due to radiolysis, the formation of the insoluble resin of poly( $\beta(-)$ pinene) was accompanied also by the formation of a pinene dimer which was soluble in the  $\beta(-)$ pinene monomer but was easily separated from the irradiated monomer when it was dissolved in acetonitrile. Elsewhere (Cataldo and Keheyan 2006) it is shown that the yield of the pinene dimer always exceeded the amount of solid resin produced, being almost double in amount with respect to the solid resin.

The poly( $\beta(-)$ pinene) appears radiostable in the sense that once formed it cannot be further decomposed or even racemized.

FT-IR spectroscopy on the radiopolymer poly( $\beta(-)$ pinene) and pinene dimer

A complete discussion of the infrared spectra of the monomer before and after the radiation treatment and in comparison with the spectra of the  $\beta(-)$ pinene dimer and the poly( $\beta(-)$ pinene) resin is reported elsewhere (Cataldo and Keheyan 2006). The infrared spectra show that  $\beta(-)$ pinene polymerizes under the action of  $\gamma$  radiation with the mechanism of ring-opening polymerization, with the shift of the double bond from the exocyclic position (in the monomer) to the endocyclic position as commonly accepted in literature also for the cationic polymerization of this monomer. In fact the radiopolymer structure appears in general analogous to that already described in literature for poly( $\beta(-)$ pinene) produced by cationic polymerization (Kennedy and Marechal 1991). However, the resin obtained by cationic polymerization shows a very limited number of infrared absorption bands, the hydrocarbon skeletal vibrations at 1,462 and 1,434  $\text{cm}^{-1}$ , the presence of the geminal methyl groups at 1,384 and 1,366  $\text{cm}^{-1}$  and the *cis* = CH wagging at 728  $\text{cm}^{-1}$ . Instead, the spectra of the poly( $\beta(-)$ pinene) resins obtained by radiopolymerization are richer in absorption bands displaying a series of additional bands which are not present at all in the spectrum of the resin obtained by cationic polymerization. This fact may suggest an higher structural regularity for the pinene radiopolymers in comparison to the resin obtained by cationic polymerization or the presence of structural fragments and units different from those commonly known in the  $\beta(-)$ pinene resin prepared by Friedel-Crafts catalysts (Cataldo and Keheyan 2006).

To go more insight into this fascinating problem, we have made an investigation on the optical properties of the resins obtained.

Polarimetric measurements on pinene radiopolymer and dimer

As shown in Table I (second column from left), pure undiluted  $\beta(-)$ pinene shows an  $[\alpha]_D = -23.1$  while the crude  $\beta(-)$ pinene collected after the radiolysis at 150 kGy brings this value to  $-22.3$  a typical trend called radoracemization which involves a drop in the optical activity as function of the radiation dose (Cataldo et al. 2004). The observed drop represents about 3% reduction in the optical activity (see Table II, second column from left), a normal trend observed also for other chiral molecules.

However higher radiation dose instead of continuing the mentioned expected trend to push the optical rotation down to  $0^\circ$  causes an increase of the optical rotation to  $-23.4^\circ$  and then to  $-25.0^\circ$  respectively at 300 and 600 kGy. This was unexpected since it involves an increment of the optical activity of about 1% at 300 kGy and 8% at 600 kGy as shown in Table II (second column from left).

In Table I (third column from left) the radiolyzed residual pinene monomer after dissolution in acetonitrile and separation of the resin and the dimer shows a trend in optical activity which follows that already discussed for the unfractionated neat samples. At

**TABLE II** Index values of optical rotation of  $\beta(-)$ pinene monomer and radiolysis products

Radiation dose (kGy)	$\beta(-)$ pinene monomer Index value	$\beta(-)$ pinene monomer <sup>a</sup> Index value	$\beta(-)$ pinene dimer Index value	$\beta(-)$ pinene resin Index value
0	100	100	100	100
150	97	89	114	172
300	101	93	132	165
600	108	100	131	170

<sup>a</sup>After dimer separation

150 kGy there is a trend to radoracemization which is followed by a recovery at higher radiations doses with an opposite trend against the racemization. As shown in Table II (third column from left) the optical activity drops of 11% at lower radiation doses but then it recovers to the original value of the pristine pinene sample at higher radiation doses.

Surprisingly, the results on the optical activity measured on the  $\beta(-)$ pinene dimer and on the resin poly( $\beta(-)$ pinene) formed from the radiopolymerization of the monomer do not show the same trend of the neat  $\beta(-)$ pinene or its fraction soluble in acetonitrile. In fact, as reported in Table I (second column from right) the dimer once dissolved in toluene displays a significantly higher optical activity than the monomer, much higher than the expected value for a  $\beta(-)$ pinene dimer (or trimer). For instance the  $[\alpha]_D$  value at 300 kGy is  $-45.6$  and should be compared with the  $[\alpha]_D$  of reference pristine  $\beta(-)$ pinene whose  $[\alpha]_D = -34.6$ . If we take that value as reference for comparison, we find that the dimer has 32% higher optical activity than the monomer (Table II, second column from right). Even much higher than the dimer was found the optical activity of the solid poly( $\beta(-)$ pinene) dissolved in toluene. Its  $[\alpha]_D \approx -59$  in the three samples taken at different radiation dose (Table I, first column in the right) is 70% higher than the value of the specific optical rotation of the monomer (Table II, first column in the right). For comparison the  $[\alpha]_D$  of the poly( $\beta(-)$ pinene) obtained by cationic polymerization on  $ZrCl_4$  is only  $-4.2$  (see experimental section), about 10 times lower than the monomer value which in toluene shows a value of  $[\alpha]_D = -34.6$ .

### General discussion

The continuous action of high energy radiation on chiral molecules in prebiotic conditions for geological time scale plays against the preservation of chirality because of the radiolysis, photolysis and the associated phenomena of true and apparent radoracemization and photoracemization (Cataldo et al. 2005). The radoracemization phenomenon has already been verified in the case of a couple of chiral terpene molecules (Cataldo et al. 2004). As shown in the previous sections, the  $\gamma$ -irradiation of  $\beta(-)$ pinene produces a white resin and a dimer as well as other products, but was a real surprise to find out that the optical activity of the crude monomer does not falls down to zero as expected but after fractionation was higher than the starting monomer. Similarly the dimer and the resin shows significantly higher optical activity per unit mass than the starting monomer. We are dealing with the phenomenon of amplification of chirality but in the present case this has been caused by the polymerization with a physical force field:  $\gamma$  radiation.

Poly( $\beta(-)$ pinene) has been prepared since long with cationic catalysis (Roberts and Day 1950), depending on the polymerization conditions the cryoscopic molecular weight was found in the range between 1,500 and 2,750 Da. Already at that time it was realized that

during the cationic polymerization the exocyclic double bond of the monomer is shifted inside the cyclohexane ring while the cyclobutane ring of the monomer undergoes a ring opening polymerization. Later studies (Modena et al. 1965; Pietila et al. 1970; Kennedy and Marechal 1991) have further elucidated the mechanism of cationic polymerization of  $\beta(-)$  pinene as well as its structure.

In the “FT–IR spectroscopy on the radiopolymer poly( $\beta(-)$ pinene) and pinene dimer” we have shown the FT–IR differences between the poly( $\beta(-)$ pinene) obtained by  $\gamma$ -radiation and by cationic polymerization. This can be viewed in conjunction with the striking differences in optical activity of the  $\beta(-)$ pinene resins obtained either by radiopolymerization or by cationic polymerization as discussed in “Polarimetric measurements on pinene radiopolymer and dimer”. These results can be interpreted in terms of a higher structural order in case of  $\beta(-)$ pinene radiopolymer which is justified by its numerous and well defined absorption bands in the FT–IR spectrum and by its much higher specific optical rotation in contrast to the poorly defined, broad absorption FT–IR bands and very low optical activity of the  $\beta(-)$ pinene resin produced by cationic polymerization. In other words the excess of chirality in  $\beta(-)$ pinene radiopolymer can be due to a special concatenation of the monomers combined with an helical structure (or another type of highly ordered superstructure) despite the relatively low molecular weight of the polymer. The simplest way to interpret the excess of chirality of  $\beta(-)$ pinene radiopolymer is to admit a special superstructure and an higher molecular weight with respect to the cationically polymerized  $\beta(-)$ pinene (Cataldo and Keheyan 2006).

An additional support to this view can be derived by the DSC data. The poly( $\beta(-)$ pinene) produced by cationic polymerization shows an onset softening point at about 102° with a peak at 140°C in complete agreement with literature data (Roberts and Day 1950) which in fact reports a peak value at 132–136°C. Instead the  $\beta(-)$ pinene radiopolymer shows an onset at about 117°C and the softening peak is recorded 160°C. The higher softening transition for the  $\beta(-)$ pinene radiopolymer is consistent at least with its higher molecular weight in comparison with the cationic poly( $\beta(-)$ pinene) and the higher enthalpy involved in softening process (370 J/g) is consistent with a different supramolecular arrangement of the  $\beta(-)$ pinene radiopolymer vs the cationic poly( $\beta(-)$ pinene) whose enthalpy is only 207 J/g.

A more complex topic involves the isomerization and racemization of the monomer before its polymerization. The cationic polymerization implies necessarily the isomerization and probably the racemization of a crucial chiral center in the structure of the monomer combined with the absence of a special polymeric superstructure. For the  $\beta(-)$ pinene radiopolymer, although we must admit the commonly accepted polymer structure, which is suggested by infrared spectroscopy, we must also admit the absence of significant racemization of the monomeric units. Furthermore, in the latter case, we may admit a certain degree of isomerization of  $\beta(-)$ pinene monomer into another structure with higher optical activity before its polymerization.

It is also useful to complete the interpretation of our results in the frame of the results of Modena et al. 1965. These authors have shown that the cationic polymerization of  $\beta(-)$ pinene produces a resin with  $[\alpha]_D = -6.2$  ( $c = 10$  benzene), thus, not so far from our  $[\alpha]_D$  value of  $-4.2$ . In contrast, the use of a highly stereospecific Ziegler–Natta catalyst applied at  $-80^\circ\text{C}$  and at low monomer conversion produced a  $\beta(-)$ pinene resin with  $[\alpha]_D = -53.7$ , hence not far from our best value for  $\beta(-)$ pinene radiopolymer  $[\alpha]_D = -59.7$ . Therefore, it appears quite clear that the use of a high stereospecific catalyst lead to a polymer with a highly ordered structure which displays very high optical activity. The same structural order appears to be achieved by radiopolymerization while it is not reached at all with cationic polymerization.

## Conclusion

The  $\gamma$  irradiation of  $\beta(-)$ pinene produces a dimer and a solid white resin of poly( $\beta(-)$ pinene). The radiolysis instead of causing the radoracemization of the enantiomerically pure monomer caused an unexpected increase in the optical activity of the system. The specific optical activity of the monomer increased after the radiolysis and the recovered  $\beta(-)$ pinene dimer and polymer showed an unexpectedly higher optical activity not explainable without admitting an highly regular polymeric superstructure. The highly regular poly( $\beta(-)$ pinene) structure, with very high optical activity has been reported in literature only for  $\beta(-)$ pinene polymerized at  $-80^{\circ}\text{C}$  with highly stereospecific Ziegler–Natta catalysts. The classical cationic polymerization of  $\beta(-)$ pinene leads to a resin with very low optical activity and structural regularity.

To the best of the author's knowledge it is the first time that at so high radiation dose, instead of observing a reduction in the optical activity of a chiral molecule, a phenomenon known as radoracemization, it is instead observed an increase in the optical activity of the system with the formation of a series of products having a much higher optical activity in comparison to the starting monomer, a phenomenon which can be described as chiral amplification. It is absolutely remarkable in the context of the prebiotic amplification of chirality that this result has been achieved simply by using  $\gamma$  radiation and a very simple terpene monomer.

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