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A Study on the Optically Active Polymer Poly- β -pinene

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Poly- β -pinene (PBP) was obtained by radiation-induced polymerization of monomer with γ radiation. The polymerizations were conducted both in vacuum and in the presence of air at different radiation doses up to 1–3 MGy. It was found that the presence of oxygen retards the polymerization rate and reduces the polymer yields and the radiation chemical yield suggesting that the polymerization mechanism involves free radicals. It is shown that PBP can also be obtained in low yields from β -(-)pinene polymerization with a free radical initiator. The chemical structures of the PBP radiopolymer and PBP obtained by a free radical initiator were studied by FT-IR and ¹³C CP-MAS NMR spectroscopy. The data shows that the PBP obtained have highly ordered structures, which is manifested also by the very high specific optical rotation which is about 3 times that of the starting monomer in the case of the radiopolymer and about 5 times in the case of the PBP prepared with the free radical initiator. In contrast, PBP obtained in high yields by cationic polymerization shows a very low specific optical rotation, much lower than that of the starting monomer and low regularity in chemical structure has been attributed to this polymer by FT-IR and ¹³C CP-MAS NMR spectroscopy. It is shown that PBP with high optical activity racemizes over an acidic catalyst.

Keywords: β -pinene; poly- β -pinene; radio polymerization; free radical polymerization; cationic polymerization; optically active polymer; optical activity; chirality; chiral polymer; racemization; chemical structure

1 Introduction

β -(-)pinene is a naturally occurring terpene which is employed, among other things, for the industrial production of a hydrocarbon or terpene resin (1). The resin finds application in the manufacture of solvent-based adhesive tapes and labels and as a plasticizer and tackifier in elastomer-based formulations (1). The production process of poly- β -pinene (PBP) involves the carbocationic polymerization with suitable Friedel-Crafts catalysts (1, 2).

It is less known that β -(-)pinene can be polymerized by Ziegler-Natta catalysts yielding an optically active polymer whose specific optical rotation exceeds that of the starting monomer (3). On the other hand, the optical activity of PBP produced by cationic polymerization is very small (4).

Recently, it has been reported that β -(-)pinene can be polymerized by γ -radiation, yielding a polymer having very high optical activity, comparable to that measured on PBP prepared on a Ziegler-Natta catalyst (4). For the first time, it has been found that high energy radiation may play a role in the so-called chiral amplification mechanism in the prebiotic world (5, 6) while it is well known that normally the action

of radiation on chiral molecules, including the prebiotic molecules, plays a key role against the preservation of chirality (7, 8).

In the present paper, we are presenting a complete study on the radiation-induced polymerization of β -(-)pinene, on the polymerization mechanism and on the structure of the resulting polymer.

2 Experimental

β -(-)pinene was obtained from Fluka or Aldrich. β -(-)pinene used in this work was >99.0% pure (by GC as the sum of enantiomers). The specific optical rotation was checked before irradiation and found $[\alpha]_D = -21.3$ (neat using $d = 0.871$ g/ml).

FT-IR spectra were recorded on liquid samples as thin film between KBr windows in transmittance mode, on solid samples embedded in KBr pellets again in transmittance mode or on a ZnSe plate on ATR accessory in reflection mode. Use was made of an IR-300 FT-IR spectrometer from Nicolet Thermo-Electron Corporation.

The electronic absorption spectra were recorded on a Shimadzu UV160A spectrophotometer using in the reference cuvette pure, not irradiated β -(-)pinene and in the sample cuvette the crude liquid β -(-)pinene after γ irradiation at

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any selected dose. The polarimetric measurements were made on a Optika polarimeter model Pol 1 using the D sodium line at 589.3nm.

Solid state ^{13}C CP-MAS NMR spectra were performed at 50.13 MHz on a Bruker ASX-200 spectrometer. The spin-rate was 8 kHz; the $\pi/2$ pulse width was 3.5 μs ; 4000 scans were acquired for each spectrum. The cross-polarization was performed applying the variable spin-lock sequence RAMP-CP-MAS, the RAMP was applied on the ^1H channel, and, during the contact time $\tau = 1$ ms, the amplitude of the RAMP increased from 50 to 100% of its maximum value.

Spectra were acquired using 1024 data points in the time domain, zero filled and Fourier transformed. The chemical shift was externally referred to tetramethylsilane. Samples were packed into 4 mm zirconia rotors, and sealed with Kel-F caps.

2.1 Irradiation Experiments of $\beta(-)$ pinene at 100, 200, 400 and 943 kGy in Vacuum

Four thick-walled glass vials charged with 18 ml of $\beta(-)$ pinene each, were sealed in a high vacuum line after repeated cycles of degassing procedure. The vials were then irradiated at room temperature. Use was made of a ^{60}Co gamma-cell as a γ radiation source at a dose rate of 2.2 kGy/h. The total radiation dose administered to the four samples was 100, 200, 400 and 943 kGy, respectively.

After the radiation treatment, the samples were stored at $+5^\circ\text{C}$ for one month before the work-up. The vials were opened at the break-seal, they were found under pressure because of the accumulated radiolysis gases and all presented a solid phase (a white solid precipitate) and a liquid phase. The solid phase (consisting in PBP) was recovered by filtration in filter paper "Rapida A", washed with methanol and left to dry in a desiccator under reduced pressure. The yield was determined gravimetrically. The crude liquid phase was studied polarimetrically, by electronic absorption spectroscopy and by FT-IR spectroscopy.

The yield of solid PBP resin over the starting monomer was 0.42% by weight at 100 kGy. At 200 kGy the yield reached 1.4% and at 400 kGy was about 6.0% $[\alpha]_{\text{D}} = -48.1$ (toluene $c = 1.3$). Finally, at 943 kGy the yield of solid PBP was 37.2% $[\alpha]_{\text{D}} = -50.3$ (toluene $c = 1.3$). The specific optical rotation was measured only on the toluene soluble fraction of the PBP resin.

In the case of the sample prepared at 943 kGy, the work-up was different. The liquid phase was present in very small amounts. The majority of the sample was under the form of a solid phase mixed with a highly viscous and tacky phase. Thus, the crude mixture was poured into an excess of methanol, refluxed and filtered warm through a paper filter. In this way, it was possible to separate the oligomeric and tacky fraction from the solid resin. In fact, the oligomeric fraction remained inside the warm methanol and separate

out during cooling, while the solid polymeric fraction was recovered on the paper filter.

2.2 Irradiation Experiments of $\beta(-)$ pinene at 1000, 2000, 3000 kGy in Closed Vials

In previous works (4, 6, 9, 10), the irradiation of $\beta(-)$ pinene was conducted in screw-cup closed vials where the air was not completely excluded. The irradiations were made at 50, 100, 150, 300, 600 kGy (4, 6, 9, 10). In the present work, the $\beta(-)$ pinene irradiations have been made at 1000, 2000 and 3000 kGy, again using the screw-cap vials (25 ml each) without the complete exclusion of air at a dose rate of 2.2 kGy/h. After the irradiation, the samples were stored at $+5^\circ\text{C}$ for a couple of weeks, and the flasks were opened. All were found under pressure because of the accumulation of the radiolysis gases. In all three cases, it was possible to recover a liquid fraction which was separated from the solid by filtration as described in section 1.1. The solid fraction was washed with anhydrous ethanol and dried in a desiccator under reduced pressure. The yield of solid PBP was determined gravimetrically. The PBP prepared at 2000, and especially at 3000 kGy, was mixed with a tacky oligomer and was thoroughly washed with anhydrous ethanol before drying and weighing.

PBP prepared at 1000 kGy $[\alpha]_{\text{D}} = -47.2$ (toluene); PBP prepared at 2000 kGy $[\alpha]_{\text{D}} = -48.9$ (toluene); PBP prepared at 3000 kGy $[\alpha]_{\text{D}} = -59.8$ (toluene) and $[\alpha]_{\text{D}} = -61.2$ (1,2,4-trichlorobenzene $c = 2.6$).

The specific optical rotation was measured only on the toluene soluble fraction of the PBP resin.

2.3 Fractionation of the Liquid Phase of the Irradiated $\beta(-)$ pinene Samples

The irradiated $\beta(-)$ pinene samples were separated by filtration from the resin formed during radiolysis and then their optical activity was checked polarimetrically on the neat samples without dilution with any solvent. Afterwards, about 6–7 g of each irradiated sample was dissolved in 50 ml of acetonitrile. The amount of insoluble fraction in acetonitrile was dependent on the radiation dose administered and separated out as a viscous oil from the solution and determined gravimetrically. The acetonitrile in the soluble fraction of each sample was then dissolved in 25 ml of toluene and the optical activity of this fraction was recorded previously (4, 6, 9, 10). More details on the fractionation of the crude irradiated $\beta(-)$ pinene have been reported previously (4, 6, 9, 10).

2.4 Preparation of $\beta(-)$ pinene Resin by Cationic Polymerization

Reference $\beta(-)$ pinene resin was prepared by treating the monomer with ZrCl_4 in toluene as detailed previously

(4, 6, 9, 10). The specific optical rotation of the resin in toluene ($c = 2$) was found $[\alpha]_D = -4.2 \pm 0.6$.

The synthesis of PBP by cationic polymerization was repeated by diluting 40 ml of $\beta(-)$ pinene in 110 ml of CH_2Cl_2 . The solution was cooled at $+5^\circ\text{C}$ in a water/ice bath and the cationic polymerization was initiated by 2.8 g of ZrCl_4 . The reaction was violent and adequate mechanical stirring and a large flask must be used. The polymerization is very fast and then the mixture was treated with 150 ml of HCl 6% under stirring. The aqueous phase was then separated from the organic phase with the aid of a separating funnel. The organic phase was then steam distilled to strip off the solvent. PBP was obtained as a bright white powder in quantitative yield. $[\alpha]_D = -9.3 \pm 1.6$ ($c = 3.2$ toluene). The PBP by cationic polymerization was completely soluble in toluene.

2.5 Preparation of $\beta(-)$ pinene Resin by Free Radical Polymerization

$\beta(-)$ pinene (30.68 g) was refluxed under a nitrogen blanket with 0.598 g of 2,2'-azobis(2-methylpropanitrile) for 37 h (oil bath temperature 195°C). On cooling, the mass appeared viscous. It was treated with an excess of warm methanol, and methanol was decanted a couple of times and replaced with fresh methanol and left in contact with the polymer overnight. After further decantation of the solvent, the mass was also treated with acetone and filtered. A white powder was recovered with a yield of 3.7 g. $[\alpha]_D = -94.7 \pm 2.7$ ($c = 1.8$ toluene).

In order to purify the $\beta(-)$ pinene monomer in some cases, we have distilled it through a 15 cm vigreux column. The residue of distillation always contained PBP, which was formed due to the high temperatures reached in the oil bath and possibly to the presence of a trace amount of some $\beta(-)$ pinene hydroperoxide. In any case, the PBP was recovered in low yield over the total mass distilled (about 2–3%), but it displays an FT-IR spectrum identical to the PBP obtained through the free radical initiator and an $[\alpha]_D = -58.2 \pm 6.4$ ($c = 1.0$ toluene). It is partially soluble in toluene.

2.6 Racemization of the Poly($\beta(-)$ pinene) Resin with Amberlyst 15 Dry

PBP resin obtained in section 2.5 (0.923 g) was dissolved in 50 ml toluene and refluxed with 2.0 g of acidic resin Amberlyst 15 dry. After refluxing, the solution was cooled and the specific optical rotation was checked. The optical activity gradually approached the zero value (see section 3.4 for further details and discussion).

2.7 Racemization of the Poly($\beta(-)$ pinene) Resin with a Friedel-Craft Catalyst

Poly($\beta(-)$ pinene) resin (200 mg) obtained at 400 kGy in vacuum was dissolved in 25 ml of toluene. In these conditions, the specific optical rotation was $[\alpha]_D = -58.8 \pm 5.9$. The

toluene solution was treated with 1.5 g of ZrCl_4 and the resulting orange mixture was refluxed for 15 min. After cooling, the reaction mixture was washed with an excess of aqueous HCl 12% to remove the catalyst and the toluene layer was separated from the aqueous solution with the aid of a separatory funnel. The optical activity of the recovered toluene solution was controlled polarimetrically; it showed the complete absence of any optical activity.

3 Results and Discussion

3.1 Yield and Radiation Chemical Yield of PBP

The radiation chemistry of pinene isomers has been studied at the beginning of the 60's (11–13). It has been discovered that the radiation chemical yield $G(-\text{monomer}) = G$ (polymer monomeric unit) was highly influenced by the presence of impurities and especially by water. In particular, it was found that water reduces the radiation chemical yield, so that a $G = 6$ molecules/100eV has been recorded for $\beta(-)$ pinene saturated with water in contrast with a $G = 22$ molecules/100 eV for the monomer dried over metallic sodium and $G = 31$ after drying over P_2O_5 . In a previous work, Cataldo et al. (9) has reported a $G = 18,6$ molecules/100 eV for a high purity commercial grade of $\beta(-)$ pinene radiolyzed in a closed flask in the presence of traces of air, hence not so far from the values of Bathes et al. (11) As shown in Figure 1, the PBP yield is linear when $\beta(-)$ pinene is irradiated in the presence of air and all the data available fit the equation:

$$Y = 7.91 \times 10^{-3} R_D \quad (1)$$

Where Y is the PBP yield in % by weight over the amount of the starting monomer and R_D is the radiation dose in kGy. A

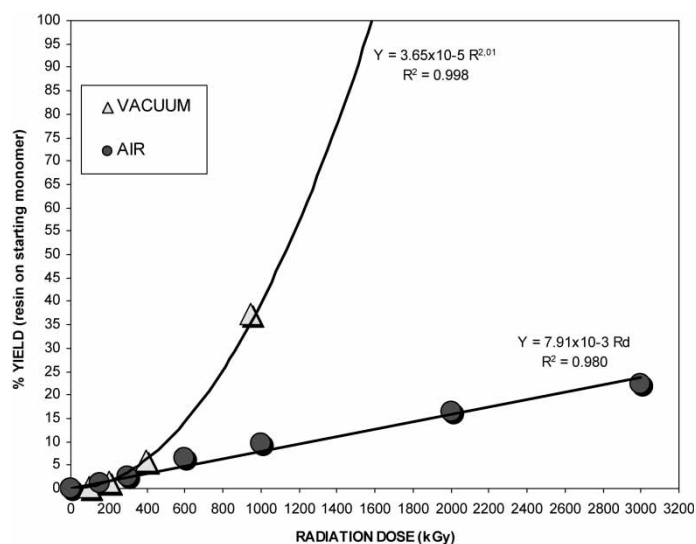


Fig. 1. Yield of solid poly- β -pinene (PBP) at different radiation dose. Note that the yield is linear in the case of β -pinene irradiation in air, but it follows a quadratic law when the irradiations are made in vacuum.

linear response has been found by other authors working under similar conditions (11). Considering all the yield data available from this and previous studies (4, 6, 9, 10), including also the data obtained at very high radiation dose of the order of MGy, the average radiation chemical yield for the β (-)-pinene polymerization in the presence of air is $G(\text{PBP})_{\text{monom}} = 6$ molecules/100 eV. The value reported considers only the amount of monomer lost in the formation of the PBP polymer and does not consider the amount of monomer lost in the formation of PBP oligomer or other possible products.

The polymerization of β (-)-pinene in vacuum shows a non-linear response in the yield as shown in Figure 1. The absence of air causes an acceleration of the polymerization reaction and at 943 kGy about 1/3 of the total monomer mass is converted into PBP and an additional fraction into PBP oligomer (not shown in Figure 1). The PBP yield data obtained in vacuum can be fitted by the equation:

$$Y = 3.65 \times 10^{-5} R_D^{2.01} \quad (2)$$

The inhibitory action of oxygen on the polymerization rate of β (-)-pinene has been observed also by Bathes et al. (11) and it can be taken as a first indication which supports the idea that the radiation-induced polymerization of β (-)-pinene follows a free radical mechanism. The reason for the non-linear response in the polymerization yield of β (-)-pinene in vacuum is not clear. Further studies are needed. A consequence of the non-linear response in the PBP yield in vacuum is that also the radiation chemical yield changes with the radiation dose. For instance at 943 kGy, $G(\text{PBP})_{\text{monom}} = 32$ molecules/100 eV, which can be compared with the values reported by Bathes et al. (11).

3.2 About the Formation of PBP Oligomer

The formation of solid white PBP by radiation-induced polymerization is also accompanied by the formation of a PBP oligomer (PBPo) (4, 6, 9, 10). Once formed, PBP precipitates out from the monomer as a solid, instead PBPo is soluble in the monomer and remains dissolved. It is possible to isolate the oligomer by diluting the irradiated monomer with acetonitrile or methanol (after the previous removal of PBP). PBPo precipitates as a white tacky mass and its yield follows that of PBP as shown in Figure 2. It is clear that PBPo has lower molecular weight than PBP and this is the reason why it remains soluble in the monomer. The radiation chemical yields discussed in the previous section, to be completed should consider both the formation of PBP and PBPo, so that $G(-\text{monomer}) = G_{\text{total}} = G(\text{PBP})_{\text{monom}} + G(\text{PBPo})_{\text{monom}}$. Since Figure 2 shows that the PBPo yield is almost double than the yield of PBP, then the $G_{\text{total}} = 3 G(\text{PBP})_{\text{monom}}$ so that $G_{\text{total, air}} \approx 18$ molecules/100 eV.

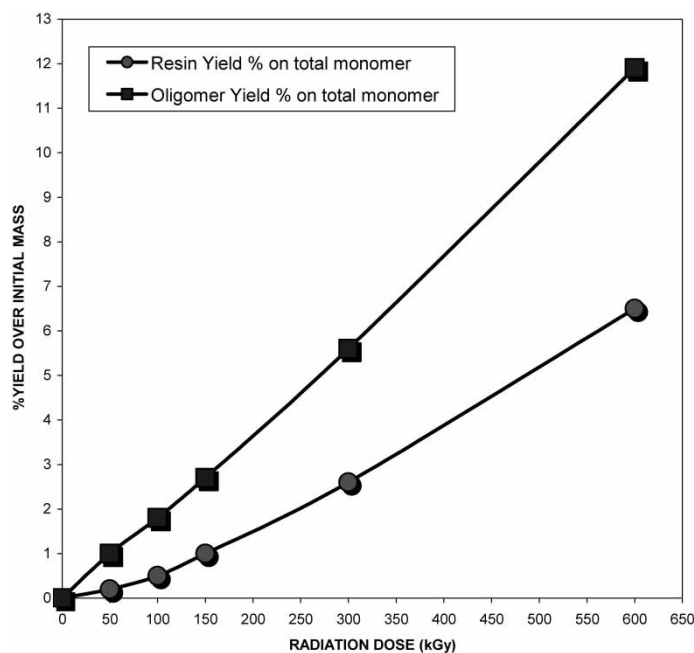


Fig. 2. Yield of white, solid, monomer insoluble PBP resin compared with the yield of oligomers of β -pinene (measured as acetonitrile insolubles). There is a linear dependence of the yield of these products with the radiation dose administered to β -pinene in the presence of air.

3.3 Electronic Absorption Spectra of Irradiated β (-)-pinene Solutions

When the electronic absorption spectrum of irradiated β (-)-pinene is recorded using a reference cuvette filled with pure β (-)-pinene a new absorption band can be observed. Such a band is located at 313 nm in the case of the samples exposed to γ radiation in vacuum and the band at 313 nm is not symmetric but also shows a shoulder at 325 nm. The β (-)-pinene samples irradiated in the presence of air show a similar absorption band but much more intense, probably also due to the higher radiation dose used. To permit the measurement of the absorbance also for all the β (-)-pinene samples irradiated in the presence of air, the samples were diluted 100 times with pure β (-)-pinene before recording the absorption spectra. The dilution causes a shift to shorter wavelengths of the absorption band to 300 and even to 295 nm. Also, in this case, the absorption band is not symmetric but shows a shoulder at higher wavelengths. Figure 3 shows the trend of the mentioned absorption bands. In the case of β (-)-pinene irradiated in vacuum, the growth of the optical density of the band is rapid and in line with the much higher radiation chemical yield for the polymerization. Instead, the growth of the band observed in the samples irradiated in the presence of air is slower, especially at lower doses. The shape is sigmoidal suggesting that initially, at low doses the band growth rate is inhibited by the presence of oxygen, afterwards when higher radiation doses are reached, the slope changes suggesting a higher growth rate because of the

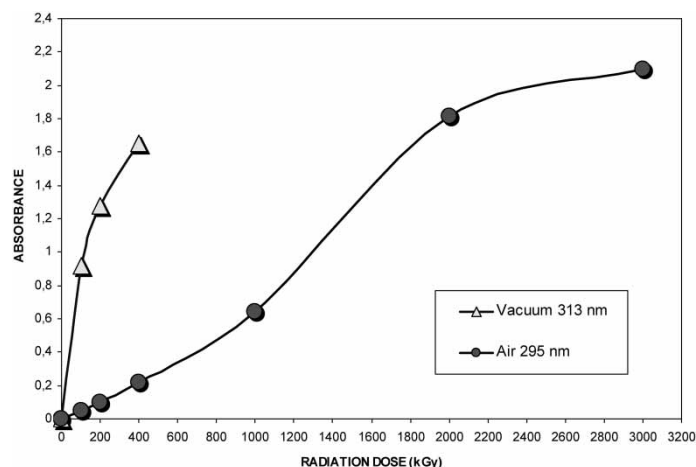


Fig. 3. Evolution of the absorption band at 313 nm for the crude β -pinene irradiated in vacuum in comparison to the absorption band at 295 nm for the crude β -pinene irradiated in air. Note the sigmoidal shape for the latter curve and the much high radiation dose administered.

disappearance of the inhibition effect (all oxygen has been consumed). Above a certain concentration, the monomer solution is saturated with the specie responsible for the absorption and its accumulation in solution is stopped.

It is reasonable to assume that the main chemical specie responsible for the absorbance at 313–295 nm is the PBPo, which being soluble in the monomer, accumulates into it as a solute.

3.4 Optical Activity of PBP and Related Topics

As general rule, the high energy radiation inevitably causes the racemization of chiral molecules, and hence plays against the preservation of the chirality; this has been widely discussed elsewhere (6–10). This fact has an impact on the pre-biotic chemistry, on the origin and on the preservation of chirality in the universe and definitely has an impact also on the origin of life. Studies on the radoracemization of chiral molecules are not numerous but have been partially reviewed (5) and have been conducted also on several terpenes (7, 8, 12). The discovery that the radiation treatment of β (-)-pinene causes an enhancement of the optical activity comes completely unexpected. In fact, earlier studies on the radiation chemistry of β (-)-pinene (11) have omitted to investigate its optical activity after irradiation and the optical activity of the resulting PBP.

Figure 4 reports the specific optical rotation $[\alpha]_D$ of β (-)-pinene irradiated in vacuum and in air after the separation of the solid PBP. Thus, the irradiated β (-)-pinene samples contain the oligomer PBPo as solute while the solid polymer has been removed. It can be observed that the $[\alpha]_D$ value passes from an original -21.3 and instead tends toward zero as a function of the radiation dose (the expected racemization trend) it increases linearly to -36.4 at 3 MGy in air and to an extrapolated value of -47 at 3 MGy in vacuum.

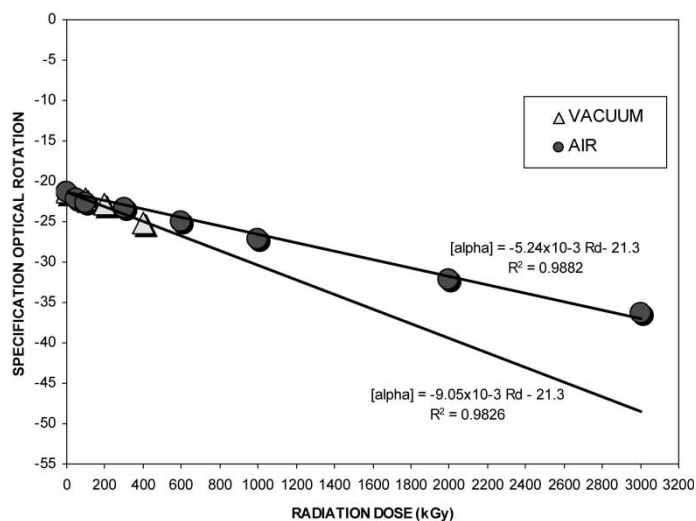


Fig. 4. Evolution of the specific optical rotation $[\alpha]_D$ of the crude β -pinene as a function of different radiation dose. The optical activity increases instead of decreasing under the action of radiation.

The equations deduced from the graph of Figure 4 are for irradiation in air:

$$[\alpha]_D = -5.24 \times 10^{-3} R_D - 21.3 \quad (3)$$

and in vacuum:

$$[\alpha]_D = -9.05 \times 10^{-3} R_D - 21.3 \quad (4)$$

showing once again that even the growth of the specific optical rotation is quite double in vacuum than in air.

The increase in the optical activity of β (-)-pinene with the radiation dose is due to the accumulation of the PBPo. In fact, the soluble oligomer has a higher specific optical rotation than the starting monomer and as solute enhances the optical activity of β (-)-pinene monomer (4, 9, 10).

PBP is partially soluble in toluene and its optical activity has been measured in that solvent on the soluble fraction which normally is roughly 35% of the total resin obtained (4). Figure 5 shows that the specific optical rotation of PBP is in the range between -50 and -60 irrespective for the radiation dose used and irrespective also for the fact that the polymer has been prepared in air or in vacuum. The data reported in Figure 5 pertain to the PBP toluene soluble fraction. However, we have also used it as a solvent where PBP is completely soluble, reducing the risk of errors due to the quantification of the soluble and insoluble fraction. In fact, we have found that 1,2,4-trichlorobenzene dissolves the PBP resin prepared at 3000 kGy in air completely. The $[\alpha]_D$ values for PBP found in trichlorobenzene agree well with the $[\alpha]_D$ values of the toluene soluble fraction (see Sections 2.1 and 2.2). For example, PBP obtained at 3000 kGy shows $[\alpha]_D = -59.8$ for the toluene soluble fraction and $[\alpha]_D = -61.2$ in 1,2,4-trichlorobenzene.

These values of specific optical rotation of PBP resin should be compared with that of the pure β (-)-pinene which

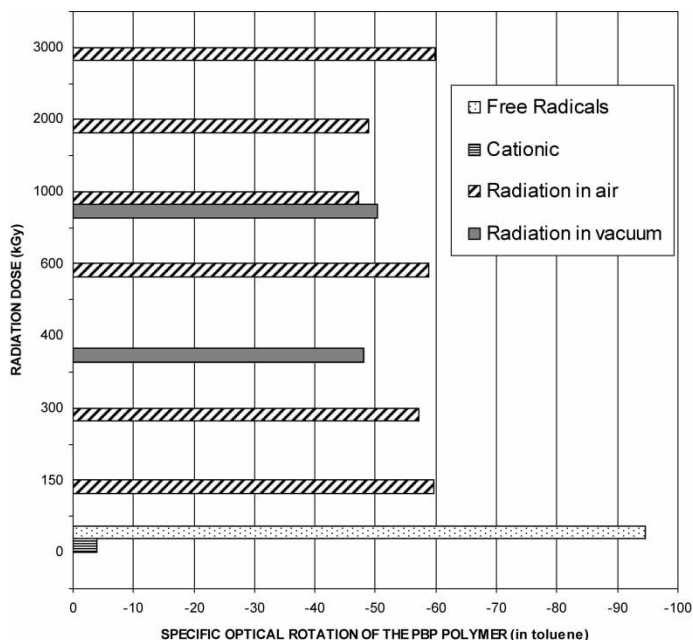


Fig. 5. Comparison of the specific optical rotation $[\alpha]_D$ of PBP resin dissolved in toluene ($1 < c < 3$). Note that the specific optical rotation of PBP is the same both for the samples prepared in the presence of air and in vacuum. The specific optical rotation of PBP prepared with cationic polymerization is very small while the highest $[\alpha]_D$ has been measured on the PBP prepared with a free radical initiator.

has $[\alpha]_D = -21.3$ (neat) or when dissolved in toluene where it displays an $[\alpha]_D = -31.6$ ($c = 3.5$). In any case, the specific optical rotation of PBP is 2–3 times that of the monomer. In the literature (3) it has been reported that $\beta(-)$ pinene polymerized on a stereospecific Ziegler-Natta catalyst at -80°C displays an $[\alpha]_D = -53.7$ (benzene, $c = 10$), thus in line with our values of $[\alpha]_D$ but obtained at room temperature and with high radiation dose. As will be discussed in the next sections, the optical activity is of course linked to the regularity of the structure of the PBP and it is quite surprising that comparable structural regularities have been observed both in the case of PBP produced with radiation and with a stereospecific catalyst.

PBP can be also obtained in high yield by cationic polymerization. However, in such a case, the specific optical rotation in toluene is very low, see Figure 5, $[\alpha]_D = -4.2$ and even if the polymerization is conducted in a low boiling solvent like CH_2Cl_2 at low temperatures, the improvement in optical activity is negligible: $[\alpha]_D = -9.3$ (see Section 2.4), a value which is considerably lower than that of the starting monomer. The point is the irregular structure of PBP obtained by cationic polymerization and the monomer and polymer racemization over the Friedel-Crafts catalyst (4–6,9, 10).

In Section 2.5, we have shown that $\beta(-)$ pinene can polymerize also with a free radical initiator. This fact was unknown to certain authors (11, 13, 14) and they were

convinced that $\beta(-)$ pinene undergoes a radiation-induced polymerization with a cationic mechanism, also because they were thinking that $\beta(-)$ pinene cannot polymerize with a free-radical mechanism.

The free radical polymerization reaction of $\beta(-)$ pinene is rather slow and the yields are low but we have not made a systematic study to select the most effective initiator at the most suitable concentration of it. In any case the reaction is easily reproducible and PBP recovered shows an astonishing optical activity in toluene with $[\alpha]_D = -94.7$, thus considerably higher than that of PBP obtained by Ziegler-Natta catalyst or with radiation (see Figure 5). A PBP analogous in terms of mechanism of formation and FT-IR spectra (see next section) to the PBP prepared with free radical initiator can be obtained as a residue of the distillation of $\beta(-)$ pinene monomer. It shows an optical activity comparable to that of the PBP radiopolymers with $[\alpha]_D = -58.2$.

In Figure 6, we have employed the PBP obtained with a free radical initiator for an interesting racemization reaction. When the PBP dissolved in toluene is put in contact and refluxed with a solid acidic resin (Amberlyst-15 dry), it undergoes a gradual racemization reaction, which can be followed easily polarimetrically. Thus, it is demonstrated that an acidic environment is able to catalyze the racemization of PBP and it is also explained why PBP produced with cationic polymerization shows very low optical activity, apart from the monomer, the PBP polymer can also racemize.

If instead of the relatively mild acidic catalyst Amberlyst-15 dry, it is employed as a strong Lewis acid like ZrCl_4 , the PBP obtained by radiation racemizes in toluene so rapidly that the racemization reaction cannot be followed polarimetrically. The recovered resin has completely lost any optical activity (see Section 2.7).

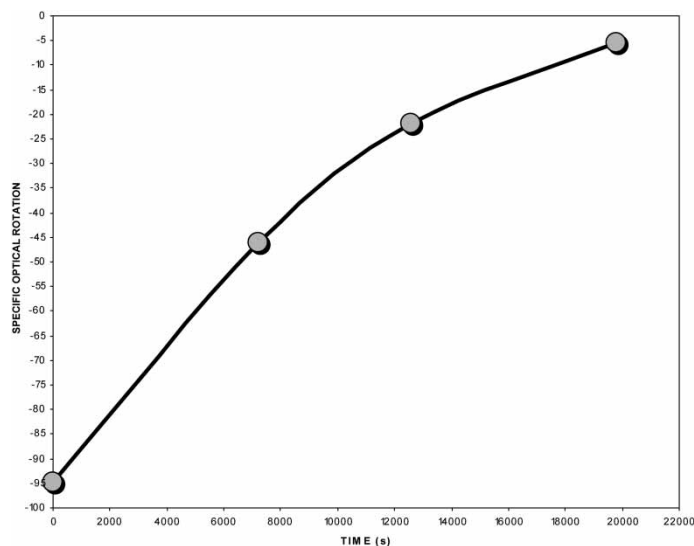
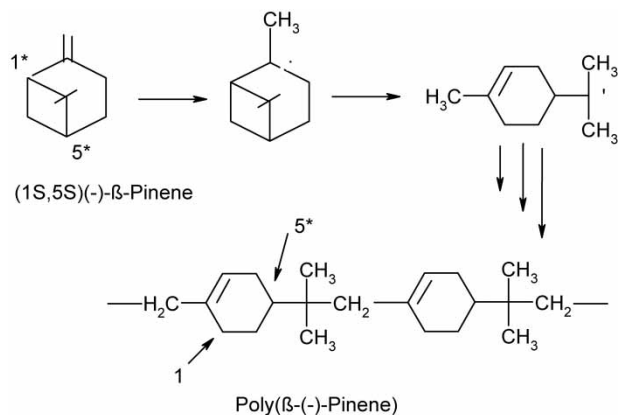


Fig. 6. Racemization of PBP on Amberlyst-15 dry ion-exchange resin at the refluxing temperature of toluene.



Sch. 1. Shows the position of the chiral centers which are present in the β (-)-pinene monomer at the positions 1 and 5. The polymerization implies the cyclobutane ring opening followed by an additional reaction of the monomeric units. The chiral center, originally in position 5, survives the polymerization, the center in position 1 is no more chiral after the polymerization.

3.5 Structure Elucidation of PBB Resin with FT-IR Spectroscopy

The simplest way to interpret the excess of chirality of β (-)-pinene radiopolymer is to admit a special superstructure

and an higher molecular weight with respect to the cationically polymerized β (-)-pinene. In fact, in terms of chiral centers, monomeric β (-)-pinene possesses two centers at 1 and 5 positions of Scheme 1 (in fact, the full name of β (-)-pinene is (1S,5S)(-)- β (-)-pinene) (15). The polymerization according to Scheme 1 implies the lost of the chiral center sited at the position 1. Only the chiral center in 5 is preserved in the polymer chain of Scheme 1. Thus, the chirality enhancement due to the polymerization cannot be attributed exclusively to the preservation of the asymmetric center in 5 position, only an ordered superstructure must be advocated to justify the chirality enhancement. The FT-IR and the NMR spectroscopy should provide some experimental support to this interpretation.

Figure 7 reports a comparison between the spectrum of β (-)-pinene monomer and the spectrum of the oligomer PBPo separated after the treatment with acetonitrile, since in this solvent only the monomer is soluble, while the PBPo precipitates as a sticky oily mass. Additionally, also the spectrum of the solid PBP resin obtained at 150kGy is shown in Figure 7. We may focus our attention on a series of key absorption bands. The monomer shows the typical absorption bands of exocyclic double bond, the $=\text{CH}_2$ moiety wagging at 875 and 854 cm^{-1} (16). Both these bands are not detectable, either in the spectrum of the PBPo nor in the spectrum of the solid PBP resin.

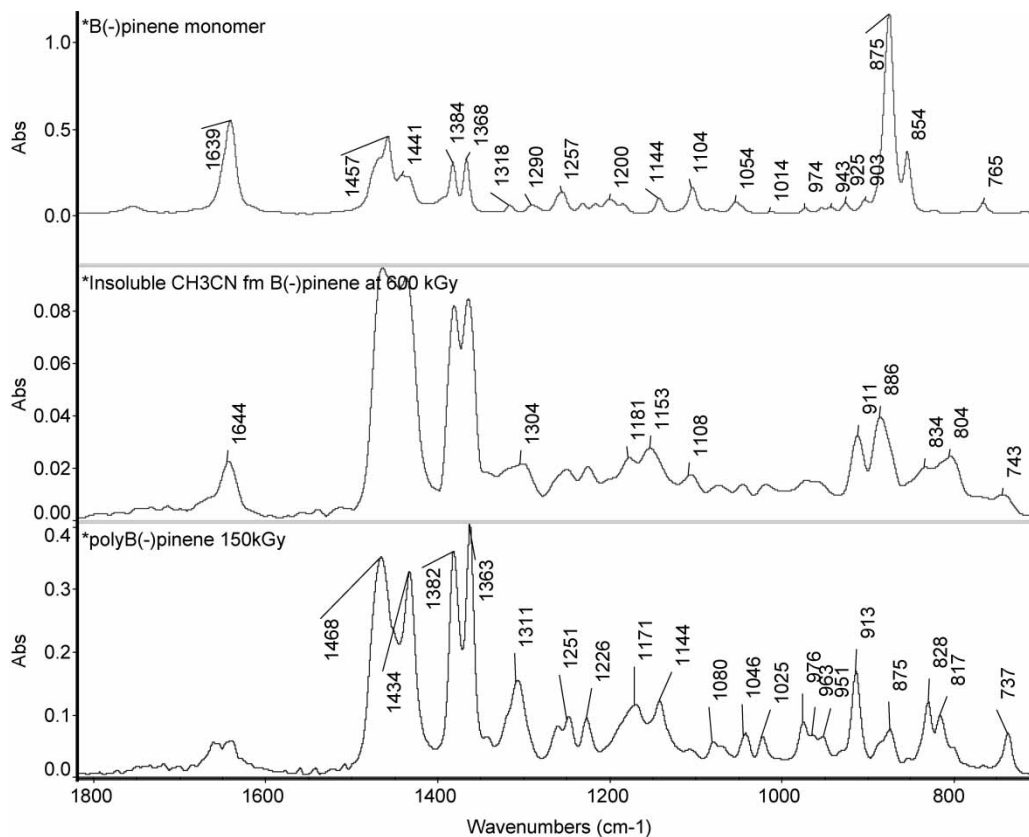


Fig. 7. FT-IR spectra. (Top): β (-)-pinene monomer before radiolysis. (Middle): PBPo recovered as insoluble fraction in acetonitrile. (Bottom): PBP solid white resin obtained after 150 kGy radiation dose.

Instead, two couples of infrared bands can be observed, two located at about 913 and 880 cm^{-1} and the other two at about 830 and 804–817 cm^{-1} in the case of PBPO and PBP, clearly confirming the disappearance of the exocyclic double bond and its conversion into an internal double bond inside the cyclohexane ring formed during the polymerization as illustrated in Scheme 1. The mentioned bands confirm the survival of the double bond and are associated to the wagging of a more substituted double bond than the original $=\text{CH}_2$ (16). Another spectral feature (not shown in Figure 7) associated to the exocyclic double bond $=\text{CH}_2$ of the monomer is the olefinic asymmetric C-H stretching at 3071 cm^{-1} accompanied by the symmetric stretching at 2980 cm^{-1} in the spectrum of the monomer (16). These bands disappear completely in the spectrum of the PBP resin and are replaced by another weaker olefinic stretching at 3043 cm^{-1} which is consistent with the survival and shift of the double bond inside the cyclohexane ring in the resin structure of Scheme 1.

In Figure 7, the *cis* $\text{RCH}=\text{CHR}$ wagging appears at about 737 cm^{-1} in the solid resin in line with the already commonly accepted structure of poly(β -pinene) of Scheme 1 with a double bond inside the six-membered ring.

The doublet at 1383 and at 1365 cm^{-1} is associated with the presence of a geminal methyl group. This group is

present in the monomer and survives the polymerization reaction since it remains present also in the PBP resin, again in agreement with Scheme 1. The spectral comparison reported in Figure 7 confirms the polymerization of the monomer and underline also the strict structural relationship between the PBPO and its solid resin of PBP radiopolymer.

Figure 8 compares the FT-IR spectra of PBP samples prepared by the radiation-induced polymerization of β -pinene in vacuum, in air and with a free radical initiator. It is immediately evident by the simple analysis and comparison of the band pattern that: (a) the band pattern and hence, the structure of the PBP resins are almost identical at any radiation dose administered in vacuum; also the PBP prepared at 940 kGy, not shown in Figure 8 displays the same spectrum; (b) the FT-IR spectra of the PBP prepared in air are identical to each other at any radiation dose up to 3000 kGy (in Figure 8 only, the spectrum of a sample prepared at 300 kGy is shown) and are also almost indistinguishable from the FT-IR spectra of the PBP prepared in vacuum; (c) the PBP prepared by a free radical initiator or by a simple thermal treatment of β -pinene, as it happens during its distillation, shows an FT-IR spectrum identical to those of PBP samples prepared by the action of γ radiation in air and in vacuum. This demonstrated that the mechanism of polymerization under the action of high energy radiation on

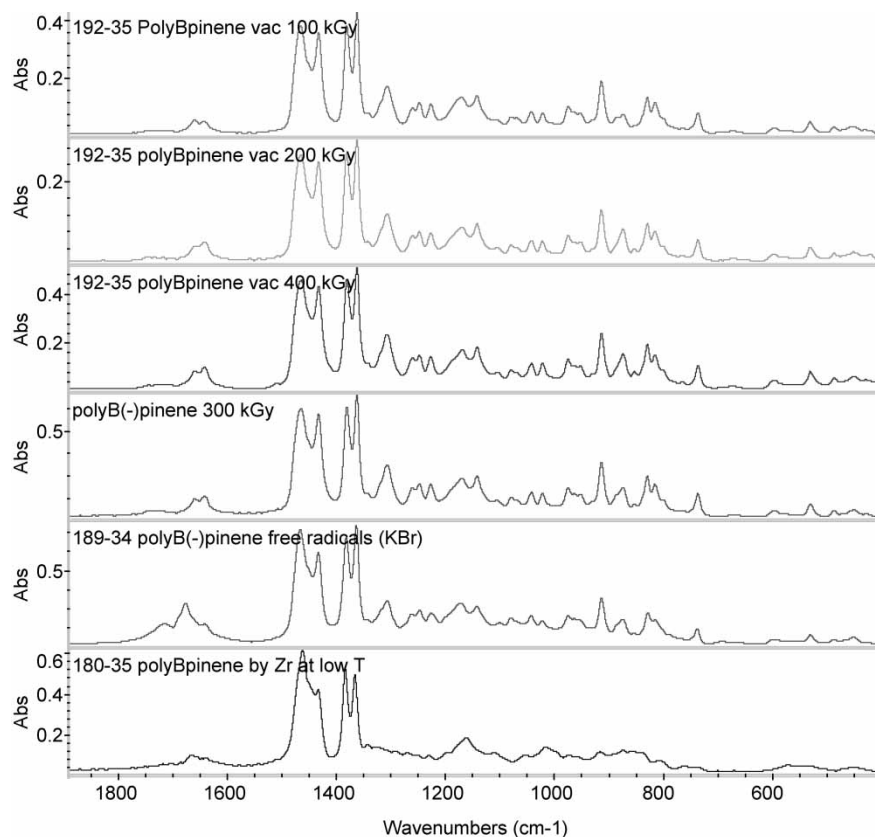


Fig. 8. Comparison of the FT-IR spectra of PBP obtained in vacuum at three different radiation doses (100, 200 and 400 kGy, respectively, the first three from top), with the spectrum of PBP obtained in air at 300 kGy (the fourth from top). PBP obtained from free radical initiator is shown at the second from the bottom and PBP prepared with cationic polymerization is the first one from the bottom.

β (-)-pinene involves free radicals and not ionic species, or at least the ionic species if present are a minority in comparison to the free radicals.

Figure 8 also shows a comparison between the FT-IR spectrum of a PBP resin obtained by cationic polymerization of β (-)-pinene with $ZrCl_4$ at low temperature and the spectra of the PBP resins samples obtained with radiation or with a free radical initiator. The resin obtained by cationic polymerization shows a very limited number of bands, the hydrocarbon skeletal vibrations at 1462 and 1434 cm^{-1} and the presence of the geminal methyl groups at 1384 and 1366 cm^{-1} . Instead, the spectra of the PBP resins obtained by radiopolymerization by a free radical initiator are much richer in absorption bands displaying a series of additional bands which are not present at all (or if present, are very weak and poorly defined) 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 β (-)-pinene resin prepared by Friedel-Crafts catalysts. Already, this observation may justify why the PBP resins prepared with radiation and with a free radical initiator display a very high optical activity, even higher than that of the starting monomer, while the PBP obtained with cationic polymerization has a very weak optical activity, smaller than that of the starting monomer.

3.6 Structure Elucidation of PBP Resin with ^{13}C CP-MAS NMR Spectroscopy

Support for the interpretation of the structures of PBP polymer is also derived from the ^{13}C CP-MAS NMR spectra. Figure 9 shows the comparison between the solid state ^{13}C CP-MAS NMR spectra of two PBP radiopolymers obtained at different radiation dose (300 and 600 kGy), with the PBP prepared with a free radical initiator and a PBP generated with cationic polymerization. The same comments we have made for the infrared spectra apply for the ^{13}C CP-MAS NMR spectra. The PBP radiopolymers display identical spectra irrespective for the radiation dose administered, also confirm the exceptional radiostability of PBP. The PBP prepared through a free radical initiator has the same well defined ^{13}C CP-MAS NMR spectrum of PBP radiopolymers confirming that it has the same chemical structure and the same ordered structure as the radiopolymers. In fact, the PBP prepared through a free radical initiator has the same well defined ^{13}C CP-MAS NMR spectrum of PBP radiopolymers. In particular, the resonances of C2 and C3 (see Scheme 2) at 134.58 and 126.28 ppm , respectively, confirm that the structure of the ring is unaffected by the irradiation. As shown in Figure 10, the PBP from a free radical initiator has possibly even a more ordered chemical structure than the PBP radiopolymers as can be derived from the sharpness of carbon resonances at 40.24 , 37.49 , 28.72 and 20.79 ppm . These facts account for the high optical activity of these

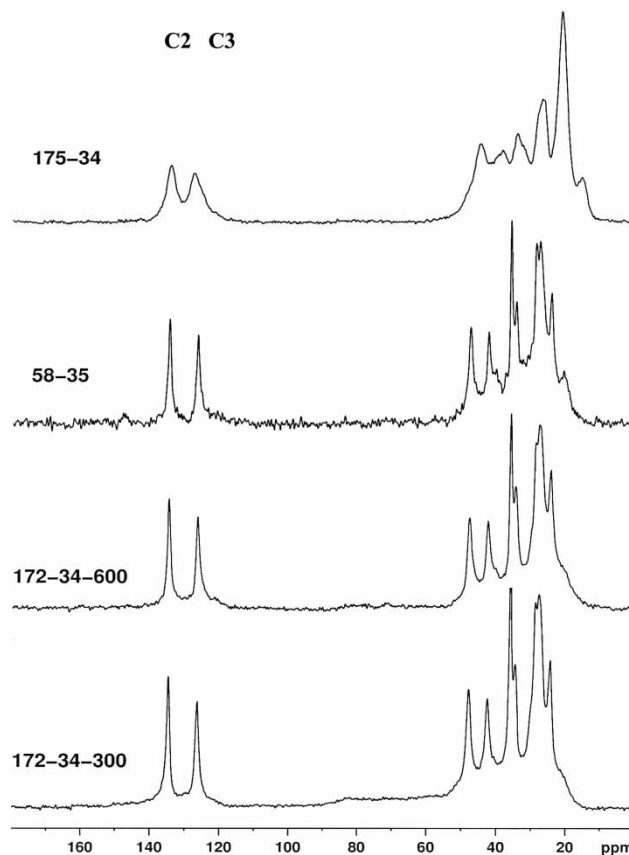
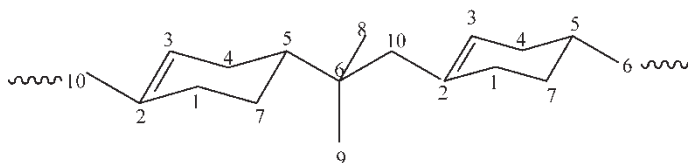


Fig. 9. Solid state ^{13}C CP-MAS NMR of PBP resins. The spectrum at the top of the figure is due to PBP prepared with cationic polymerization. The second spectrum from top, labelled 58–35 is due to PBP prepared with a free radical initiator. Finally, the last two spectra are due to PBP radiopolymers prepared respectively at 600 and at 300 kGy in the presence of air. Spectra shown in the figure were processed applying an exponential multiplication with a line broadening of 8 Hz. Note that the C2 and C3 labels refer to the PBP structure reported in Scheme 2.

PBP polymers and in particular, for the exceptionally high optical activity of the PBP prepared with free radicals. In contrast, the ^{13}C CP-MAS NMR spectrum of PBP prepared with cationic mechanism shows broader resonances, which suggest a less ordered structure and possibly a partial racemization of the chiral center. As discussed earlier, the structural irregularity may derive from the racemization and isomerization of the monomer prior the polymerization and mainly from the racemization of the resulting PBP on the Lewis



Sch. 2. Reports a three-dimensional schematic structure of poly- β -pinene.

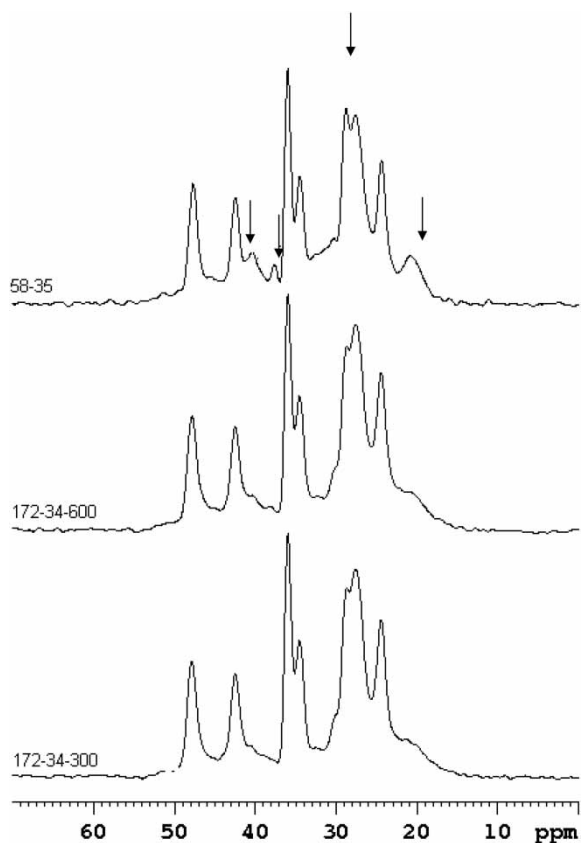


Fig. 10. ^{13}C CP-MAS NMR of PBP resins. The spectrum at the top is due to PBP prepared with free radical initiator, the last two spectra are due to PBP radiopolymers prepared respectively at 600 and at 300 kGy in presence of air. In the figure is shown only the region between 0–70 ppm. These spectra were processed applying a gaussian multiplication with a line broadening of -32 Hz and $\text{GB} = 0.2$ Hz.

acid which is used as Friedel-Crafts catalyst for the cationic polymerization.

4 Conclusions

$\beta(-)$ pinene polymerization can easily be achieved by γ -radiation treatment of the monomer both in vacuum and in the presence of air. Higher PBP yields and radiation chemical yields are ensured when the radiation polymerization is conducted in vacuum. It was found that the presence of oxygen retards the polymerization and the retardation is consistent with a free radical mechanism. Furthermore, the PBP yield is linear with the radiation dose when the air is present, but follow a quadratic law when the irradiation is conducted in vacuum.

The PBP formed precipitates from the monomer as a white solid, while the oligomer PBPO remains dissolved in the monomer and enhances the optical activity of the crude monomer. PBP is partially soluble in toluene and the

toluene-soluble fraction displays a higher optical activity than that the starting monomer. In fact, if the starting monomer has a specific optical rotation $[\alpha]_{\text{D}} = -21.3$ (neat) and the best $[\alpha]_{\text{D}}$ value measured on the PBP radiopolymer has been found -61.2 in trichlorobenzene. PBP can be obtained also by a free radical initiator and in such a case, the specific optical rotation has been found $[\alpha]_{\text{D}} = -94.7$ in toluene, about five times the value of the monomer. In contrast, PBP obtained in high yields by cationic polymerization shows a very low specific optical rotation, much lower than that of the starting monomer. With FT-IR spectroscopy and ^{13}C CP-MAS NMR spectroscopy it has been shown that there is a correlation between the chemical structural regularity of the PBP and its optical activity. The regularity appears very low in the case of PBP prepared with cationic catalysis. It has been shown that PBP with very high optical activity racemizes on acidic catalysts. Thus, the low optical activity on PBP prepared with cationic mechanism shows low optical activity because of its racemization due to the catalyst acidity.

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