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Radiation-Induced Inclusion Polymerization of $\beta(-)$ Pinene In Deoxycholic Acid

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For the first time, $\beta(-)$ pinene has been successfully polymerized by the radiation-induced inclusion polymerization technique in deoxycholic acid (DOCA) crystals. The resulting poly- $\beta(-)$ pinene (pBp) has been isolated in the pure form from the host matrix in very high yield (nearly 100% on the starting monomer at 320 kGy), while the pBp yield from bulk radiolysis of $\beta(-)$ pinene is very low $\approx 3\%$. The clathrate complex pBp@DOCA and the pure pBp from inclusion polymerization have been studied by FT-IR spectroscopy, thermogravimetric analysis (TGA and DTG) and by differential thermal analysis (DTA). The optical activity of pBp from inclusion polymerization has been investigated by polarimetry and by optical rotatory dispersion (ORD) spectroscopy. Evidences have been found about the phenomenon of asymmetric induction “through space” caused by the chiral host matrix on the guest pBp molecules.

Keywords: Clathrates; $\beta(-)$ pinene; inclusion polymerization; radiation-induced polymerization; supramolecular chemistry; chiral polymer; poly- β -pinene

1 Introduction

It is known for a long time that bile acids are able to form clathrate compounds with a number of different molecules having considerably different dimensions (1, 2). In these compounds, the guest is retained in closed cavities or cages provided by the crystalline structure of the host. The most common inclusion compounds of bile acids can be prepared with deoxycholic acid as host matrix and the resulting inclusion compounds are known as choleic acid (1–3). Numerous other related hosts are known such as cholic and apocholeic acids (3). Such inclusion compounds are used in supramolecular chemistry (3) molecular recognition (4), in chiral selection (5–7). Stereospecific radiation-induced polymerization has been achieved inside deoxycholic acid channels and in related hosts by the inclusion of opportune diene monomers (8–10). In some special cases, the chiral arrangement of the host matrix has

acted “through space” as chiral inductor during the polymerization of the prochiral monomer included as complex (11).

Recently, we have expanded the study of the inclusion polymerization to various host matrices (12, 13) and have also successfully achieved the inclusion polymerization of isoprene and phenylacetylene as clathrates in deoxycholic acid (14, 15).

We have dealt with the bulk radiation-induced polymerization of $\beta(-)$ pinene monomer and have discovered certain peculiarities of the resulting polymer, poly- $\beta(-)$ -pinene (pBp), ranging from the radiation driven free radical polymerization mechanism to its chemical structure, to its almost unique higher specific optical rotation, much higher than that of the starting monomer (16–19) with implications on the abiotic origin of the chirality (20,21), and with potential applications in chiral selection and separation (22). Thus, it was a natural step to explore the possibility to study the inclusion polymerization of $\beta(-)$ pinene as guest in deoxycholic acid (DOCA) host matrix. After all, it is well known that DOCA forms inclusion compounds with 2:1 stoichiometry with a bicyclic terpene such as (+)-camphor (23) so, it should form such complex also with $\beta(-)$ pinene which has similar molecular dimensions as (+) camphor.

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The present work is a full account on the inclusion polymerization of $\beta(-)$ pinene in DOCA and represents the first report on this specific topic.

2 Experimental

2.1 Materials and Equipment

$\beta(-)$ pinene was purchased from Fluka (Switzerland) and used as received. Deoxycholic acid was a high purity grade from Fluka or Sigma (USA). Absolute ethanol was from Fluka.

Irradiations were made in a Gamma cell from Atomic Energy of Canada at a dose rate of 2.0 kGy/h. The FT-IR spectra were recorded on samples embedded in KBr pellets in transmittance mode or in reflectance mode (ATR) on ZnSe crystal. The specific optical rotation of poly- β -pinene (pBp) was determined in tetrachloroethane on a Jasco spectropolarimeter model P2000 using the D line of Sodium at 589 nm. Additionally, the optical rotatory dispersion curve of pBp was determined in tetrachloroethane by using an external dedicated monochromator attached to the polarimeter. Thermogravimetric analysis with simultaneous differential thermal analysis was recorded under a nitrogen flow at a heating rate of 10°C/min in a Linseis apparatus model L81+DTA.

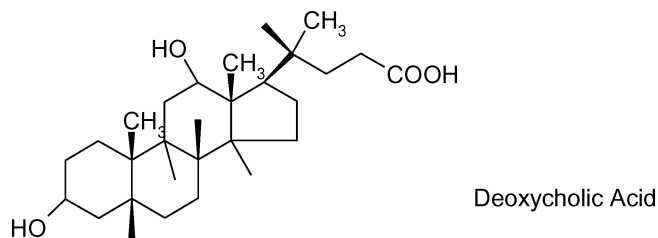
2.2 Inclusion Polymerization of $\beta(-)$ Pinene in DOCA

Deoxycholic acid (13.8 g) was contact imbibed with $\beta(-)$ pinene (8.6 g) with the aid of a spatula. The resulting homogeneous mass was prepared inside a glass vial having a volume of 25 ml which was then tightly closed with a screw cap. Three vials were prepared as described and irradiated with γ rays at 75, 150 and 320 kGy, respectively. After irradiation, the samples were stored for two months at +10°C and then opened. In all cases, a homogeneous and rather compact white powder was easily recovered from the irradiated vials. The powder was extracted with 200 ml of abs. ethanol by heating to refluxing temperature for 1 h and then filtering with an aspirator the insoluble fraction. The filtration was made by pouring the warm ethanol solution and the insoluble fraction on the filter. The insoluble fraction consisting of poly- β -pinene (pBp) was washed thoroughly with additional warm ethanol, then with cold acetone and left to dry in air. The pBp yield was determined gravimetrically.

3 Results and Discussion

3.1 General Properties of DOCA

Deoxycholic acid (DOCA) belongs to the class of steroids and its chemical structure is shown in Scheme 1. DOCA is a naturally occurring molecule present in the bile acids



Sch. 1. Chemical Structure of Deoxycholic Acid (DOCA)

of humans and of animals (3). It is produced in liver and together with other bile acids possesses dispersing, micelle-forming properties promoting the digestion and facilitating the absorption of fats and fat-soluble vitamins in the small intestine (3). DOCA is able to form inclusion compounds with a number of different molecules of considerably different shapes and sizes (1–3). In contrast with urea and thiourea, other well known molecule able to form clathrates (1), DOCA has the peculiarity of not being size selective. In fact, DOCA crystallizes with an open structure leaving free channels in the center (1–3). The *c* axis of the cavity is 0.75 nm, a value which should be compared with that of urea 0.52 nm and thiourea 0.61 nm (1,9) and with the diameter of the channels of perhydrotriphenylene 0.55 nm (9). More in detail, the host matrix of DOCA possesses the unique properties to adapt its dimensions as function of the shape and size of the guest molecules. Therefore, even molecules of the size of phenanthrene or dibenzathracene have been included in DOCA (1).

3.2 Inclusion Polymerization of β -Pinene and Yield of pBp

The bulk radiolysis of $\beta(-)$ pinene produces poly- β -pinene (pBp) in low yield. For instance, the pBp obtained at 150 kGy is approximately 1% by weight over the mass of the starting monomer and becomes 2.5% at 300 kGy (16–18). The pBp yield is enhanced considerably when $\beta(-)$ pinene is irradiated in presence of silica (22) and part of the pBp results grafted on silica surface. As shown in Figure 1, the yield of pBp calculated on initial monomer exceeds 20% by weight when irradiated with deoxycholic acid (DOCA). $\beta(-)$ pinene was absorbed in DOCA matrix simply by direct contact imbibition a technique which was successfully adopted by Allcock (24, 25) in the preparation of inclusion compounds of diene monomers in a series of cyclotriphosphazene derivatives and successfully adopted also in the isoprene and phenylacetylene inclusion polymerization in DOCA (14, 15). This approach facilitates the sample preparation avoiding the tedious and even complex co-crystallization technique achievable by dissolving the monomer and DOCA in ethanol and then crystallizing the solution (1–3). Of course the drawback of the contact imbibition technique regards the precise knowledge of the host-guest stoichiometry, which in the present case, implies always a nominal excess of monomer guest over the host

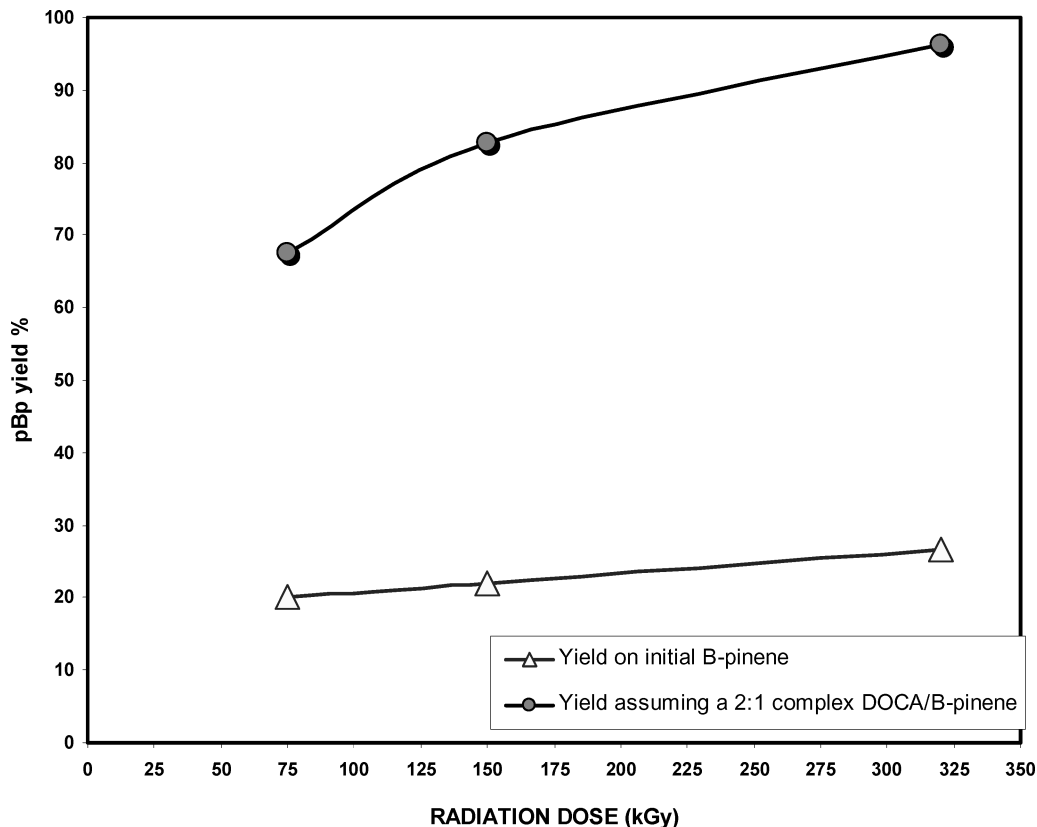


Fig. 1. Yield of pBp over initial $\beta(-)$ pinene monomer (triangles) and calculated assuming the formation of a DOCA / $\beta(-)$ pinene complex having a 2:1 molar ratio (circles).

compound. As shown in the experimental section we have worked with a nominal molar ratio $\beta(-)$ pinene/DOCA = 1.8:1 while it is known that in the inclusion complexes is DOCA in excess over the guest molecule. For instance, with the (+)camphor, a terpene having roughly the same dimensions of $\beta(-)$ pinene, DOCA forms a DOCA/camphor clathrate with a 2:1 molar ratio (23). Assuming that also in the case of pinene, the clathrate compound between DOCA and $\beta(-)$ pinene has a molar ratio 2:1, then the yield of pBp over the included $\beta(-)$ pinene becomes close to 100% at 320 kGy and is considerably high also at lower radiation dose, as illustrated in Figure 1. A similar phenomenon has been observed in the case of the inclusion polymerization of phenylacetylene in DOCA (15).

3.3 FT-IR Spectroscopy of the pBp Synthesized by Inclusion Polymerization in DOCA

The irradiation of $\beta(-)$ pinene included in DOCA produces (at any radiation dose) a homogeneous and dry powder with a weak odour of free $\beta(-)$ pinene. Such powders are the inclusion complexes of pBp in DOCA (pBp@DOCA). The FT-IR spectra of these products are shown in Figure 2 in comparison to a reference spectrum of pure DOCA. The spectra of pBp@DOCA at any radiation dose are very

similar to that of pure DOCA. This implies that pBp is almost completely retained inside the DOCA channels. In fact, the ketone band of the DOCA carboxylic group at about 1700 cm^{-1} and the OH stretching band at 3380 cm^{-1} are present in all the samples of Figure 2. Additionally, Figure 2 shows that the band pattern of pBp@DOCA in the “fingerprint” spectral region between 1500 and 700 cm^{-1} is very similar to that of pure DOCA suggesting indeed that large part of the pBp is retained inside the DOCA matrix.

Washing pBp@DOCA with warm ethanol permits us to remove DOCA almost completely and to isolate pure pBp. The FT-IR spectra of the purified pBp are shown in Figures 3 and 4: the removal of DOCA from pBp has been complete since the typical bands of DOCA, for instance, at about 1700 and 3400 cm^{-1} disappeared. Additionally, Figures 3 and 4 show that pBp produced as inclusion in DOCA has almost the same chemical structure of the pBp prepared by radiation-induced polymerization of $\beta(-)$ pinene in bulk. This can be deduced at first glance by comparing the band pattern of the reference pBp prepared by bulk radiolysis at 400 kGy in vacuum with the three spectra of the purified pBp prepared by inclusion polymerization in DOCA respectively at 75, 150 and 320 kGy (Figs. 3 and 4).

The chemical structures of pBp synthesized with radiation, free radicals initiator, cationic and Ziegler-Natta

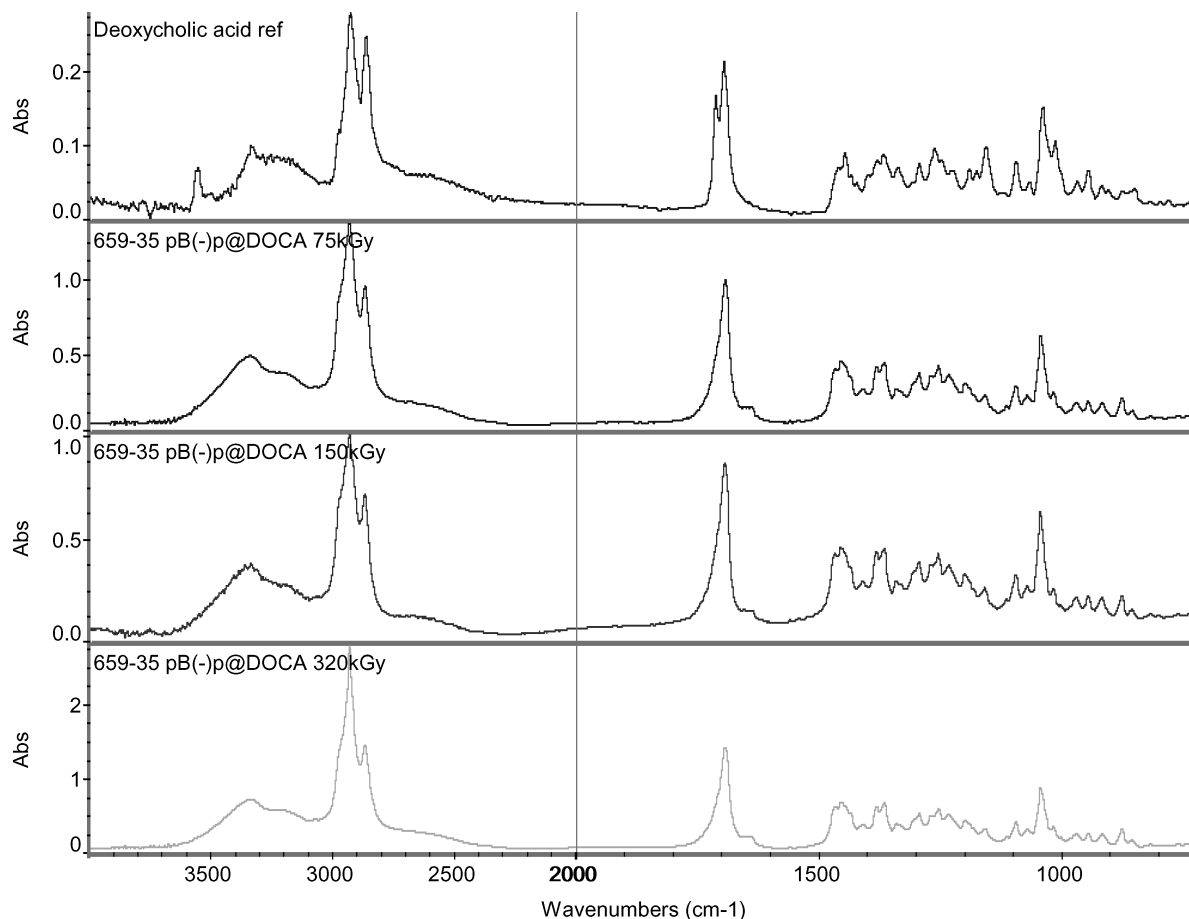
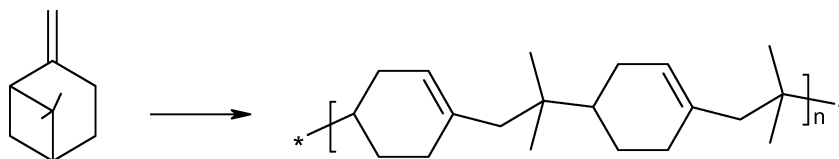


Fig. 2. FT-IR spectra (ATR, ZnSe crystal); from top to bottom: pure deoxycholic acid; pBp included in DOCA 75 kGy; pBp included in DOCA 150 kGy; pBp included in DOCA 320 kGy.

catalysts (16–18) have been investigated in detail, also with high resolution and other sophisticated NMR techniques (19). It has been found that the radiation-induced polymerization of $\beta(-)$ pinene yields the pBp with the most regular chemical structure (see Scheme 2), in comparison to other polymerization routes. In particular, the p-menthene repeating unit of pBp prepared by bulk radiolysis are regularly connected in 2,5–2,5–2,5 triad sequences with a negligible degree of crosslinks, in contrast with other pBp prepared by cationic or Ziegler-Natta catalysts which instead present high degrees of irregularities both for the presence of the 2,1–2,5–2,5 triads, but also for the presence of other chain defects, including crosslinks with adjacent chains (19). Such structural irregularities derive from the

isomerization reactions occurring when the monomer is in contact the catalyst (Wagner-Meerwein isomerization) and may happen also on the pBp polymer chain once it is formed in an acidic medium (17–19). Instead, because of the absence of any catalyst, the pBp prepared by radiation or by a free radical initiator is extremely regular because the Wagner-Meerwein isomerization cannot occur at all (18, 19).

Indications about the high regularity of the pBp from inclusion polymerization in DOCA can be deduced also from the FT-IR spectra (16–18). For instance, from the well resolved doublet at 1381 and 1361 cm^{-1} due to the geminal methyl groups shown in the pBp structure of Scheme 2 and by the corresponding doublet at 1175 cm^{-1} with



Sch. 2. Ring-opening polymerization of $\beta(-)$ pinene to pBp

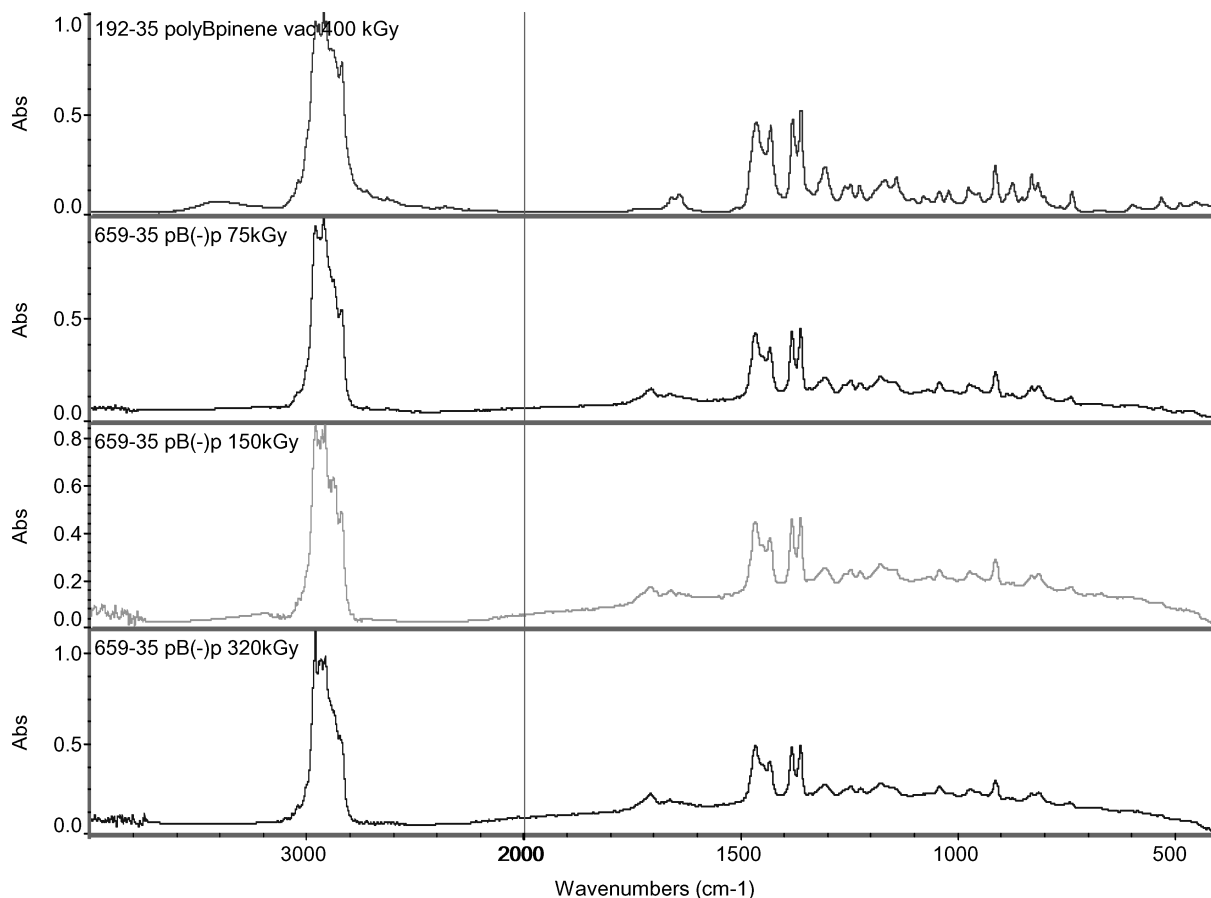
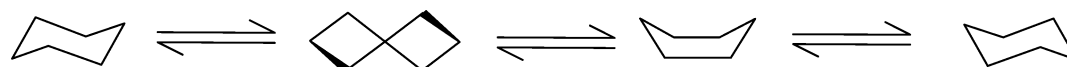


Fig. 3. FT-IR spectra (KBr); from top to bottom: reference pBp prepared by bulk polymerization at 400 kGy in vacuum; purified pBp from inclusion polymerization in DOCA 75 kGy, purified pBp from inclusion polymerization in DOCA 150 kGy, purified pBp from inclusion polymerization in DOCA 320 kGy.

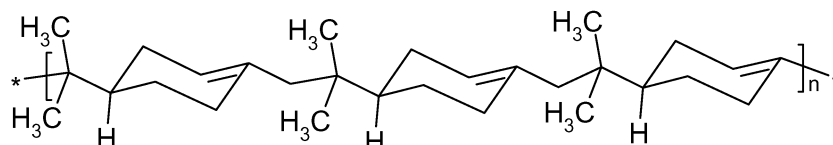
shoulder at 1145 cm^{-1} which confirms the presence of geminal methyl groups (26). The doublet at about 1465 and 1432 cm^{-1} are due to the cyclohexene ring of pBp (Scheme 3) coexisting in different ring configurations (27, 28). Curiously, the FT-IR spectrum of pBp synthesized by inclusion polymerization in DOCA shows different relative intensity of the two bands at 1465 and 1432 cm^{-1} in comparison to the FT-IR spectrum of reference pBp from bulk radiopolymerization, with the former band more intense than the latter (Figs. 3 and 4). Additionally, the spectrum of pBp from inclusion polymerization shows an additional weak feature at 1451 cm^{-1} , which is absent in the reference pBp from bulk radiopolymerization (Fig. 4). This suggests that in the pBp from inclusion polymerization the cyclohexene ring assumes certain configurations which were not present in the cyclohexene ring of reference pBp. This fact is a powerful argument suggesting that the polymerization occurred in a constrained environment.

As shown at the top of Scheme 3, the cyclohexane ring undergoes a continuous change in its conformation interconverting between the two “chair” structures. The interconversion occurs through two intermediate structures, the

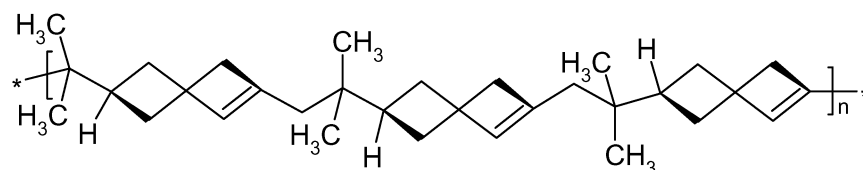
“twist” and the “boat” structure (29–31). Although more strained because of the presence of a double bond, also the cyclohexene ring undergoes such kind of conformational equilibrium (29, 31). Of course, the conformational equilibrium is “frozen” when cyclohexane or cyclohexene rings are linked with bulk substituents (30,31), precisely as it happens in the case of pBp where the rings are connected each other through a branched alkyl chain. This implies that the cyclohexene ring may assume any of the possible conformations in the short interval of time occurring during the polymerization process and comprised from the opening of the cyclobutane ring of the $\beta(-)$ pinene monomer to the formation of the pBp chain shown in Scheme 2 and 3. Once the pBp chain is formed a given ring conformation becomes a permanent configuration. During bulk polymerization there are no constraints and a “natural” largely mixed configuration can be assumed by the cyclohexene ring (e.g. in one monomeric unit: chair, in another monomeric unit: twist, in another one: boat configuration) and in fact, the two infrared bands at 1465 and 1432 cm^{-1} have approximately the same intensity. Instead, in the case of pBp prepared in a constrained environment, inside the



Conformational changes of cyclohexane ring



pBp with cyclohexene ring in "chair" configuration



pBp with cyclohexene ring in "twist" configuration

Sch. 3. pBp with cyclohexene ring in different configurations: "chair" or "twist"

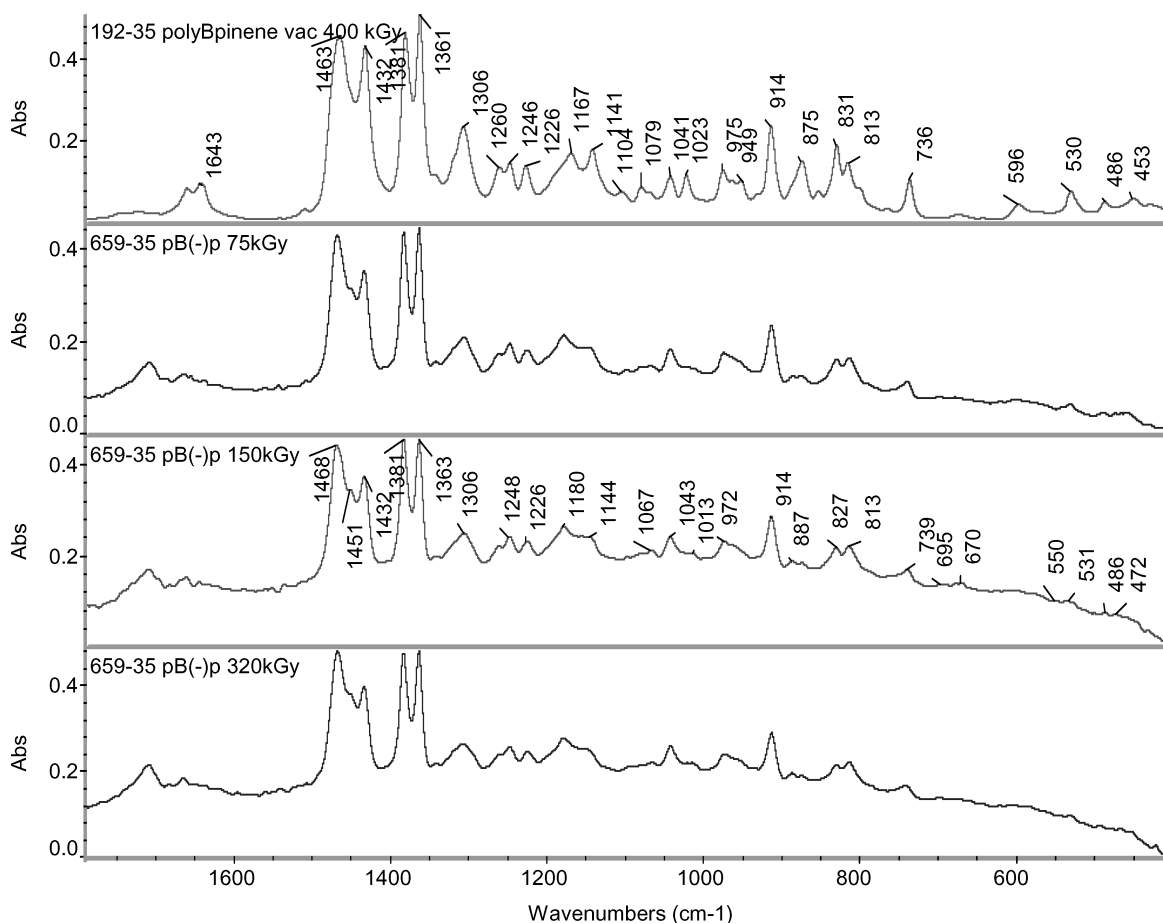


Fig. 4. FT-IR spectra (KBr), detail of the "fingerprint" region; from top to bottom: reference pBp prepared by bulk polymerization at 400 kGy in vacuum; purified pBp from inclusion polymerization in DOCA 75 kGy; purified pBp from inclusion polymerization in DOCA 150 kGy; purified pBp from inclusion polymerization in DOCA 320 kGy.

DOCA channels, the most compact configuration should be prevalent, may be the chair structure, and indeed the infrared band at 1465 cm^{-1} is more intense than the band at 1432 cm^{-1} . The additional infrared band at 1451 cm^{-1} suggests that an additional unusual configuration is formed as well in the constrained medium. The two pBp structures in Scheme 3 illustrate schematically the cyclohexene ring in chair and in twist configuration respectively.

3.4 Optical Activity and Optical Rotatory Dispersion (ORD) of pBp Synthesized by Inclusion Polymerization in DOCA

The $\beta(-)$ pinene polymerization presents a unique feature: the specific optical rotation $[\alpha]_D$ of the resulting pBp is much higher than that of the starting monomer. In fact, a solution of $\beta(-)$ pinene monomer in toluene ($c = 3.5$) has an $[\alpha]_D = -31.6$, while pBp obtained by radiation-induced polymerization in bulk of $\beta(-)$ pinene has an $[\alpha]_D = -59.7$ ($c = 1.5$, toluene) (16–18,20), almost double than that of the starting monomer. The reason of this radical change in the specific optical rotation resides in the cyclobutane ring-opening polymerization mechanism of $\beta(-)$ pinene so that a bicyclic terpene is transformed into a

cyclohexene-based resin (Scheme 2). As discussed elsewhere (16), the polymerization causes the loss of one of the two chiral centers of $\beta(-)$ pinene monomer, while the other is preserved but in a complete different molecular configuration. This is the root of the enhancement of the specific optical rotation observed in pBp and in irradiated solution of $\beta(-)$ and $\beta(+)$ pinene (21).

Instead of measuring the specific optical rotation $[\alpha]$ at a single wavelength, the D line of sodium at 589 nm, in the present work, we have measured the optical rotatory dispersion (ORD) i.e., $[\alpha]$ at different wavelengths (32, 33). Such curves are characteristic of chiral molecules and macromolecules and are sensitive to conformational, configurational or even supramolecular changes (32, 33). The solvent of choice for ORD measurements was tetrachloroethane (TCE) where pBp shows more solubility than in toluene.

Figure 5 shows the ORD curve of pBp prepared by bulk radiolysis of $\beta(-)$ pinene at 948 kGy in vacuum in comparison to that of pBp prepared by a free radical initiator. It can be observed that the two ORD curves are completely overlapped and the specific optical rotation becomes more intense at shorter wavelengths. On the other hand, the pBp synthesized by inclusion polymerization in DOCA and obtained both at 75 and 320 kGy, shows, ORD curves which

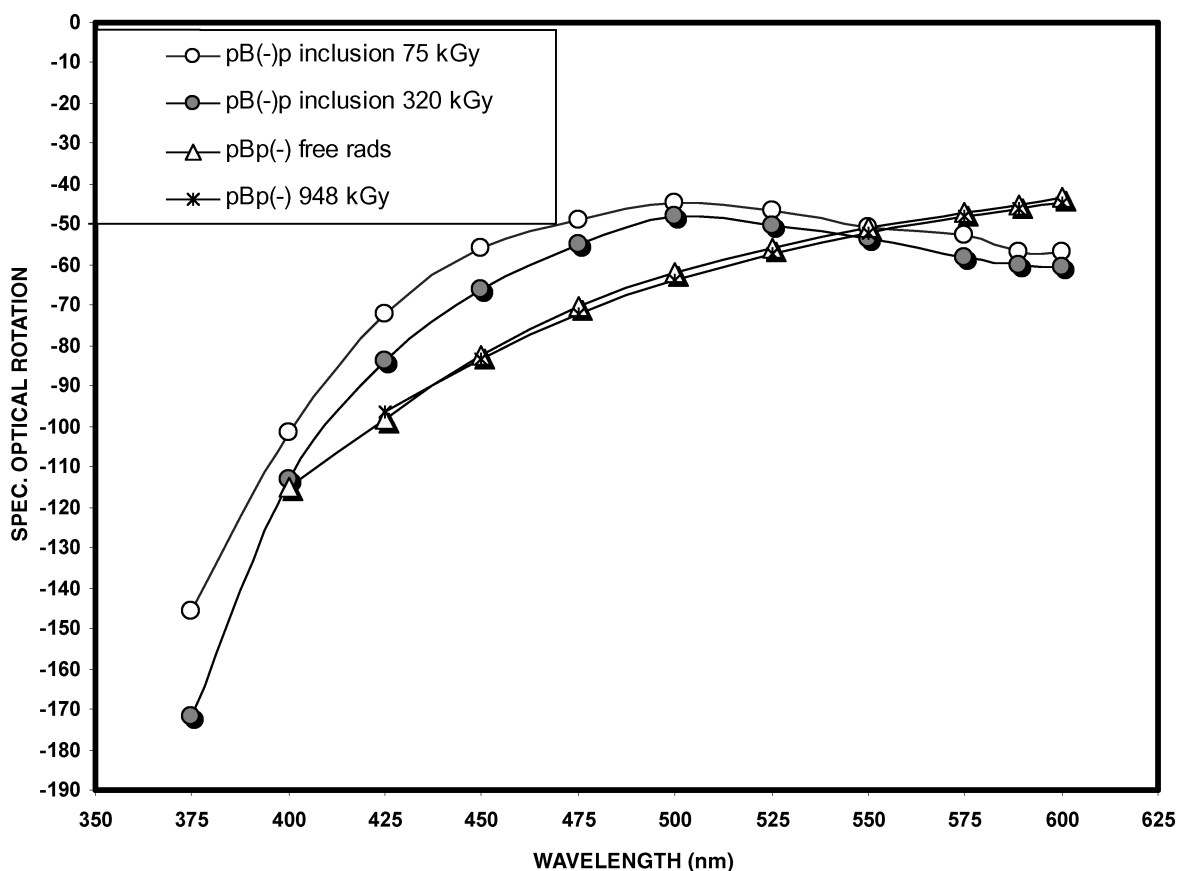


Fig. 5. Optical rotatory dispersion (ORD) curves in tetrachloroethane (TCE) of pBp synthesized by inclusion polymerization at 75 and 320 kGy in comparison to ORD curves of pBp synthesized by bulk radiolysis of $\beta(-)$ pinene or by a free radical initiator.

run parallel each other but which are different from the ORD curves of pBp synthesized in bulk. In particular, at longer wavelengths and at shorter wavelengths the specific optical rotation of pBp prepared by inclusion synthesis is more pronounced and the opposite happens at intermediate wavelengths. The differences in the two families of ORD curves imply that the pBp obtained by inclusion polymerization have a different configuration than that of the pBp obtained by bulk polymerization. This interpretation is completely in line with the FT-IR spectra discussed in the previous section which indeed suggest such different configurations of the cyclohexene rings of the two pBp families. The polymerization in constrained media such as the channels of DOCA necessarily induces some limitations in the configuration of the pBp molecules with a prevalence of the most compact structure and this can be observed both by FT-IR spectroscopy and by differences in ORD curves and hence in optical activity. Additionally, it is worth mentioning here that in TCE the $[\alpha]_D$ of the pBp derived from inclusion polymerization are in the range of -57 to -60 while in the same solvent the pBp prepared in bulk shows $[\alpha]_D = -45.5$. The higher optical activity of the pBp prepared by inclusion polymerization and the different ORD curve can be attributed to the phenomenon of asymmetric induction “through space” caused by the chiral host matrix on the guest molecules advocated by Audisio and colleagues for inclusion polymerization in a chiral medium (11).

3.5 Thermal Properties of pBp Synthesized by Inclusion Polymerization in DOCA

The melting point of pure DOCA as measured by differential thermal analysis (DTA) occurs at 183°C and DOCA decomposes at 396°C under N_2 . The inclusion complex pBp@DOCA shows a broader melting point at 186°C and decomposes at lower temperature than pure DOCA: 386°C . The decomposition of pure DOCA and the complex pBp@DOCA can be observed also in Figure 6. The first derivative of the thermogravimetric curve (DTG) confirms the DTA data since pure DOCA reaches the maximum decomposition rate at 397°C , while the complex pBp@DOCA decomposes at 10°C lower temperature: 386°C . Figure 6 shows also that the maximum decomposition rate of the purified pBp prepared by inclusion polymerization is practically coincident with that of pBp prepared by bulk polymerization: 406°C and 411°C respectively. Figure 7 reports the DTA of the pBp samples prepared by inclusion polymerization in DOCA at three different levels of radiation dose (75, 150 and 320 kGy) in comparison with a reference pBp resin synthesized by bulk polymerization. The DTA shows that all the pBp samples decompose at about 406°C under N_2 . Instead the softening-melting behaviour of the pBp samples is a rather complex process (17) and the DTA of Figure 7 confirms this fact. It begins with an endothermic transition at about 120°C for the pBp samples from

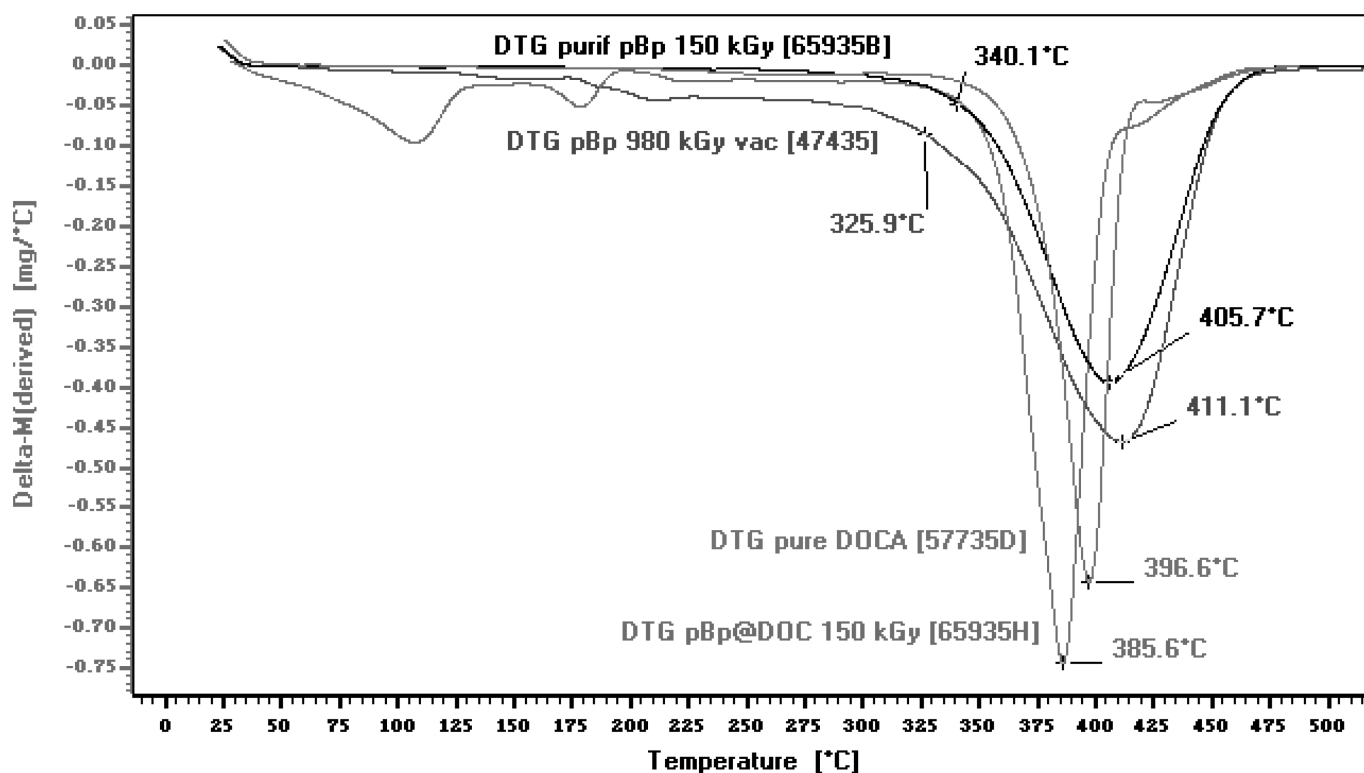


Fig. 6. Differential thermogravimetry (DTG) of pBp prepared by inclusion polymerization in comparison to a pBp prepared by bulk polymerization: the maximum decomposition rate occurs at 406°C and 411°C , respectively. The decomposition of the complex pBp@DOCA occurs at 386°C , while pure DOCA decomposes at 397°C .

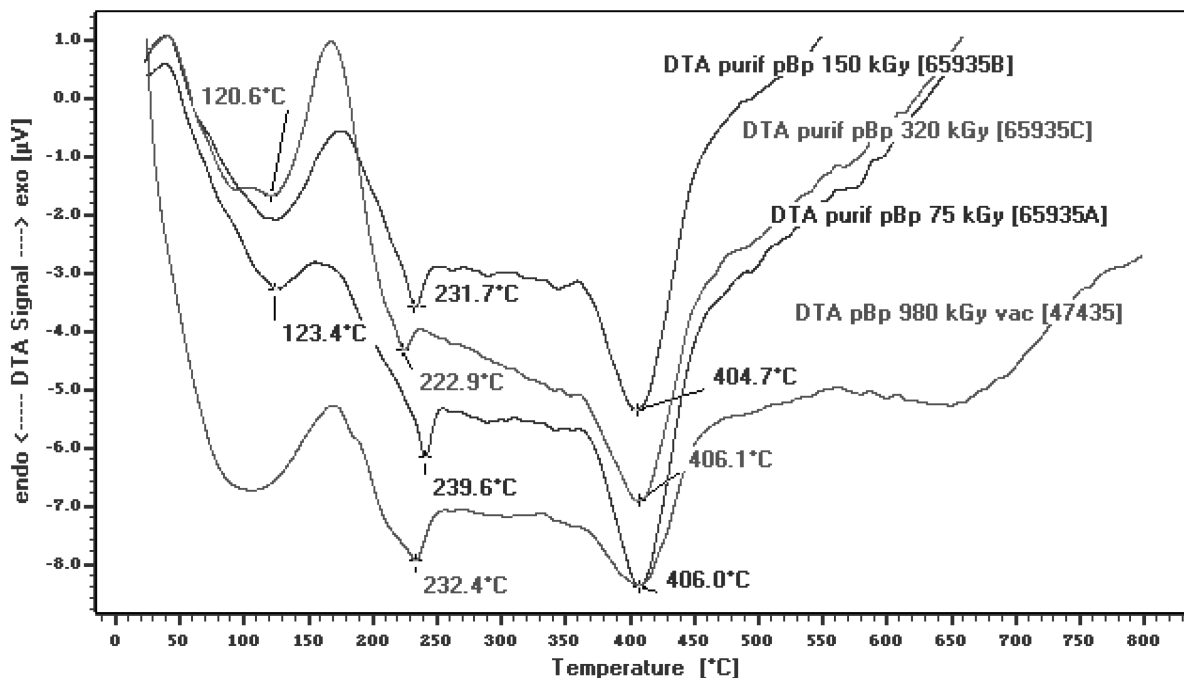


Fig. 7. DTA under N_2 flow. The thermal behaviour of the three pBp samples obtained by inclusion polymerization in DOCA is compared with the thermal properties of a pBp sample prepared by bulk polymerization with γ radiation.

inclusion origin and 100°C for the pBp from bulk polymerization followed by a weakly exothermal transition at $160\text{--}170^\circ\text{C}$ for all samples. The softening-melting process ends with an endothermal sharp transition at $223^\circ\text{--}239^\circ\text{C}$. Curiously, such a transition occurs at the highest temperature for the pBp sample prepared at 75 kGy: 239.6°C , at 231.7°C for the pBp sample obtained at 150 kGy and at the lowest temperature, 223°C , for the pBp prepared by inclusion polymerization at 320 kGy. The reference pBp sample prepared from bulk polymerization melts completely at the intermediate temperature of 232°C .

From Figure 7, it appears evident also from the thermal behaviour the identity of the pBp resins prepared by inclusion polymerization with that prepared by bulk polymerization although some peculiarity of the pBp derived from the inclusion synthetic process has been evidenced.

4 Conclusions

$\beta(-)$ pinene forms an inclusion complex with deoxycholic acid (DOCA) crystals and when irradiated at 75, 150 or 320 kGy with γ radiation, it undergoes a radiation induced polymerization to poly- $\beta(-)$ pinene (pBp) in very high yield. The yield is nearly 100% at 320 kGy. Such high yields cannot be achieved at all by radiation-induced bulk polymerization of $\beta(-)$ pinene. The pBp from inclusion polymerization shows the same FT-IR spectrum of the reference pBp prepared by bulk radiolysis although some spectral feature suggests a different cyclohexene ring configuration for the pBp from inclusion polymerization: an

evidence of the fact that the polymerization occurred in a constrained environment.

Furthermore, the specific optical rotation and the optical rotatory dispersion (ORD) of the pBp from inclusion polymerization in DOCA appears different than the optical properties of pBp prepared by bulk polymerization. The difference has been attributed to the phenomenon of asymmetric induction "through space" caused by the chiral host matrix on the guest molecules. The thermal properties of pBp from inclusion polymerization studied by TGA, DTG and DTA appear similar to those of reference pBp prepared in bulk. Additionally, also the thermal properties of the inclusion complex pBp@DOCA have been studied.

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