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ARTICLE

Intercalate Co-Crystals of Syndiotactic Polystyrene with Benzyl methacrylate and Radiation-Induced Guest Polymerization

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ABSTRACT: The formation of a cocrystalline phase of syndiotactic polystyrene (s-PS), presenting layers of benzyl methacrylate (BzMA) guest molecules *intercalated* with layers of closely packed alternated enantiomorphous polymer chains, is presented. The distance between these polymer layers, which for the nanoporous δ phase of s-PS is of 1.05 nm increases up to 1.61 nm, due to the guest intercalation. The proximity of the BzMA molecules in the guest layers makes possible their irradiation-induced polymerization inside the cocrystalline film. The polymerization products are expelled from the crystalline host phase, and the latter, as a consequence of guest exclusion, reorganizes in a lower order helical mesomorphic phase.

1. Introduction

In recent years, chemical reactions in the solid state are widely investigated mainly because often proceed giving a single product without producing solvent waste and, as a consequence, are ideal for green chemistry technologies.[1] Some of these solid-state chemistry studies have been devoted to polymerization reactions, like, e.g., crystal to crystal topochemical polymerizations (mainly of diacetylenes[2] and muconic esters)[3] or solid state polymerization of monomers (mainly dienes) included as guest in channels of host organic crystalline phases.[4]

As for host polymeric cocrystalline phases, only intramolecular solid-state guest reactions have been until now reported.[5] In particular, the photoisomerization reaction of norbornadiene to quadricyclane in its cocrystalline phase with syndiotactic polystyrene (s-PS), has been suggested as a recording reaction for advanced optical materials.[5]

The lack of intermolecular guest reactions in host polymeric crystalline phases, is not surprising because the cocrystalline phases (formed by many stereoregular polymer like, e.g., syndiotactic polystyrene,[6−8] syndiotactic poly(*p*-methylstyrene),[9] syndiotactic poly(*p*-chlorostyrene),[10] poly(ethylene oxide),[11] syndiotactic poly(methyl methacrylate),[12] isotactic poly(4-methylpentene)[13]), in most cases exhibit clathrate structures, i.e. include low-molecular-mass guest molecules being isolated between polymer chains.

In recent years, for s-PS, a cheap and robust commercial polymer,[14] two different classes of cocrystalline phases presenting rows[7] or layers[8] of contiguous (rather than isolated)[6] low-molecular-mass guest molecules have been described. This opens the possibility to obtain solid-state intermolecular reactions between contiguous guest molecules.

In fact, s-PS is able to form cocrystalline phases with a large number of guest molecules,[6−8] always assuming the s(2/1)2 helical conformation, with a repetition period of nearly 0.78 nm. Most s-PS cocrystals[6,7] are characterized by the *ac* layers of close-packed alternated enantiomorphous helices, typical of the nanoporous monoclinic δ form (Figure 1A),[15] and hence have been defined as δ *cocrystals*.

These δ cocrystals in most cases are δ *clathrates*; i.e., the guest molecules are imprisoned into isolated cavities (cooperatively generated by two enantiomorphous helices of two adjacent *ac* layers), as shown for instance in Figure 1B for the δ *clathrate* phase with toluene.[6a] δ clathrate cocrystalline phases are generally characterized by a molar ratio between styrene units and guest molecules (SU/G) equal to 4 and have been also obtained with reactive guest molecules (like, e.g., classical olefin and diene monomers: ethylene,[16a] butadiene,[16b] styrene[16c]). However, because of the isolated arrangements of the guest molecules these clathrate cocrystalline phases are unsuitable for solid-state intermolecular guest reactions.

A second class of s-PS δ cocrystals, defined as δ *intercalate* (or simply intercalates),[7,17] has been suggested on the basis of qualitative interpretation of X-ray diffraction data since 1996[17] but corresponding crystalline structures have been established only in recent years.[7] In the δ intercalates, the guest molecules are not isolated into host cavities but contiguous inside layers intercalated with the polymer layers, as shown for instance in Figure 1C for the δ intercalate phase with norbornadiene.[6a] These intercalate structures present a higher guest content with respect to the clathrate structures and SU/G ratio generally is 2 rather than 4 (Figure 1C).[5] Intercalate co crystalline structures, being characterized by the *ac* layers of helices alternated with layers of contiguous guest molecules,[7] could bring in principle to guest proximity and orientations suitable for intermolecular reactions.

Recently, a third class of s-PS cocrystals has been obtained by guest sorption in the nanoporous orthorhombic ε phase of s-PS.[18] In these cocrystals, defined as ε *clathrates*, guest molecules are imprisoned into channels passing the unit cells of the ε form from side to side along the *c* direction.[8] Also for guests of ε clathrates, the guest proximity and orientations could be, in principle, suitable for intermolecular reactions.

In the first part of this contribution, the formation of an *intercalate* cocrystalline phase of s-PS with benzyl methacrylate (BzMA), a vinyl monomer used as a base of UV curable imprinting resins,[19] is presented. In the second section of the paper, the BzMA guest polymerization, as induced by γ-irradiation, is reported.

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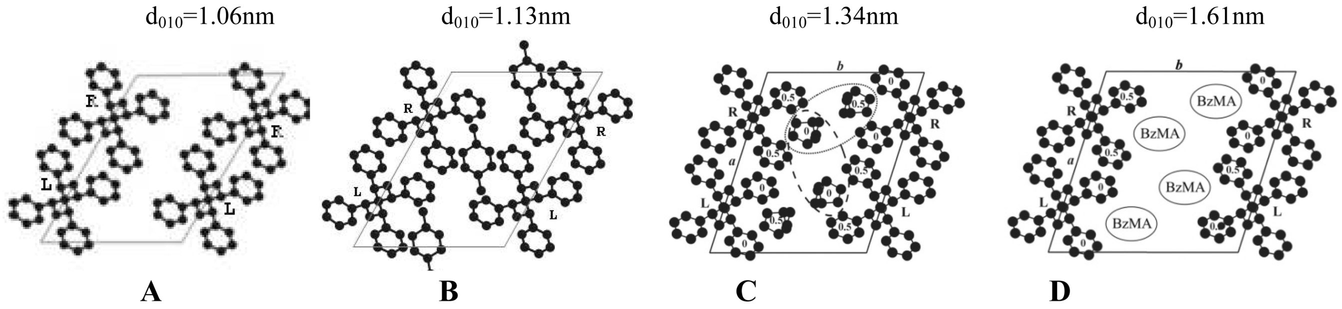


Figure 1. Schematic projections along the chain axis of s-PS s(2/1)2 helices, showing the crystal structure: (A) empty δ phase; (B) δ clathrate phase with toluene (SU/G = 4); (C) δ intercalate phase with norbornadiene (SU/G = 2); (D) δ intercalate phase with benzyl methacrylate (BzMA), as proposed on the basis of the results of the present paper (SU/G = 2). All these structures exhibit the same high-density *ac* layers of close-packed enantiomorphous helices.

2. Experimental Part

2.1. Materials. s-PS was manufactured by Dow Chemical Company under the trademark Questra 101. The ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be M_w 3.2×10^5 with the polydispersity index $M_w/M_n = 3.9$.

Benzyl methacrylate, the commercial poly(benzyl methacrylate) (PBzMA) and solvents were purchased from Aldrich and used without further purification.

2.2. Preparation of the Samples. Uniaxially oriented s-PS amorphous films were obtained by stretching of extruded sheets, at draw ratio $\lambda \equiv$ (final length/initial length) = 3, at strain rate of 10/min, in the temperature range 105−110 °C with a dynamometer INSTRON 4301. Uniaxially oriented films, presenting the s-PS/BzMA cocrystalline phase, were obtained from oriented films, by immersion in BzMA at room temperature for 5 days. The orientation of the crystalline phase is characterized by a high degree of parallelism of the chain axes with respect to the stretching direction (Herman's orientation factor f_c is close to 0.95).

s-PS/BzMA cocrystalline films presenting the $a_{\parallel}c_{\parallel}$ uniplanar orientation,[20] i.e. with the *ac* planes preferentially parallel to the film surface, were obtained by immersion in BzMA for 3 days of δ-form films, in turn prepared by casting from a s-PS chloroform solution.

The content of the guest molecules in the films was determined by thermogravimetric (TGA) and Fourier transform infrared (FTIR) measurements.

The molecular volume of the guest molecules has been simply evaluated from their molecular mass (M) and density (ρ):

$$V_{\text{guest}} = M/\rho N_{\text{A}}$$

where N_A is Avogadro's number (6,02 × 10^{23} molecules/mol).

2.3. Fourier Transform Infrared Measurements. Fourier transform infrared (FTIR) spectra were obtained at a resolution of 2.0 cm^{-1} with Bruker spectrometers (Vertex70 and Tensor27) equipped with deuterated triglycine sulfate (DTGS) detector and a KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He−Ne laser. 32 scans were signal averaged to reduce the noise.

The degree of crystallinity was evaluated by the FTIR procedure described in ref 21.

2.4. X-ray Diffraction Characterizations. Wide-angle X-ray diffraction (WAXD) patterns with nickel filtered CuKα radiation were obtained, in reflection, with an automatic Bruker diffractometer. Wide-angle X-ray diffraction patterns were also obtained, in transmission, by using a cylindrical camera (radius = 57.3 mm). In the latter case the patterns were recorded on a BAS-MS imaging plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800). In particular, to collect the diffraction of the film with uniplanar orientation,[20] photographic X-ray diffraction patterns were taken by having the X-ray beam parallel (EDGE) and perpendicular (THROUGH) to the film surface and by placing the film sample parallel to the axis of the cylindrical camera. The degree of orientation of the crystal plane exhibiting 010 Miller indexes (f_{010}), with respect to the film plane, has been formalized on a quantitative numerical basis, in analogy with the Hermans' orientation functions, and evaluated as described in ref 20d.

2.5. Nuclear Magnetic Resonance (NMR) Measurements. ^{13}C NMR spectra were recorded on an AM 300Bruker spectrometer operating at 75.47 MHz at 298 K.

The spectrum of the commercial PbzMA was obtained after dissolution of 0.1 g in 0.5 mL of deuterated chloroform. The spectrum of the polymer obtained by γ-irradiation of BzMA guest molecules was measured after extraction of the s-PS host film by deuterated chloroform. Tetramethylsilane was used as internal chemical shift reference.

2.6. Electronic Paramagnetic Resonance (EPR) Measurements. Films of s-PS containing BzMA monomer were sealed under high vacuum in quartz tubes and irradiated at 77 K in a 60-Co source at the dose rate of 0.35 kGy/h with a total doses of 7−14 kGy. After the irradiation and elimination of the quartz paramagnetic centers using the sliding technique, the EPR spectra were recorded as a function of the temperature from 120 K up to room temperature, using a Bruker EMX/12 spectrometer. Low microwave power (0.1 mw) suited for avoiding saturation and attaining optimum signal-to-noise ratio coupled with best line resolution was adopted. The spectral analysis was carried out by computer simulation using a spin Hamiltonian including the Zeeman electron and nuclear terms and the hf isotropic and anisotropic interactions.

3. Results and Discussion

3.1. Intercalate s-PS Cocrystals with BzMA. The formation of an intercalate cocrystalline phase of s-PS with BzMA has been reported by Rastogi and co-workers since 1998.[22] However, mainly due to the use of only unoriented samples, few diffraction peaks and only preliminary ideas relative to the crystalline structure have been reported.[22d]

The X-ray diffraction pattern of an axially oriented s-PS film, exhibiting the nanoporous δ phase (Figure 2A), after absorption of BzMA is modified as shown in Figure 2B. For the pattern of Figure 2B, the main features of the observed reflections (layer-line, Bragg spacing, diffraction angle and relative intensity) are collected in the first four columns of Table 1. The changes of the X-ray diffraction pattern, as shown in Figure 2 (e.g., the intense 010 reflection of the δ form become negligible after BzMA sorption),[6,7] clearly confirm the formation of a cocrystalline phase.[15a]

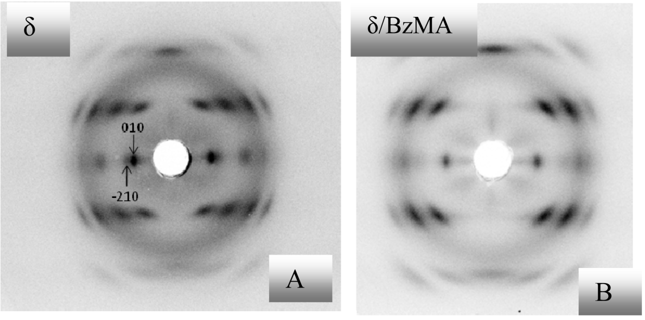


Figure 2. X-ray fiber diffraction patterns (CuKα) of an axially oriented film, obtained on an imaging plate with a cylindrical camera, exhibiting the (A) nanoporous *δ* phase and the (B) intercalate cocrystalline phase with BzMA, as obtained by guest sorption into the *δ* phase. The layer-lines, Bragg spacings, diffraction angles and relative intensities of the reflections observed for the s-PS/BzMA cocrystalline phase (B), are reported in the first four columns of Table 1.

Table 1. Bragg Distance (*d*), Miller Index (*l*), Diffraction Angle (2*θ*), and Relative Intensity (*I*, v = Very, s = Strong, m = Medium, w = Weak) and Azimuthal Angle (*χ*) of Observed Reflections for Film Exhibiting the Axial or Uniplanar Orientations of the s-PS/BzMA Intercalate Phase[a]

				$a_{\parallel}c_{\parallel}$ uniplanar				
	axial			edge			through	
d (nm)	*l*	$2\vartheta_{obs}$	I_{obs}	$2\vartheta_{obs}$	I_{obs}	χ_{obs} (deg)	$2\vartheta_{obs}$	I_{obs}
1.52 (010)				5.8	s	0		
0.89	0	9.9	s	9.9	s	90	9.9	s
0.8 (020)				10.9	w	0		
0.56	0	15.7	vw				15.7	vw
0.5 (030)				17	ms	0		
0.48	0	18.6	m	18.7	ms	53	18.8	s
0.54	1	16.3	s	16.5	ms	48		
0.45	1	19.6	s	19.5	s	90		
0.43	1	20.8	vw				20.8	vw
0.38	1	23.5	m	23.4	m	90	23.3	m
0.38	2	23.6	m					
0.32	2	27.9	m	27.9	m	90	27.5	mw
0.39 (002)	2	22.7	s					

[a] For the uniplanar film the data collection has been effected with both *edge* and *through* geometries, i.e., with X-ray beam parallel or perpendicular to the film plane, respectively. In the first column the three Miller indexes of some relevant reflections are also indicated.

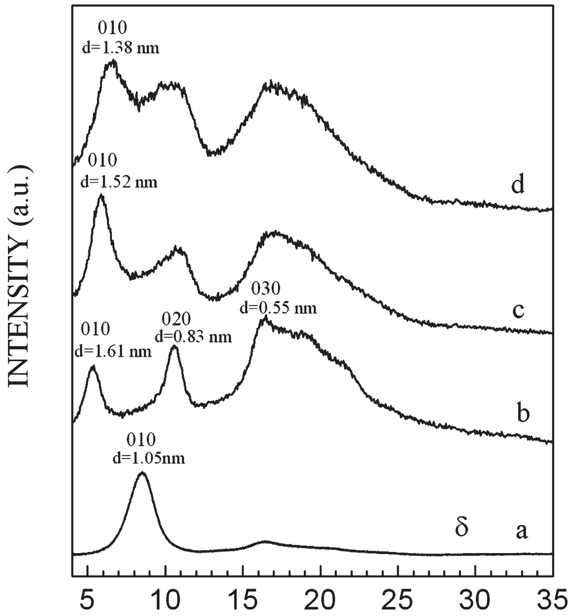


Figure 3. X-ray diffraction patterns (CuKα), as taken with automatic powder diffractometer of s-PS films exhibiting uniplanar orientation of the crystalline phases ($f_{010} \approx 0.75$): (a) nanoporous *δ*; (b–d) intercalate cocrystalline, with different BzMA content of (b) 35%, (c) 21%, and (d) 13%.

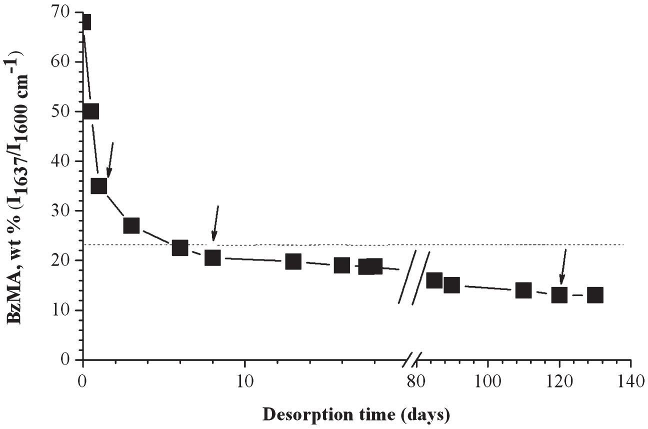


Figure 4. Desorption kinetics of BzMA at room temperature from a s-PS film, with $a_{\parallel}c_{\parallel}$ uniplanar orientation of the cocrystalline phase, as obtained by room temperature sorption of the liquid in films initially exhibiting the nanoporous *δ* phase. The symbols indicated by arrows correspond to the samples as characterized by the X-ray diffraction patterns of Figure 3b–d. The horizontal dashed line represents the guest content of a film presenting a degree of crystallinity of 35% and including BzMA only in the cocrystalline phase (with SU/*G* = 2).

Relevant additional information relative to this cocrystalline phase can be obtained by X-ray diffraction patterns of s-PS/BzMA cocrystalline films exhibiting the $a_{\parallel}c_{\parallel}$ uniplanar orientation, i.e., presenting an orientation of the *a* and *c* unit axes preferentially parallel to the film plane.[20d]

As discussed in detail in previous papers,[20a,d] the $a_{\parallel}c_{\parallel}$ uniplanar orientation maximizes the 0k0 reflections in simple X-ray diffraction patterns, as taken by automatic powder diffractometers. This makes easy the evaluation of the distance (d_{010}) between the *ac* layers of close-packed alternated enantiomorphic helices,[20a,d] which allows to discriminate between *δ* clathrates and intercalates.[7b]

For the *δ* form s-PS film, whose X-ray diffraction pattern is shown in Figure 3a, exhibiting uniplanar orientation of the cocrystalline phase ($f_{010} \approx 0.75$), sorption and desorption kinetics of BzMA at room temperature have been studied in some detail. In particular, the BzMA uptake after 3 days of sorption (essentially corresponding to an equilibrium uptake) is close to 70 wt %. The corresponding room-temperature desorption kinetics, as obtained by the intensity ratio between two BzMA (1637 cm^{-1}) and s-PS (1600 cm^{-1}) absorbance FTIR peaks, is shown in Figure 4. It is clearly apparent that most of the solvent rapidly desorbs from the polymer film while a part of the solvent (15–20 wt %) remains in the film also after many days of desorption.

The X-ray diffraction patterns, as taken by an automatic powder diffractometer, of this $a_{//}c_{//}$ uniplanar film after 1 day, 8 days and 4 months of BzMA desorption are shown in Figure 3b–d, respectively. All patterns present, as expected, an intense 010 peak whose periodicity is always much higher than for the starting *δ* form film (1.05 nm) and significantly decreases (1.61, 1.52, and 1.38 nm) with the desorption time and hence with the guest content (35, 21, and 13 wt %, respectively). These data clearly indicate that BzMA molecules are hosted as guest of the s-PS cocrystalline phase mainly by increasing the distance between the *ac* layers

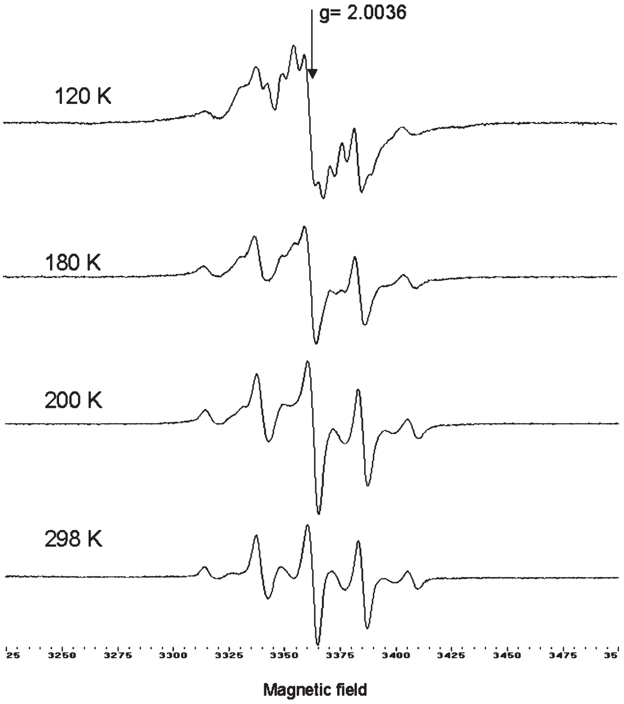


Figure 5. EPR spectra of an intercalate cocrystalline films of s-PS with BzMA, γ irradiated at 77 K and recorded after the irradiation at the temperature shown aside.

(d_{010}), thus forming an intercalate structure (which typically present d_{010} spacing higher than 1.3 nm).[7b]

As the desorption time increases, there is a progressive loss of crystalline order (both of crystal perfection and size), as clearly pointed out by the increasing broadness of the diffraction peaks (compare Figure 3b with Figure 3d). Hence, the most informative is the pattern of Figure 3b, which corresponds to the s-PS/BzMA intercalate cocrystalline phase exhibiting a maximum degree of order. For this uniplanar film, X-ray diffraction data have also been collected with both *edge* and *through* geometries (i.e., with X-ray beam parallel or perpendicular to the film plane) and the main features of the observed reflections are reported in Table 1 in columns 5−7 and 8−9 respectively. The comparison between the diffraction angles of the peaks of the sample exhibiting the axial orientation (column 3 of Table 1) and of the sample exhibiting uniplanar orientation (columns 5 and 8) shows that the same intercalate cocrystalline phase has been achieved in both samples.

It is worth adding that the desorption kinetic of Figure 4 indicates that, as usual for guest molecules of s-PS cocrystalline films, there is a fast guest desorption (mainly from the amorphous phase) followed by a much slower guest desorption, essentially involving guest molecules of the crystalline phase.

Hence, the desorption kinetics suggest a guest content in the intercalate cocrystalline films being in the range 20−25 wt %, which combined with a degree of crystallinity (as evaluated by the FTIR method described in ref 21) in the range 35−40%, roughly correspond to a molar ratio SU/G = 2. This is the molar ratio found for most s-PS intercalate cocrystalline phases and in particular for intercalates whose guest molecular volume is similar or smaller with respect to that one of BzMA (V_{mol} = 0.281 nm^3), i.e., with norbornadiene[7a] (V_{mol} = 0.169 nm^3), 1,3,5-trimethylbenzene[7b,23] (V_{mol} = 0.230 nm^3), 1,4-dimethylnaphthalene[7b] (V_{mol} = 0.255 nm^3) and 2,2,6,6-tetramethylpiperidinyl-N-oxyl, TEMPO[17f-h] (V_{mol} = 0.283 nm^3).

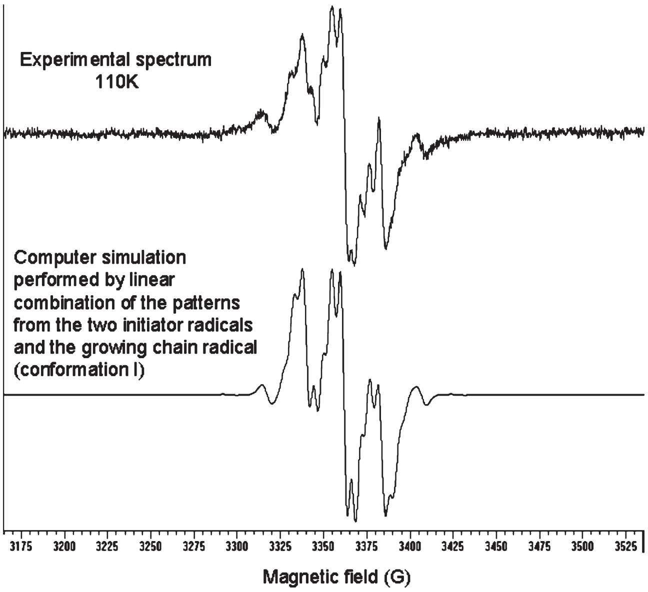


Figure 6. Computer simulation of the EPR spectrum recorded at 110 K after γ irradiation at 77 K.

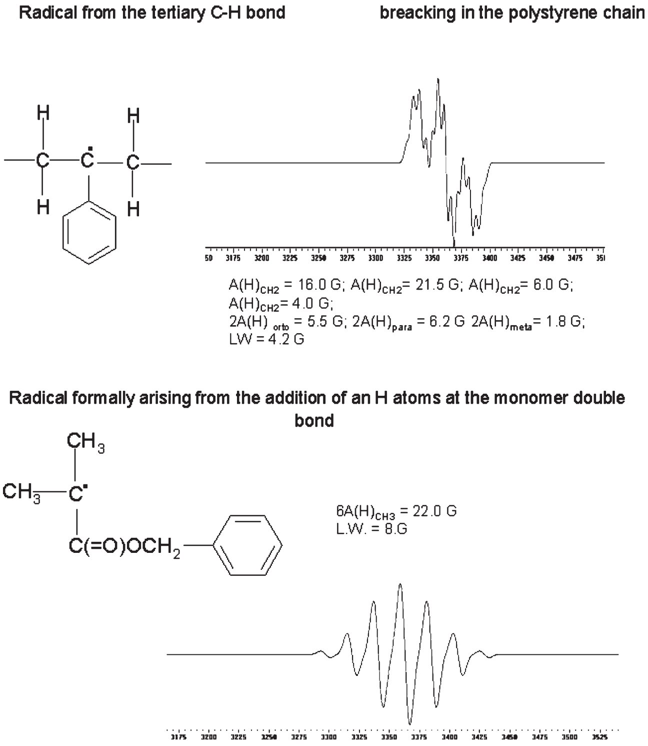


Figure 7. Computer simulations of EPR spectra of the supposed initiator radicals.

It is worth adding that a higher SU/G molar ratio (4 rather than 2) has been until now found only for the intercalate cocrystalline phase with a bulkier guest molecule (a styrene dimer with V_{mol} = 0.36 nm^3).[17e]

On this basis, it is possible to propose for the s-PS/BzMA intercalate cocrystalline structure the BzMA guest locations schematically shown in Figure 1D, similar to those of the 1,4-dimethylnaphthalene[7b] or TEMPO[17h] in their intercalate cocrystalline structures.

3.2. γ-Irradiation of Polymer Cocrystalline Films. Films of s-PS having a thickness of 20−30 μm, exhibiting the uniplanar orientation of the intercalate cocrystalline phase with

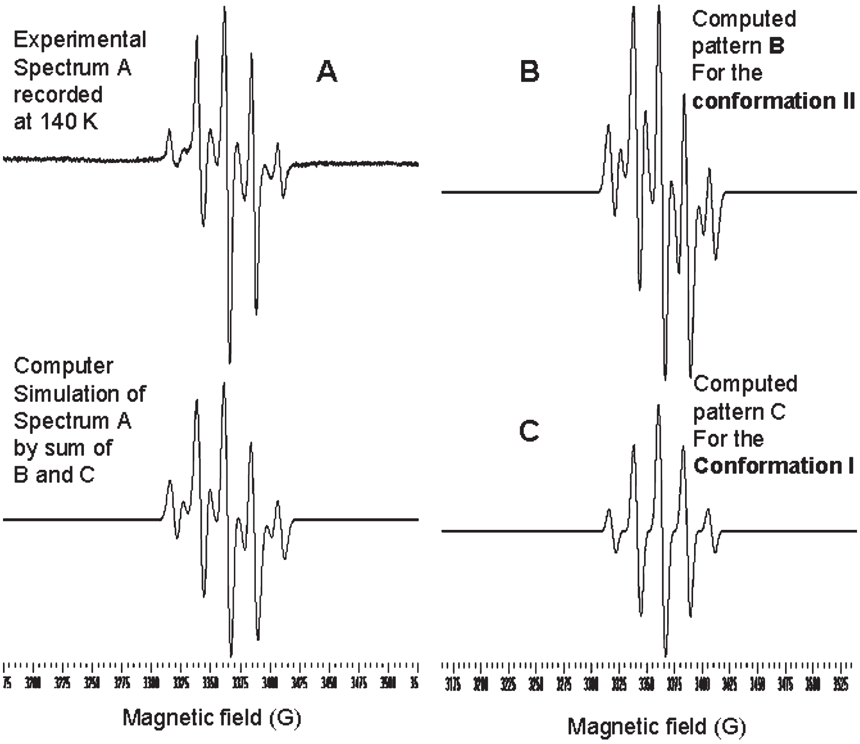


Figure 8. Computer simulation of the EPR spectrum of the growing chain radical within the s-PS intercalate phase. The simulation was obtained by linear combination of the spectra arising from the conformation I and II.

BzMA (similar to that one of Figure 3d, with a guest content close to 15 wt %) have been irradiated at 77 K in a 60-Co source with total doses of 7−14 Kgy, as described in the Experimental Part.

3.2.1. EPR Study of the Irradiated Guest Molecules. The sequence of the EPR spectra recorded as a function of the temperature is shown in Figure 5. The initial spectrum belongs to the initiating radicals, consisting mainly of the polystyrene radicals, formally arising from the loss of an H atom at the tertiary CH bond, and the radical formed by H atom addition at the monomer double bond. The final spectrum, recorded at 298 K, is the well-known pattern belonging to the growing chain radicals of methacrylate monomers.[24]

This EPR change can be reckoned with the initiation of a radical polymerization reaction of the guest molecules of the intercalate cocrystalline phase, following the increase of the temperature. The decay of the initiating polystyryl radical is complete at 180 K, which implies that the addition to the monomer starts at lower temperatures:

The identification of the initiating radicals is based on the computer simulation of a 110 K spectrum recorded at lower power to enhance line resolution at expenses of some worsening of the signal-to-noise ratio (Figure 6).

The proton coupling constants used for simulations are reported in Figure 7. The characteristics of the EPR spectrum of the polystyryl radical needs some comment. The major structure is a triplet 1:2:1 of about 19 G average splitting with each line being further split into a multiplet with average splitting of 5.5 G. The inequivalence of the four methylene protons is due to a conformation which causes the dihedral angles between the symmetry axis of the unpaired electron and the C−H$_\beta$ bond of one proton in each methylene groups to be $<60°$. The other two C−H$_\beta$ bonds are closer to the nodal plane giving the smaller splittings. A similar conformation leading to a triplet EPR signal through the prominent interaction by two protons is observed also in the radicals from irradiated atactic polystyrene.[25a,b] The other four minor splittings of 5−6 G are those expected for the ortho and para positions in a benzyl type radicals.[25c] The irradiation of benzene and aromatic compounds usually also leads to the formation of cyclohexadienyl radicals formally arising from the addition of H atoms at the ring. Such radicals have also been detected in minor relative abundance in irradiated polystyrene[25a,b] giving broad doublets and triplets of about 47.G splitting. In this work, due also to the overlapping signal by the guest molecules it was not possible to definitely assess the presence of such species which are expected to afford a minor contribution to the initiation of the polymerization and grafting of BzMA.

With respect to the corresponding spectrum of Figure 5, the recording of the experimental spectrum has been performed at lower microwave power and lower modulation amplitude to enhance line resolution at expenses of the signal-to-noise ratio.

The growing chain radical spectrum recorded at room temperature shows the typical nine line pattern which is reckoned with a slightly asymmentrical conformation with dihedral angles 65° and 55°. In order to correctly reproduce the intensity of the central line in the experimental spectrum (Figure 8) another more asymmetrical conformation had to be considered which is prevalent at low temperature (Figure 5, spectra recorded at 180 and 200 K). This conformation gives a binomial quintet because of the accidental equivalence of the three methyl proton and one of the methylene proton, the other methylene proton being too small foe being resolved (Figure 9). The quintet structure of the growing chain radicals had to be added to the patterns of the initiating radicals in order to improve the simulation of the 120 K experimental spectrum (Figure 6). This implies that some addition to the monomer has already occurred at such low temperatures.

3.2.2. FTIR and WAXD Characterization of the Irradiated s-PS Films. The FTIR spectrum of the s-PS films, exhibiting

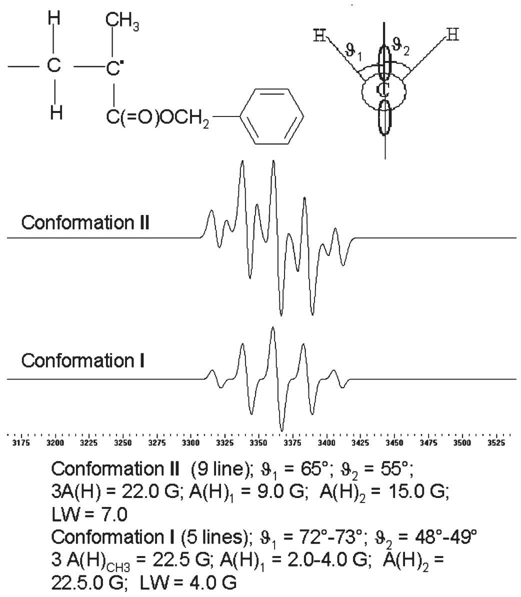


Figure 9. Computer simulation and hf parameters of the EPR spectra of the two conformation of the BzMA growing chain radical. The two patterns have been used for the simulation of the experimental spectrum (Figure 8).

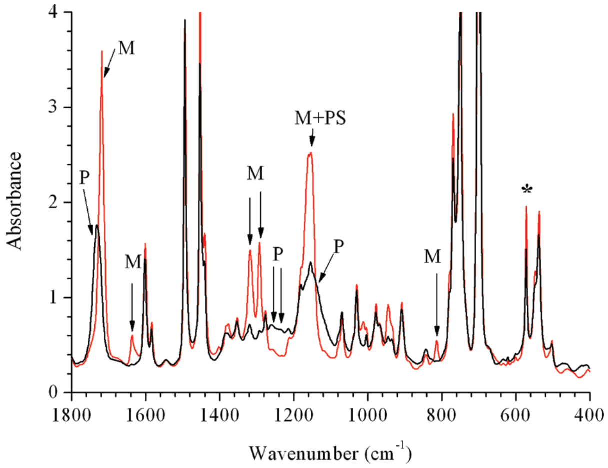


Figure 10. FTIR spectra in the wavenumber range 1800−400 cm^{-1} of s-PS films, exhibiting the cocrystalline phase with BzMa, before (red thin line) and after (black thick line) γ-irradiation.

a cocrystalline phase with BzMa (guest content nearly equal to 10 wt %) is shown as a red thin line in Figure 10, where the main absorbance peaks of BzMA have been labeled as M (monomer). The FTIR spectrum of the same s-PS films, after γ irradiation in a 60-Co source with a total doses of 100 KGy is also shown in Figure 10, as a black thick line. It is clearly apparent that, after irradiation, all the monomer peaks disappear, while new minor peaks appear at 1730, 1260, 1233, and 1143 (shoulder) cm^{-1}. These peaks are close to the main infrared peaks observed for poly(benzyl methacrylate)[26] and hence have been labeled as P (polymer) in Figure 10.

The FTIR spectra of Figure 10 also show that the helical polymer conformation, typical of all cocrystalline and nanoporous phases of s-PS is essentially preserved. In fact, for instance, the peak at 572 cm^{-1} (indicated by a star in Figure 10, typical of the s(2/1)2 helix and mainly corresponding to a CH$_2$ group torsion)[27] reduces its intensity of only 16%.

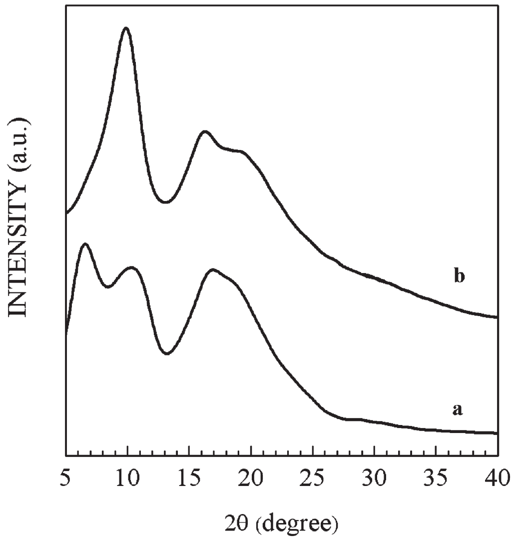


Figure 11. X-ray diffraction patterns, as taken by an automatic powder diffractometer (CuKα), of s-PS films, exhibiting the cocrystalline phase with BzMa, before (a) and after (b) γ-irradiation.

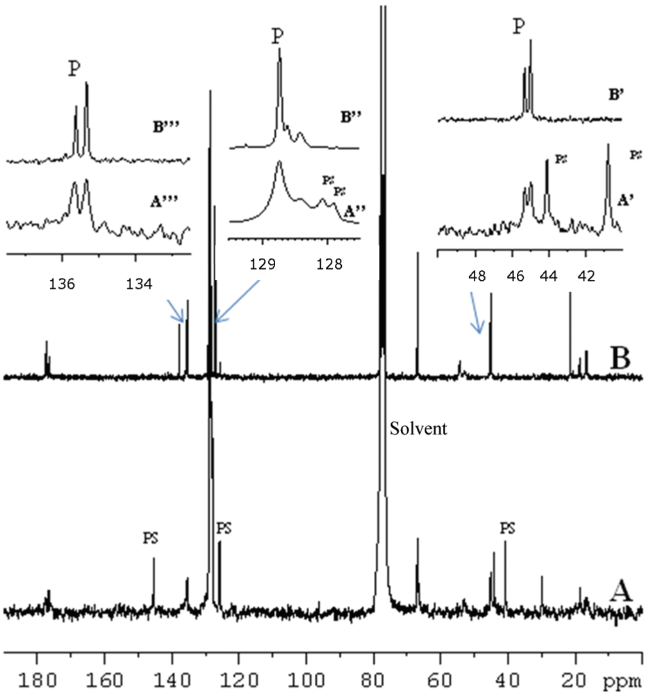


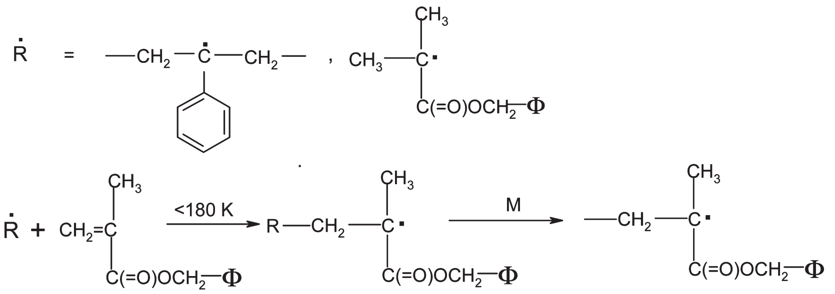
Figure 12. ^{13}C NMR spectra: (A) the reaction product of the γ irradiation of the s-PS/BzMA intercalate cocrystalline film, as extracted by CDCl$_3$; (B) a commercial PBzMA. The insets show enlarged regions with intense and well-resolved peaks of PBzMA (labeled as P). The peaks labeled as PS correspond to a minor amount of s-PS extracted with PBzMA.

The X-ray diffraction patterns, as taken by an automatic powder diffractometer of the same s-PS films whose FTIR spectra are reported in Figure 10 (thin and thick lines) are shown in Figure 11, parts a and b, respectively.

The pattern of the irradiated uniplanar film (Figure 11b) exhibits broad peaks suggesting the formation of the mesomorphic helical phase[28] (also called intermediate phase).[28c]

In summary, the FTIR and WAXD analyses clearly indicate that, after irradiation, no monomer is left in the sample and at least part of the monomer has been transformed in a polymeric product, which is expelled from the crystalline phase leaving a mesomorphic helical phase.

Scheme 1



3.2.3. ^{13}C NMR Characterization of the Radiation-Induced Reaction Products. The reaction products of the γ-irradiation procedures on s-PS/BzMA intercalate cocrystalline films, have been also studied after extractions from the s-PS films.

In particular, the ^{13}C NMR spectrum of a sample extracted by $CDCl_3$ (at room temperature for 2 days) from a γ irradiated s-PS/BzMA intercalate film is shown in Figure 12A. For the sake of comparison the analogous spectrum of a commercial PBzMA has been reported in Figure 12B.

The extracted sample present the typical resonances at 44.9, 45.3 ppm (B′), at 128.7 ppm (B″), and at 135.3, 135.6 ppm (B‴) of PBzMA, clearly indicating the formation of an atactic polymer.[29]

The spectrum of Figure 12A clearly shows also peaks corresponding to a minor amount of extracted s-PS (see peaks labeled as PS in Figure 12, parts A, A′, and A″). This PS fraction includes chains chemically bonded to the formed PbzMA, according to the initiating radical mechanism of Scheme 1.

4. Conclusions

The formation of an *intercalate* cocrystalline phase of s-PS with BzMA, a vinyl monomer used as a base of UV curable imprinting resins, is presented.

X-ray diffraction patterns of s-PS films presenting axial and uniplanar orientations have allowed to establish that, for this intercalate cocrystalline phase, the distance (d_{010}) between the high density *ac* planes (of closely packed alternated enantiomorphous helices) is much higher than for the starting δ form film (1.05 nm) and can assume values as high as 1.61 nm.

Guest desorption kinetics associated with evaluations of degrees of crystallinity of the films indicate that, for the intercalate cocrystalline phase, the molar ratio between the styrenic units and BzMA is close to 2. This is the molar ratio already observed in all known s-PS intercalates with guests having molecular volumes similar or smaller than BzMA.

An EPR study of γ-irradiated s-PS films exhibiting the intercalate cocrystalline phase with BzMA has shown that the initiating radicals (observed at low temperatures, 120 K) mainly consist of the polystyrene radicals, formally arising from the loss of an H atom at the tertiary CH bond, and of the radical formed by H atom addition at the monomer double bond. The EPR study at room temperature shows the well-known pattern belonging to the growing chain radicals of methacrylate monomers.

The formation of poly(benzyl methacrylate), as a consequence of γ irradiation of the s-PS/BzMA cocrystalline films, has been shown by FTIR spectra of the films as well as by ^{13}C NMR spectra of the products, as extracted by $CDCl_3$ from the host s-PS films.

As for the crystalline structure of the polymer host, the FTIR spectra show that the ordered helical s(2/1)2 polymer conformation is essentially preserved, after the considered irradiation procedures. However, the X-ray diffraction patterns of the irradiated films indicate the exclusion of the reaction products from the crystalline phase leading to empty mesomorphic helical phases.

In summary, the proximity of the BzMA guest molecules in layer intercalated to s-PS *ac* layers makes possible their irradiation-induced polymerization. However, the polymerization products are expelled from the crystalline host phase, and the latter, as a consequence of guest exclusion, reorganizes in a lower order helical mesomorphic phase.

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