Chapter 4 MMA-co-POSS copolymers: synthesis, characterization, structure, morphology and properties

MMA-co-POSS random copolymers have been synthesized and characterized in order to exploit the effect of the POSS objects both on the nanostructuring and on the properties. Structure and morphology have been determined as well as thermal and surface properties. Two types of POSS have been used and the synthesized systems have been compared with commercially available MMA-co-POSS copolymers.

4.1 Synthesis and chemical characterization of MMA-co-POSS copolymers

The aim of the synthesis is to obtain random copolymers of MMA and POSS, with a structure similar to the one in figure 4-1:

![Figure 4-1](image)

The R groups can be either isobutyl or cyclohexyl.

The values of m and n are random and vary as a function of POSS concentrations.

The values of m and n, that is the ratio between the methacrylate and the POSS monomers, is intended to be random, still respecting the condition that its average would be equal to the molar ratio MMA/POSS.
To better identify the different copolymers used in this research the following nomenclature will be used:

MMA-co-x% CyPOSS-INSA identifies the copolymers synthesized from free radical polymerization with x mol % CyPOSS (with respect to the total number of moles of all the monomers). Similar notation will be used for the iBuPOSS copolymers, with the obvious difference of iBuPOSS instead of CyPOSS.

MMA-co-x% iBuPOSS-Aldrich identifies the copolymers commercially available containing x mol % iBuPOSS.

4.1.1 Composition of commercially available MMA-co-POSS copolymers

The MMA-co-iBuPOSS copolymers are commercially available from Aldrich Chemicals. The structure of these random copolymers is not specified by the producer. $^{13}$C NMR data, which will be displayed further, suggests that these copolymers are random copolymers.

The compositions available are:

- MMA-co-1.5mol % iBuPOSS, identified as MMA-co-1.5% iBuPOSS-Aldrich
- MMA-co-2.9mol % iBuPOSS, identified as MMA-co-2.9% iBuPOSS-Aldrich
- MMA-co-9.6mol % iBuPOSS, identified as MMA-co-9.6% iBuPOSS-Aldrich

These compositions have been determined via elemental analysis.

4.1.2 Synthesis and purification of MMA-co-POSS-INSA copolymers

MMA-co-POSS copolymers have been synthesized by free radical polymerization. This technique has been chosen because of its wide application in polymer science [Bra03, Bub94, Chi95, Ell02, Fuk92, Kas03, Lov03, Moa95, Wei99, Zhu89], thus it has been possible to synthesize hybrid copolymers by an easy adaptation of a synthesis procedure well-established in polymer science. A purification procedure with a solvent-non-solvent system was used to separate the final system from unreacted or partially reacted reagents. Toluene was used as a solvent and methanol as non-solvent. Methanol has been chosen because it is a good solvent for the reagents [Biz04, Bra03], while it is a non-solvent for the MMA-co-POSS copolymers [Hyb05], which therefore tend to precipitate once in the toluene-methanol mixture.
- **Experimental conditions**

Methylmethacrylate, MMA, was purchased from Janssen Chimica. Azobisisobutyronitrile AIBN, a thermal free radical initiator, was purchased from Fluka. The POSS used are the two monofunctional ones, iBuPOSS and CyPOSS, described in Chapter II. All reagents were used as received, except CyPOSS which was purified by recrystallization in methanol, as detailed in Chapter 2. Random copolymers were prepared with POSS amount varying from 0 to 10mol %. All the copolymers have been prepared in a 0.5M solution of toluene. 0.25 mol % (with respect to the total number of moles of all the monomers) of AIBN was used. In standard conditions, a 250 ml reactor has been used. The reactor was equipped with a condenser and calcium carbonate cage to avoid moisture absorption. All the components (i.e. reactor, condenser and calcium carbonate cage) were stored in a humidity-free oven at 110°C prior to use. All the joints have been sealed with Teflon band and no silicon grease has been used to reduce the possibilities of contamination. 100 ml MMA-POSS-AIBN solution was poured in the reactor and then stirred via an oval magnetic bar for 48 hrs at 70°C in an oil bath. A flux of argon was used to maintain the inert atmosphere inside the reactor. Once the reaction was completed, the solution was allowed to cool down slowly.

The toluene was evaporated at 25°C overnight and then 20 ml of fresh toluene were used to re-dissolve the system. After complete dissolution, the solution was added to 5-fold methanol. Precipitation of the copolymers took place steadily and the system was afterwards kept 2 hrs at 5°C to increase the amount of precipitated material. The precipitated material was separated from the solution through filtration via a Buchner funnel equipped with paper filters. Precipitated material was then re-dissolved in 20 ml fresh toluene.

At this step, the part soluble in methanol was analysed by SEC to check if some residual monomers, either POSS or MMA, were unreacted, and the results are shown in figure 4-2:
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Figure 4-2 Spectra of the refractive index detector in SEC analysis. The products analysed are reported on the right of each spectrum. The circles represent the three main chemical species: (green) MMA monomer, (orange) CyPOSS monomer, (pink) MMA-co-CyPOSS. The data are offset for clarity.

As can be observed in figure 4-2, residual POSS can be seen at an elution time $t_e$ equal to 16.5 min while no peak is observed at $t_e=21.5$, which is the elution time of the MMA monomer. Therefore, it could be stated that the MMA has fully reacted. On the same curves relative to the soluble materials is visible also a peak at $t_e \approx 12.5$ min. This corresponds to an average molar mass of $\sim 20000$ g.mol$^{-1}$ and therefore this peak may well due to a polymer (with an average molar mass lower than the final copolymer) removed by the purification process. Therefore the purification procedure has the twofold effect of removing the unreacted monomers and at the same time the low-molar mass copolymers, this resulting in a final copolymer with lower polydispersity.

This procedure of purification was repeated three times and the final precipitate was then dried up in several steps: 25°C/12hrs, 60°C/2hrs, 80°C/2hrs, 100°C/2hrs, 120°C/2hrs, 140°C/2hr, 160°C/1hr under vacuum. The final products are in the form of white powder similar to PMMA-INSA powder. An example of the chromatogram of one of the copolymers is plotted in figure 4-2 (curve in pink): no trace of monomer is evidenced, while the final copolymer has a molar mass higher than the polymer soluble in methanol.

To prepare the 100µm thick films the powders were dissolved in chloroform, then poured in a PTFE mould. The films were slowly heated up to 140°C (above the glass transition temperature)
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temperature, \( T_g \), of the films, in the range 70-135°C) at atmospheric pressure and hold at 140°C up to complete evaporation of the solvent.

- **Chemical characterization**

The yield of the reaction was varying from ~95% for the pure PMMA to ~70% of the systems with higher amount of POSS. This is explicable in terms of the lower reactivity of the POSS monomers with respect to the MMA [Hyb05]. This difference of reactivity is reflected also in the POSS concentration in the copolymers, which is lower with respect to the reactive mixtures, as it will be shown further in table 4-1. This phenomenon, shown by NMR and elemental analysis, has a similar extent of what is present in the literature for copolymers POSS-styrene [Rom98, Xu02, Zhe01a]. In any case, the difference in between the POSS concentration in the reactive mixtures and in the copolymers is relatively low, and this confirms indirectly the capacity of the POSS to polymerise. It is to be noted that these compositions are effectively average value of the chains compositions. The first chains formed present a lower concentration of POSS than the last ones [Biz04].

In table 4-1 are reported the data of the chemical characterization of all the copolymers studied: molar fraction of POSS in the reactive mixtures, molar fraction of POSS in the final systems, average molar mass \( \bar{M}_n \), degree of polymerization \( \bar{DP}_n \) and the polydispersity index \( Ip \).
Table 4-1 Chemical characterization of the MMA-co-POSS copolymers.

* = data from elemental analysis; ** = data from SEC, triple detection, with THF as mobile phase.

Where the SEC data are not present, the system was not soluble in THF.

<table>
<thead>
<tr>
<th></th>
<th>POSS mol % in the reactive mixture</th>
<th>POSS mol % in the copolymers*</th>
<th>POSS wt % in the copolymers *</th>
<th>Yield % (by differential weight)</th>
<th>$\bar{M}_n$ (g*mol$^{-1}$) **</th>
<th>$\overline{D}_{pm}$</th>
<th>$I_p$ **</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>95</td>
<td>28000</td>
<td>280</td>
<td>1.31</td>
</tr>
<tr>
<td>MMA-co-CyPOSS-INSA</td>
<td>2.5</td>
<td>1.8</td>
<td>17.1</td>
<td>89</td>
<td>32100</td>
<td>271</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.9</td>
<td>31.4</td>
<td>83</td>
<td>40700</td>
<td>291</td>
<td>1.58</td>
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<tr>
<td></td>
<td>7.5</td>
<td>6.4</td>
<td>43.5</td>
<td>77</td>
<td>61500</td>
<td>371</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8.8</td>
<td>52.1</td>
<td>70</td>
<td>66100</td>
<td>347</td>
<td>1.59</td>
</tr>
<tr>
<td>MMA-co-iBuPOSS-INSA</td>
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<td>1.9</td>
<td>15.5</td>
<td>90</td>
<td>36000</td>
<td>310</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.4</td>
<td>30.3</td>
<td>84</td>
<td>31700</td>
<td>231</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>8.9</td>
<td>48.0</td>
<td>75</td>
<td>29000</td>
<td>166</td>
<td>1.54</td>
</tr>
<tr>
<td>MMA-co-iBuPOSS-Aldrich</td>
<td>Not available</td>
<td>1.5</td>
<td>12.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Not available</td>
<td>2.9</td>
<td>22.0</td>
<td>-</td>
<td>33400</td>
<td>268</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Not available</td>
<td>9.6</td>
<td>50.1</td>
<td>-</td>
<td>34000</td>
<td>188</td>
<td>2.26</td>
</tr>
</tbody>
</table>

All the copolymers were well soluble in THF, except the MMA-co-1.9% iBuPOSS-Aldrich, only partially soluble. Thus the data relative to this sample have not been presented because it was not possible to determine the concentration of the sample in the THF solution, therefore the SEC analysis was unreliable in this case.

The molar masses of the copolymers are in the same range of PMMA, therefore one can sensibly compare the properties of these copolymers with the neat PMMA.

The POSS present different influences on the molar mass and the polydispersity index of the copolymers. The CyPOSS tend to increase both the $\bar{M}_n$ and $I_p$, as already present in the literature for linear copolymers [Rom98, Zhe01a]. This effect can be explained in terms of the
lower termination rate of the MMA-co-POSS co-polymerization with respect to the MMA polymerization [Biz04]. In fact, during the radical polymerization of vinyl polymers, like the PMMA, the presence of bulky side groups decrease the termination rate of the polymerization, this in turn increasing the molar mass of the polymers [Ito79]. The POSS, and the CyPOSS in particular, therefore decrease the termination rate, and therefore increasing both the molar mass and the degree of polymerization of the MMA-co-POSS copolymers. On the other hand, MMA-co-iBuPOSS-INSA present only a slight decrease of the molar mass but a marked decrease of the degree of polymerization. It could be that the presence of the flexible isobutyl groups (instead of the rigid cyclohexyl ones) does not get the POSS to reduce massively the termination rate of the polymerization, as in the CyPOSS. However, the explanation of this effect is still partially unclear.

4.1.3 Influence of the POSS on the tacticity of the MMA-co-POSS copolymers

The influence of POSS on the tacticity of the MMA-co-POSS copolymers has been determined with $^{13}$C NMR. These data were also in agreement with the $^1$H NMR data. The results are shown in figure 4-3:

![Figure 4-3](image)

**Figure 4-3** Percentage of triades mm, mr and rr as a function of POSS type and concentrations.

The PMMA synthesized via free radical polymerization is atactic. The POSS seem to have no influence on the tacticity of the copolymers. This can be to the large hindrance of the bulky cubic cage to a regular arrangement of the POSS in either a isotactic or a syndiotactic fashion.
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This in turn allows us to compare the properties of the different systems without considering the influence of the tacticity.

4.2 Structure-Morphology Analysis of the random copolymers

This section shows the differences in the structures and morphologies as visualized by means of WAXS, TEM and AFM. The samples analysed were films 100 µm thick, of which the preparation is described in the section 4.1.2.

Each “family” of copolymers will be presented separately in each sub-section, then general conclusion will be drawn in the sub-section 4.2.4.

4.2.1 Structure-Morphology of MMA-co-CyPOSS-INSa

WAXS has been used to analyse the structure of all the copolymers, giving in some cases valuable indications for further analysis. This was the case for the MMA-co-CyPOSS-INSa, where the WAXS has supplied the basis for hypothesis successively confirmed by other techniques.

In figure 4-4 are reported the WAXS patterns of the various MMA-co-CyPOSS-INSa copolymers:
Figure 4-4 WAXS patterns of MMA-co-CyPOSS-INA copolymers. The POSS molar percentages are reported on the right of the figure. The data are offset for clarity.

The PMMA is amorphous and it present a pattern in good agreement with the existing literature [Mil84], with a broad peak at $2\theta \sim 13.5^\circ$. The CyPOSS, as already viewed in the chapter 2, has a crystalline structure and it is reported on the top of figure 4-4, as 100% POSS percentage.

The presence of small quantities of POSS in the copolymer chain, as in the case of MMA-co-1.8% CyPOSS-INA, modify the anomalous behaviour of the PMMA in terms of scattering, giving a pattern more similar to other methacrylates, like the cyclohexyl methacrylate [Mil84]. Despite the high crystallinity of the neat CyPOSS, the pattern of MMA-co-1.8% CyPOSS-INA is still amorphous. This does not exclude a priori the existence of a crystalline structure inside this copolymer because the crystal peaks may be not resolved due to the lack of good scattering intensity from the crystalline phase or due to a possible very small size of the crystallites, therefore giving rise to very broad peaks [Klu54, War90]. These considerations are in agreement with the micrograph taken with the TEM, as shown in the figure 4-5:
This copolymer presents a multi-scale morphology and it appears clearly as a three-regions material. One region constitutes the very most part of the copolymer and it looks bright and uniform in the TEM pictures. This region is likely to be mainly composed of PMMA (PMMA-rich region), as no evidence of POSS has been found. Therefore, it is not surprising that the scattering pattern of MMA-co-1.8% CyPOSS-INSA is amorphous. The second region is represented by apparently inhomogenously dispersed objects, with the sizes ranging from 10 to 80 nm. A third region is constituted by aggregates of needle-like objects, with the size of the aggregates in the range 2-3 µm. The needle-like objects present a length of about 200 nm and their orientation looks random. These needle-like objects should have an ordered, crystalline structure, according to the existing literature [Mat04, Zhe04]. The lack of a crystalline contribution to the scattering pattern can be due to the fact that the organisation is not enough to have a real crystallinity of these objects.
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For a CyPOSS molar fraction of 3.9%, there is the appearance of a semicrystalline pattern. The crystalline part of the WAXS pattern of MMA-co-3.9% CyPOSS-INSA has been analysed focusing on the two sharpest peaks, respectively at 2\(\theta\)~8° and ~18°. The peak at 2\(\theta\)~8° has a full width at half maximum, FWHM, of 0.6°, while the FWHM of the peak at 2\(\theta\)~18° is 1.15°. The difference of the FWHM of these peaks at 2\(\theta\)~8° and ~18° tends to indicate an anisotropic shape of the crystals, as it was already reported in the Chapter 1.

In fact, as previously noted, there are significant spatial constraints on the crystal shape assumed by POSS attached as side groups to the polymer chains. This crystal shape could be either columnar or lamellar, with the polymer chains located on the external faces of the crystals.

This anisotropic shape could in principle give rise to a difference in the breadth of the X-ray peaks associated with directions parallel or perpendicular to the long direction of the crystallites. As one can see in the table 2-3 in the Chapter 2, the two peaks at 2\(\theta\)~8° and 18°, having respectively as crystallographic indexes (hkl)=(101) and (hkl)=(011), correspond to two non-parallel sets of crystallographic planes. This, in turn, enforces the hypothesis that the difference in the FWHM of the two peaks is an indication of the existence of two-dimensional POSS crystalline assembling in the copolymers. Therefore it could be assumed that, in the MMA-co-CyPOSS-INSA, the CyPOSS organize themselves either in columnar or lamellar morphology.

To further test this hypothesis ultramicrotomed samples of the films were analyzed with the TEM, shown in figure 4-6:
The morphology is of the type islands-in-the-sea. Again there is the co-existence of three regions. The first two regions look essentially unaltered by the increase of the POSS molar fraction, while the third region is massively changed. First of all, the size of the aggregates now ranges in between 4-5µm. The needles now, still with a random orientation, organise themselves in what it may be called a “lamellar” or raft-like morphology, as shown already in the literature [Jeo00, Mat04, Mat99, Zhe04]. The needles are therefore likely to be constituted by the piling of POSS objects, and the stacking of these piles creates the lamellar morphology displayed. Increasing the POSS content these needles increase in number and sizes, with the remarkable feature to arrange themselves in a raftlike structure, as the ones presented in the section 1.3 for other POSS-based copolymers. The reason of the CyPOSS self-assembling into needles and then raftlike structures could be sought in the specific POSS-POSS interactions developed by the cyclohexyl groups.
A schematic representation of the three-region morphology present in the MMA-co-3.9% CyPOSS-INSAs copolymers is reported in figure 4-7:

Figure 4-7 Schematic representation of the three-region morphology of the copolymers MMA-co-3.9% CyPOSS-INSAs. In the frames indicated by the letters A, B and C are respectively indicated the needle, the aggregates, and the lamellar structures. The rest of the copolymers is here represented in the frame D as a polymer chain with dangling POSS units randomly distributed along the chain.

The assembling of POSS in the raftlike structure is represented in figure 4-7 as bidimensional, even if it would be more logic to be tri-dimensional, as in the model of Zheng et al. [Zhe02a] in figure 4-8 (with obviously the MMA instead of the PE as organic co-monomer):
According to the Zheng’s model [Zhe02a], the PMMA chains are supposed to be situated external to the lamellae, thus no polymer chains are supposed to lay in between the platelets. The lamellae do not look like a continuous region, like in the case of POSS-Butadiene [Zhe04]. This is likely to be due to the high rigidity of PMMA chains, which therefore hinders the arrangement of the POSS units in a continuous lamellar region inside the material, like the much softer butadiene chains can allow.

A confirmation of these results comes from AFM analysis on one of these domains, as displayed in figure 4-9:

![AFM analysis image](image)

**Figure 4-9** Phase image of AFM analysis on one of the domains displayed in figure 4-5. The sample was fractured at RT. The scale is indicated.
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The AFM image shown is the phase image. In the image are visible in white several objects long tens of nm and apparently wide only few nm. These can be the needles seen in figure 4-6, made less clear by the tip broadening intrinsic to any AFM analysis [VEE05]. Therefore section analysis has been performed on this image to clarify whether or not the same objects were visualized with the two techniques. The results are reported in figure 4-10:

![Section Analysis](image)

**Figure 4-10** Section analysis on the phase image in figure 4-9.

The section analysis shows the presence of some peaks likely due to the raftlike structure but it does not reveal a clear regularity of the peaks. It could be stated that this raftlike structure does not give rise to a long range order, as seen by AFM, and SAXS confirmed this finding.

The presence of a crystalline phase inside this copolymer is evident also from DSC, as can be see, in figure 4-11:

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As seen in the figure, while the PMMA-INSA exhibits only one transition in this temperature region, corresponding to the glass transition at T~107 °C, the MMA-co-3.9% CyPOSS-INSA shows, apart of the glass transition, another endothermic peak, at ~180°C, with an enthalpy of 2.25 J/g. It has to be noted that neither the neat CyPOSS nor the other CyPOSS copolymers display any transition in this region. This phenomenon can be explicable in terms of melting of the CyPOSS lamellar crystallites. Another possible reason can be the glass transition of the polymer chains bond to the lamellar structure, which in principle could have a higher Tg because the hindering effect on the polymer motion constituted by the POSS presence [Lee05].

Increasing even more the content of CyPOSS leads to an apparent decrease of the semicrystalline character of the X-ray patterns. For example, for the case of MMA-co-6.4% CyPOSS-INSA copolymers, the WAXS patterns presents essentially two halos centred at 2Ω~8° and 18°. This phenomenon could be surprising considering the high crystallinity of the neat CyPOSS. On the other hand, the crystallization of CyPOSS in the copolymers with high POSS content may be hindered by the increase in the viscosity of the copolymers due to the POSS presence [Kop04, Kop05]. This increase in viscosity in principle could make harder for the POSS to re-arrange in the raftlike structure shown for the MMA-co-3.9% CyPOSS-INSA. This decrease in the crystalline nature of the nanostructures formed by the CyPOSS is in good agreement with the TEM results shown in figure 4-12:
As can be seen in figure 4-12 (A), (B) and (C), the morphology of this copolymer is not homogenous, showing clearly two distinct regions. In figure 4-12 (A) are visible some aggregates of ~500 nm in size and these aggregates represent the second region inside the material. Once zoomed on it, this second region, especially visible in the centre of the figure 4-12 (C) and in figure 4-12 (D), presents again a needle-like morphology, as the MMA-co-1.9% CyPOSS-INSA copolymer. The needles, as shown in figure 4-12 (D), do not seem to arrange in a lamellar or raftlike structure as regularly as in the MMA-co-3.9% CyPOSS-INSA. Furthermore, the first region, which can be reasonably supposed to be PMMA-rich, looks spotted (see figure 4-12 (B)), as if there was a lack of homogeneity of the material at a scale lower than the resolution of the TEM. This in turn can be due to the presence of CyPOSS aggregates in this material. This is a very difficult structure to resolve, even if an indirect indication of its existence may come from the visual appearance of the WAXS pattern for MMA-co-6.4% CyPOSS-INSA, which is very different from the PMMA-INSA one. Therefore, considering that the WAXS analysis has been carried out in the region...
corresponding to interaction distances from 3.5 to 17.5 Å, it can qualitatively be stated that the CyPOSS may form nanostructures with the characteristic size in this Å range, which corresponds to the molecular level.

Looking to the WAXS pattern of MMA-co-8.8% CyPOSS-INSA in figure 4-4 it can be seen that it looks very similar to the one of the MMA-co-6.4% CyPOSS-INSA. The TEM micrographs, reported in figure 4-13, are also very similar to the ones of MMA-co-6.4% CyPOSS-INSA:

In figure 4-13 (A) can clearly be seen that the few aggregates in figure 4-12 (A) are not present anymore. At their place it is possible to find some cylindrical features. Zooming on one of them, as in figure 4-13 (D), reveals again the presence of needle-like structure, likely to be due to the piling of CyPOSS, as in the case of MMA-co-1.8% CyPOSS-INSA. In this case the needles, with a size range of 100-200 nm, are less in number than in MMA-co-6.4% CyPOSS-INSA (see figure 4-12 (D)) and furthermore even the small regularity in their
arrangement present in MMA-co-6.4% CyPOSS-INSA seems to be not present anymore. The so-called PMMA-rich region is more spotted than in the MMA-co-6.4% CyPOSS-INSA, and this can be again an indication of the presence of molecular structures inside the materials.

It is to be noted that DSC analysis on the MMA-co-6.4% CyPOSS-INSA and MMA-co-8.8% CyPOSS-INSA copolymers did not reveal any other transition than the glass transition of the copolymers. This is in agreement with the results from WAXS, which did not show any crystallinity, and therefore may lead to conclude that the second transition viewed in the case of the MMA-co-3.9% CyPOSS-INSA is effectively the melting of the CyPOSS raftlike crystals.

Summarising the results shown in this section, it can be concluded that the nanostructures present in the MMA-co-CyPOSS-copolymers are very dependent on the POSS concentration. A critical composition for the existence of a raftlike nanostructure can be found to be as high as 3.9% CyPOSS in the copolymers. In fact, at CyPOSS concentration both lower and higher, the POSS form only one-dimensional nanostructure (the needles) showing few or no lamellar structure. The POSS aggregation in an ordered structure is driven by their partial immiscibility inside the PMMA system and it is hindered by the increase in the viscosity due to the POSS presence. The coexistence of these two phenomena may produce the variation in the structures with the POSS concentration. A possible explanation could be the following: at low concentration, the POSS-rich chains are immiscible in the PMMA-rich region, which leads to the aggregation of POSS as needles. Their amount in the MMA-co-1.8% CyPOSS-INSA copolymers is not enough for them to arrange in a raftlike structure. At a concentration of 3.9% CyPOSS, the CyPOSS-rich chains are still not miscible in the PMMA-rich region, but their concentration is high enough for them to arrange in a lamellar structure. Increasing more the POSS molar percentage, the CyPOSS-rich copolymer chains are still not miscible in the PMMA-rich region, but the probable increase in viscosity due to their presence hinders their arrangement in a lamellar structure. The POSS could therefore form aggregates below the TEM resolution, which can be the reason for the spottiness of the TEM micrograph for MMA-co-6.4% CyPOSS-INSA and MMA-co-8.8% CyPOSS-INSA.
4.2.2 Structure-Morphology of MMA-co-iBuPOSS-INSA

In figure 4-14 are reported the WAXS patterns of the various MMA-co-iBuPOSS-INSA copolymers:

![WAXS patterns of MMA-co-iBuPOSS-INSA copolymers. The POSS molar percentages are reported on the right of the figure. The data are offset for clarity.](image)

Despite the high crystallinity of neat iBuPOSS, all the MMA-co-iBuPOSS-INSA copolymers present fully amorphous patterns. The WAXS pattern for the lowest iBuPOSS content (1.9 mol % iBuPOSS) is very similar to the pattern for the copolymer with equivalent CyPOSS content. Above this POSS molar percentage, the WAXS patterns of the two POSS groups differ significantly. The WAXS pattern of the MMA-co-iBuPOSS-INSA for iBuPOSS molar percentage of 4.4% displays two broad halos centred at 2θ~8° and ~18°, while the pattern of the MMA-co-8.9% iBuPOSS-INSA exhibits mostly the halo at 2θ~8° and a very small halo at 18°. Therefore, there is no hint of the existence of a crystalline phase, which, according to certain authors [Con04], is on its own a clear indication of POSS aggregation. On the other hand, the shift of the halo of PMMA-INSA at 2θ~14° to higher angles (i.e. 2θ~18° for the MMA-co-1.9% iBuPOSS-INSA) may indicate a re-arrangement of the polymer chains induced by the POSS presence, likely associated to a change of the interactions at the Van der Waals distance [Mil84].

It could therefore be assumed that the iBuPOSS are well dispersed in the MMA-co-iBuPOSS-INSA copolymers, maybe even at the nanometre level. This assumption is in good agreement with the TEM pictures shown in figure 4-15, 4-15 and 4-16:
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Figure 4-15 TEM micrographs of MMA-co-1.9% iBuPOSS-INSA at various magnifications.

Figure 4-16 TEM micrographs of MMA-co-4.4% iBuPOSS-INSA at various magnifications.
The TEM pictures of all the MMA-co-iBuPOSS-INSA do not show any POSS aggregation, even at very high magnification. The nano-features visible at high magnification are very likely to be artefacts of the TEM analysis. Furthermore, even AFM revealed a very homogenous structure at a nm level, as shown in figure 4-18:

The scale is indicated.
As can be clearly seen, the AFM phase image of the fracture surface of MMA-co-4.4% iBuPOSS copolymers is featureless. The scale used is the same of the figure 4-9, where the MMA-co-3.9% CyPOSS-INS displays clear features with high phase contrast.

To better see this difference in between CyPOSS and iBuPOSS copolymers with similar POSS content it is also possible to compare the section analysis in figure 4-10 and 4-19:

![Section Analysis](image)

Figure 4-19 Section analysis of the phase image in figure 4-18.

The section analysis reveals no particularly distinctive features at all. Therefore it can be concluded that the iBuPOSS are likely to be dispersed at a molecular level in the MMA-co-iBuPOSS-INS copolymers. The extent of this dispersion is the same for all the compositions, even in the case of high POSS molar percentage.
4.2.3 Structure-Morphology of MMA-co-iBuPOSS-Aldrich

In figure 4-20 are reported the WAXS patterns of the various MMA-co-iBuPOSS-Aldrich copolymers:

![WAXS patterns of MMA-co-iBuPOSS-Aldrich copolymers](image)

Figure 4-20 WAXS patterns of MMA-co-iBuPOSS-Aldrich copolymers. The POSS molar percentages are reported on the right of the figure. The data are offset for clarity.

From WAXS patterns, MMA-co-iBuPOSS-Aldrich copolymers are amorphous and they look very similar to the ones of MMA-co-iBuPOSS-INSA. The MMA-co-1.5% iBuPOSS-Aldrich copolymer presents a WAXS pattern very similar to the one of PMMA. The MMA-co-2.9% iBuPOSS-Aldrich shows a broad halo at $2\theta \approx 8^\circ$ and an apparent superimposition of several other halos for $2\theta$ higher than $10^\circ$. The MMA-co-9.6 % iBuPOSS-Aldrich resembles closely the MMA-co-1.9% iBuPOSS-INSA, with the presence of two broad halos centred at $2\theta \approx 8^\circ$ and $18^\circ$.

Despite the close resemblance among the WAXS patterns of the MMA-co-iBuPOSS-INSA and MMA-co-iBuPOSS-Aldrich there are remarkable differences in the morphologies of the two families of copolymers. In fact, when the MMA-co-iBuPOSS-INSA displayed no features at a nm level, the MMA-co-iBuPOSS-Aldrich present the so-called “salami morphology” [Bra98, Sch03, Sch96], as can be seen in figure 4-21, 4-21 and 4-22:
Chapter IV MMA-co-POSS copolymers

Figure 4-21 TEM micrographs of MMA-co-1.5% iBuPOSS-Aldrich at various magnifications.

Figure 4-22 TEM micrographs of MMA-co-2.9% iBuPOSS-Aldrich at various magnifications.
The three copolymers display very similar morphologies, with the presence of three distinct regions, as in the MMA-co-CyPOSS-INSA, but with the important difference of having salami morphologies instead of raftlike ones. The presence of these features should be somehow connected with the synthesis protocol, but unfortunately no information are available from the producer about this aspect of the material preparation. It can be simply remembered that in the literature are reported two procedures to synthesize POSS-MMA copolymers, the free radical polymerization or the ATRP (atom transfer radical polymerization). In the light that the free radical polymerization has been used to synthesize the MMA-co-iBuPOSS-INSA copolymers (which do not display any nanostructuration at the TEM resolution), it could be supposed that ATRP was used to synthesize the MMA-co-iBuPOSS-Aldrich copolymers. Allegedly random copolymers, the MMA-co-iBuPOSS-Aldrich copolymers could be block copolymer as well because the ATRP can be used either for random, graft and block copolymerization [Lee03]. Supposing that the MMA-co-iBuPOSS-Aldrich copolymers are random, it could be possible to propose the following explanation of the phenomenon of POSS arrangement in salami morphologies. Salami morphologies are formed usually during the “grafting-from” polymerization of a monomer B in a solution of copolymer PA/PB, with A and B general monomers [Sch03]. During the polymerization of B there is the phase-separation of the domains inside the three component
system. Usually, PB is an elastomeric polymer while PA is a more rigid thermoplastic polymer. In a common case, PA is represented by polystyrene and PB is polybutadiene [Bra98, Sch96]. A clear visualization of the salami morphologies can be found in figure 4-24:

![Figure 4-24 TEM micrograph of stained sample of high-impact polystyrene. The polybutadiene is in black and the polystyrene is in white [Sch03].](image)

The detailed description of this phenomenon is beyond the scope of this manuscript, but the reader may find it in Schierholz et al. [Sch03]. In this case it is possible to suppose that PA is represented by PMMA and PB by the Poly-iBuPOSS. The iBuPOSS is less reactive than the MMA, as already stated, therefore it is possible that PMMA chains are formed first, then PMMA-POSS chains afterwards. In the light also that in all the figures 4-21 – 4-23 the POSS (not stained, because the contrast was enough) and the butadiene (stained) are shown in black, it could be supposed that the situation would be as if the iBuPOSS was polymerizing in PMMA-POSS environment, like butadiene does in PS/PB system. Therefore the formation of the salami morphologies would be a direct (and automatical) effect of the phase separation of iBuPOSS due to change of their miscibility in the solution of PMMA-iBuPOSS during the iBuPOSS polymerization in the MMA-co-iBuPOSS solution, as described by Schierholz et al. [Sch03] for the butadiene in PS/PB solution.
It is not clear why this phenomenon does not happen when iBuPOSS and MMA are randomly copolymerized with a free radical reaction. It could be that the probability of “grafting-from” in free radical polymerization is lower than in ATRP, or that the concentrations of the reactive mixtures were different for the two families of copolymers. However, an explanation of the different morphologies of MMA-co-iBuPOSS-INSA and MMA-co-iBuPOSS-Aldrich copolymers can not be complete and precise without a precise knowledge of the synthesis and purification procedure for the commercial products.

Giving a glimpse to the morphologies present in the three family of copolymers analysed, it is worthy to note that, for similar concentrations, the POSS can be present in the copolymers either as finely dispersed objects (MMA-co-iBuPOSS-INSA) either as crystalline (MMA-co-CyPOSS-INSA) or non-crystalline aggregates (MMA-co-iBuPOSS-Aldrich).

4.3 Thermal properties of MMA-co-POSS copolymers

As shown in chapter 1, thermal properties in POSS-based nanocomposites and copolymers have been widely investigated. Usually POSS influences significantly the glass transition temperature of the pristine polymer and the degradation-oxidation resistance, as shown in §1.4.1. In this section the influence of the POSS on the glass-transition temperatures of the MMA-co-POSS copolymers and on the pyrolysis-oxidation resistance will be discussed, with a particular attention on the effect of the organic groups borne by the POSS and on the morphologies-structure of the POSS (along with their dispersion) in the copolymers.

4.3.1 Glass transition temperature of the MMA-co-POSS copolymers

The glass transition temperatures \(T_g\) have been measured with scanning differential calorimeter (DSC), with a scan rate of 10°K/min under nitrogen. A preliminary heating-cooling step (respectively 20°K/min-5°K/min) has been used to remove the effect of physical ageing on the glass transition [Str78, Van97]. The results of this analysis are shown in figure 4-25:
The three families of copolymers display different influence on the glass transition temperatures of the copolymers. The CyPOSS tend to increase the Tg linearly with respect to the POSS content, up to an increase of 25°C for MMA-co-8.8% CyPOSS-INSA. The MMA-co-iBuPOSS-INSA have a Tg rather similar to the of neat PMMA-INSA, with the remarkable exception of MMA-co-8.9% iBuPOSS-INSA which shows a decrease of 10°C of the Tg. On the other hand, the commercial MMA-co-iBuPOSS-Aldrich displays a very notable decrease of 16°C even at the lowest POSS content, while at a POSS molar percentage of 9.6% the Tg is decreased of 37°C with respect to the neat PMMA-INSA.

The reasons of the increase of the Tg due to the CyPOSS may be due to two different factors: the rigidity of the cyclohexyl groups and the presence of needles and raftlike morphologies. The first two factors, especially the first one, pose physical hindrance to the movement of the polymer chains, as shown widely in chapter 1. This physical hindrance, due to the bulkiness of the cubic cage and the rigidity of the organic cyclohexyl groups, reduces the motion of the polymer chains and therefore increase the values of the glass transition temperature. The morphologies may play a minor role in slowing down the motion of the copolymers chains, acting as potential anchor points for the polymer bound to the needle-raftlikes.
The MMA-co-iBuPOSS-INSA have no or slight variation of the Tg up to 4.4mol %, then the Tg for the MMA-co-8.9% iBuPOSS-INSA drops to 97°C. Any consideration about the influence of the morphology on the glass transition temperatures should just take into account the very fine dispersion of the POSS into the copolymers. Therefore it could be reasonably supposed that their effect is present effectively in a similar amount on the most part of the chains. The hindrance of the POSS cubic cage to the physical movement of the polymer chain can be overcome by the flexibility of the isobutyl groups. The effect of side groups in methacrylate copolymers has been early investigated in the literature [Kar68, Spe92, Van97]. Generally, isobutyl-methacrylate polymers have a Tg lower than methyl-methacrylate polymers which show a Tg similar to cyclohexyl-methacrylate polymers. It could be that the hindrance effect is predominant for POSS percentage up to 4.4%, while the flexibility of the isobutyl plays a bigger role for high POSS content, when the isobutyl groups contribute effectively for 20% of the weight of the total copolymer.

Using molecular modelling, Bizet [Biz04] found the very same trend of the Tg’s with the POSS type and concentration that it has been just shown here as issued experimentally. Bizet justified this difference in the influence of the POSS on the Tg’s of the copolymers as due to (I) the increase in the free volume due to the POSS presence (valid for both the POSS types) and (II) the flexibility of the isobutyl groups, which enhances the chain cooperative motion, also with respect to the more rigid cyclohexyl groups.

This difference in between the effects on the Tg of CyPOSS and iBuPOSS is also similar to what Haddad et al. reported for the copolymerization of POSS with styrene [Had02].

A completely different situation happens in the MMA-co-iBuPOSS-Aldrich for which the Tg massively decreases at every POSS concentration. The explanation of this decrease is not clear. It could be that the POSS arrangement in the salami morphologies shown in the section 4.2.4 decrease the POSS-polymer interactions [Jeo00, Mat99], as well as the polymer-polymer interactions which are supposed to decrease in most of the POSS-containing system [Li01a, Xu02a, Xu02]. Therefore, because of the arrangement of the POSS in the salami morphologies, the reduction of polymer-polymer interactions is not counterbalanced by the establishment of POSS-polymer interactions, like in the MMA-co-CyPOSS-INSA or the MMA-co-iBuPOSS-INSA.
4.3.2 Thermogravimetric analysis of the MMA-co-POSS copolymers

The purpose of this research is to study the effect of the POSS on the degradation-oxidation behaviour of POSS-MMA copolymers, always with respect to the neat PMMA polymer.

The weight loss of PMMA [Fer03, Hir85, Kas85, Man86, Man89a, Man91, Man88, Man89b] is the final result of a complex degradation process consisting of chain initiation by random scission and disproportionation reactions, plus the transport of the decomposition products through softened PMMA from the inside of the sample to the outside.

From a chemical point of view it could be considered that there are two factors which can control the weight loss in PMMA: (1) the chemical process of degradation and (2) the transport of the degradation products (by bubbles and diffusion) in softened PMMA. According to certain authors [Hir85], the second factor is preponderant for thermogravimetric analysis with a heating rate above 3°K/min. In the light that the thermogravimetric analysis in this research has been performed at 10°K/min, the results in this manuscript will be discussed considering the second factor as predominant in controlling the degradation process.

The TGA-DTG results in an inert atmosphere for PMMA are displayed in figure 4-26:

![Figure 4-26](image_url) TGA (axis on the left) and DTG (axis on the right) results for thermal degradation of PMMA-INSA under He at 10°K/min. The numbers in the box indicate the 4-step mechanisms involved in the degradation.
The degradation of PMMA in an inert atmosphere consist of four steps, indicated in figure 4-26 by the number in the boxes, which have been assigned [Fer03, Kas85, Kas86, Kas02, Man89a, Man91, Man88, Man89b] to the following phenomena:

1) T~170-180°C : initiated by scission of head-to-head linkages, which are less stable than C=C double bonds in the polymer chain backbone. Any reaction able to generate free radicals is able to degrade the PMMA, and the source of these radicals are usually impurities and oligomers [Fer03,Man89a,Man89b].

2 and 3) T~270-300°C : initiated by scission at unsaturated ends (results of termination by disproportionation) involving a homolytic scission β to the vinyl group. The presence of weak H-H bonds promotes facile homolytic scission of the chain[ Fer03].

4) T~370°C : random scissions within the polymer chains.

The final result is a mix of depolymerization, homolytic and random scissions in the main chain. It should be noted that the most important steps are the (1) and the (4). In fact, the step (1) happens in the temperature range (160°C-240°C) at which usually the PMMA is processed [Bra03], while the step (4) involves the biggest weight loss of the whole degradation process (final decomposition temperature). The attention therefore will be focused on the effect of POSS on the temperature of the steps (1) and (4) and on the char yield.

In figure 4-27 and 4-27 are shown the effects of the POSS on the temperature of the degradation step (1), respectively, in helium (degradation) and in air (oxidation). This temperature, which corresponds to the maximum weight loss rate in the step (1), is indicated by the common parameter $T_5$ (defined at the temperature at which 5% of the original polymer weight is lost):
As seen in the figures 4-26 and 4-27, both in air and in inert atmosphere the POSS tend to increase the $T_5$ temperature, albeit not with a linear relation with the POSS content, as
observed already in the literature [Eis02b, Kim02, Zhe01c, Zhe02b]. Therefore generally POSS tend to shift to higher temperatures this first step of degradation, in this way stabilizing the PMMA. A possible reason can be that the POSS may facilitate the recombination of the free radicals created during the degradation, as observed by Zheng et al. [Zhe01c] in POSS-polyolefine copolymers.

The MMA-co-iBuPOSS-INSa copolymers display a relatively uniform trend, in contrast with the other systems. This can be due to the more homogenous morphology present in these copolymers with respect to the lamellar or salami features of the other two families. As already stated, the first step of degradation is connected with the generation-recombination of free radicals. It is likely that the morphology influences this generation-recombination of free radicals by simple trapping them. Therefore different morphologies can have a wide influence on the onset of the degradation via changing the radicals generation-recombination. So, on the one hand, the trend of the $T_5$ for the MMA-co-CyPOSS-INSa and MMA-co-iBuPOSS-Aldrich is probably influenced also by the different morphologies displayed by these materials. On the other hand, the very homogenous morphology of the MMA-co-iBuPOSS-INSa copolymers, as shown in the § 4.2.3, makes more uniform the positive influence of the iBuPOSS on the increase of the $T_5$.

It can be noted that this increase in the $T_5$ temperature is more remarkable for TGA analysis in inert atmosphere than in air. For example, in the case of MMA-co-8.8%CyPOSS-INSa, the maximum increase of the $T_5$ is of ~70°C in inert atmosphere and ~11°C in air. A possible explanation could be that the effect of oxygen on the step (1) simply overcomes any possible influence of POSS on the mechanisms connected to oxidation resistance at this temperature range (160-240°C). It has been observed, in fact, that the $O_2$ may likely suppress the end initiation process as a result of some $O_2$-induced modification of the unsaturated C=C at one end of the polymeric chain [Hir85].

Another important parameter obtainable from the DTG-TGA analysis is the maximum weight loss temperature, $T_{\text{max}}$, which is defined as the peak on the DTG curve. The results for the $T_{\text{max}}$ in inert atmosphere are reported in figure 4-29:
The POSS tend in general to increase the maximum weight loss temperature during degradation in inert atmosphere, and this increase is larger for the MMA-co-iBuPOSS-Aldrich copolymers at high POSS content. This increase is somehow related to the recombination of the free radicals generated during the degradation process, which delays the random scission in the polymer chains [Kas85, Kas86, Kas02]. On the other hand, it is unclear why this increase is more linear and more marked for the MMA-co-iBuPOSS-Aldrich than for the other two families of copolymers.

A different situation happens when the $T_{\text{max}}$ is analyzed in oxidation experiments. The DTG curve (from which the $T_{\text{max}}$ is usually determined) relative to the PMMA-INSA shows clearly three peaks, among which the highest one (corresponding to $T_{\text{max}}$-PMMA-INSA) is at $\sim$365°C. Generally, the POSS presence complicates the trend of these curves, causing the apparition of more DTG peaks, the shifting of the highest one to lower temperatures as well as a general broadening of the peaks, as can be seen in figure 4-30 for the MMA-co-CyPOSS-INSA copolymers:
Figure 4-30 DTG curves of MMA-co-CyPOSS-INSA copolymers. Test in air at 10°K/min.

It is difficult therefore determining which values the $T_{\text{max}}$ assume in the oxidation experiments. Apparently there is the coincidence of more degradation mechanism at the same time, evidenced by the presence of more DTG peaks along with the broadening of most of them. It should be noted that the POSS form a silica layer during the degradation in air. This layer may trap the degradation products (as will be shown later in this section by the residual weight) thus perhaps giving rise to the coexistence of more than one of the four mechanisms shown above for the PMMA degradation.

The third parameter studied in the thermogravimetric analysis is the char yield. As char yield is identified the residual weight percentage after the completion of the test, i.e. at 750°C. According to Van Krevelen, the char yield is an important parameter to evaluate the flame resistance: the higher the char yield (especially in inert atmosphere), the higher the flame resistance [Van97, Van75]. It is also widely accepted that the char play a role of protection towards degradation [Aja03, Kas02, Ni04]. In PMMA this is even more important because the formation of a char can help to reduce or prevent the transport phenomena of the decomposition products from the inside of the sample to the outside [Kas02]. The POSS in this case can be a sort of ideal material for flame-resistant polymeric materials [Li01a] because their inorganic core supplies a good thermal resistance while the organic groups ensure the solubility in the reactive mixtures and the tailoring of the dispersions in the final hybrid copolymers.
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The char yields for the three families of copolymers under helium or air are displayed in figure 4-31 and 4-32:

**Figure 4-31** Char Yield of the various POSS-MMA copolymers as a function of POSS molar percentages: MMA-co-CyPOSS-INS A (■ ■ ■), MMA-co-iBuPOSS-INS A (● ● ●) and MMA-co-iBuPOSS-Aldrich (▲ ▲ ▲). Test in He at 10°K/min.

**Figure 4-32** Char Yield of the various POSS-MMA copolymers as a function of POSS molar percentages: MMA-co-CyPOSS-INS A (■ ■ ■), MMA-co-iBuPOSS-INS A (● ● ●) and MMA-co-iBuPOSS-Aldrich (▲ ▲ ▲). Test in air at 10°K/min.
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To better discuss these data, they will be firstly compared to the ones of the neat POSS, subsequently an explanation of the different mechanisms influencing the char yield in the different copolymers will be proposed.

It is worthy to resume here the most important features of the char yield of the POSS during degradation or oxidation analysis, already presented in detail in Chapter 2. The CyPOSS leaves a residue of 11% in He and of 42% (which is equal to the theoretical value for the complete conversion of (SiO\(_{1.5}\)) to silica (SiO\(_2\)), while the iBuPOSS do not leave any residue under He (complete sublimation) and under air they give as char yield 36.5% (in contrast with the theoretical one of 50.9% for the complete transformation of all the inorganic cages to silica). In the table 4-2 the theoretical (due to the complete trasformation of the cubic cage in silica) and experimental char yield are compared for all the copolymers.

Table 4-2 Comparison between experimental and theoretical Char Yields for MMA-co-POSS copolymers.

<table>
<thead>
<tr>
<th>POSS molar percentage in the copolymers</th>
<th>POSS mass fraction in the copolymers</th>
<th>Char Yield Theoretical He %</th>
<th>Char Yield Real He %</th>
<th>Char Yield Theoretical air %</th>
<th>Char Yield Real air %</th>
<th>Char Yield Theoretical air calculated with Char Yield air of iBuPOSS = 36.5%</th>
</tr>
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<tbody>
<tr>
<td>PMMA-INSA</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MMA-co-CyPOSS-INSA</td>
<td>1.8</td>
<td>17.1</td>
<td>1.9</td>
<td>7.0</td>
<td>7.2</td>
<td>8.2</td>
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<tr>
<td></td>
<td>3.9</td>
<td>31.3</td>
<td>3.4</td>
<td>7.1</td>
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<td>14.3</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>43.5</td>
<td>4.8</td>
<td>6.1</td>
<td>18.3</td>
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<td>5.7</td>
<td>5.9</td>
<td>21.9</td>
<td>24.4</td>
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<tr>
<td>CyPOSS</td>
<td>100.0</td>
<td>100.0</td>
<td>-</td>
<td>11.0</td>
<td>42.0</td>
<td>42.0</td>
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<td>15.4</td>
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<td>7.9</td>
<td>6.2</td>
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<td>24.4</td>
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<td>0.4</td>
<td>6.4</td>
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</tr>
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<td></td>
<td>9.6</td>
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<td>0.0</td>
<td>2.4</td>
<td>25.5</td>
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</tr>
<tr>
<td>iBuPOSS</td>
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<td>100.0</td>
<td>-</td>
<td>0.0</td>
<td>50.9</td>
<td>36.5</td>
</tr>
</tbody>
</table>

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The theoretical char yields of the CyPOSS-copolymers have been calculated using as basis the values of 11% (in He) and 42% (in air). For the CyPOSS-copolymers it can be noted that the experimental char yields, both in He and in air, are always higher than the theoretical ones. This deviation can be due to the entrapment of polymer into the needle-lamellar morphologies. In fact the transport phenomena can be in principle slowed down by the persistence of an inorganic phase inside the materials even at high temperature, as shown in Chapter 1 for other POSS-polymer systems. Besides, in the oxidation tests, the char yield increases with the POSS content, as can be logic considering the conversion of the inorganic cage to silica. It should be remembered that this inorganic phase will be effectively a silica layer in the case of POSS-copolymers oxidation, and, when this layer is homogenous, it can act as a shield to the further degradation of the copolymer both stopping the degradation products to “fly away” and reducing the oxidation effect of the air on the copolymers.

The char yields for thermal degradation under inert atmosphere of both groups of iBuPOSS copolymers are higher than the value obtained for the neat iBuPOSS, equal to 0%. A possible explanation could be that part of the MMA, bond to the iBuPOSS, is trapped inside the sample, therefore creating a char having the general formula $C_n(SiO_{1.5})_m$ [Man96].

For the char yields of iBuPOSS-copolymers in air it has been necessary to take into account the differences in the theoretical and experimental values found for the neat iBuPOSS. Therefore the last column in table 4-2 reports the calculation made considering as a neat iBuPOSS char yield the value of 36.5%, when in the column “Char Yield Theoretical air %” are reported the results for the same calculations using 50.9% as char yield of the neat iBuPOSS in air. It can be therefore seen that the experimental char yields are always comprized in between the two theoretical values. A possible explanation of this may be that more POSS are converted to silica in the copolymers than in the neat iBuPOSS. A more logical reason could be the entrapment of part of the copolymers inside the silica layer formed. To better understand the origin of this difference in between experimental and theoretical values it could be useful to know the composition of the char, for instance using the elemental analysis.

The MMA-co-iBuPOSS-INSA copolymers display generally a better degradation-oxidation char yield than the MMA-co-iBuPOSS-Aldrich for similar POSS content. This can be addressed to the differences in the dispersion among the two families of copolymers. According to Ni et al. [Ni04], the higher the dispersion, the higher the degradation-oxidation
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resistance, thus higher the char yield both in He and in air. Therefore, the very fine dispersion of POSS in the MMA-co-iBuPOSS-INSa copolymers can be the reason of the higher char yields with respect to the MMA-co-iBuPOSS-Aldrich copolymers.

The CyPOSS-copolymers have better char yields than the iBuPOSS copolymers. In this case, the needle-raftlike morphologies are apparently effective in reducing the amount of copolymers loss, probably trapping material in between these nano-features.

4.4 Surface properties of MMA-co-POSS copolymers: Nanoindentation

Nanoindentation has been used to determine the mechanical properties of films of MMA-co-POSS copolymers. The mechanical properties investigated were the Young moduli and the hardness. Nanoindentation has been chosen to investigate the mechanical properties because the very low amount of material requested for such analysis permitted a high number of test on the same sample, this improving the statistics of the mechanical properties. Furthermore, the use of other technique such as DMTA was not feasible because of the low toughness of the copolymers, due to the low molar mass [Pre85].

It is to be noted that, for several reasons, the nanoindentation hardly gives the real values of the hardness and the Young Moduli, giving rather pseudo-values [Aim94, Du01, Mil03, Tsu01]. Therefore in this study it has been preferred to normalise all the data obtained for the copolymers with the value obtained for the PMMA-INSa. In this way it would not be possible to determine the absolute values of hardness and E, but only the influence of POSS on these properties. On the other hand, all the problems connected with the nanoindentation analysis (like tip geometry influence on the final modulus [Du01]) will be simply avoided with the procedure of normalization. Therefore the definitions Pseudo-E normalized and Pseudo-Hardness normalized will be used. The details of the nanoindentation analysis can be found in the Annexes.

The results of the Pseudo-E normalized (Pseudo-Young Moduli normalized) for different copolymers as a function of POSS type and concentration are reported in figure 4-33:

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As can be clearly seen in figure 4-33, the presence of POSS decreases the pseudo-Young moduli of the copolymers with respect to the PMMA-INS. Furthermore, the trend of decrease is very similar for all the POSS-copolymers. The effect of the POSS on the pseudo-E is rather surprising because the POSS influence on the Pseudo-E seems independent both of the particular type of POSS copolymerized with the MMA and of the structure-morphologies originated in the hybrid systems. This is quite peculiar among all the different properties analysed in this research, which shown a clear effect of the structures-morphologies on them.

A possible explanation of this diminution can be found in the molecular simulation analysis performed by Bizet [Biz04]. It was found that the copolymerization of POSS with MMA causes a diminution of the cohesive energy density (CED) of the final copolymers with respect to the neat PMMA-INS. It was shown also that the organic groups borne by the POSS molecules have no influence on the CED of the copolymers, as can be seen in the figure C-15, Chapitre II – partie C - pag. 163 in [Biz04].

In these copolymers the Young modulus is directly proportional to the CED at temperature below the Tg (which was the case for these tests, done at ~25°C when the lowest Tg among the copolymers is of ~70°C, as can be seen in figure 4-25). The CED of a material is due to the presence of intermolecular interactions in the system. Decreasing the intermolecular
interaction means decreasing the CED, that is, in these copolymers, decreasing the Young Moduli.

The question now is why and how the POSS decrease the intermolecular interactions of the MMA-based copolymers?

From a chemical point of view, each hybrid copolymers studied in this research was mostly composed by MMA units. Therefore each consideration should be based on the intermolecular interactions present in the PMMA. The CED of PMMA is mainly ensured by Van der Waals forces, and the hydrogen bonds, due to the carbonyl groups present on the methacrylate arm, play a minor role in it.

The POSS, independently from their organic groups, should in principle give rise to dispersive interactions with the neighbouring atoms, as seen by Bharadwaj et al. [Bha00]. The inorganic cage is logically not supposed to lay any role because the isobutyl and cyclohexyl groups simply shield its effect. So, when the POSS are present as pendent groups in a methacrylate copolymer, they mostly decrease the polar interactions. Also the Van der Waals interactions are decreased by the POSS presence [Biz04], even though it is not so clear the reason of this decrease.

Resuming, the copolymerization of POSS decreases (linearly with POSS content) both the polar and non-polar interactions inside the copolymers, thus decreasing the CED and the Young moduli of the systems, in a fashion independent from the organic groups borne by the POSS. In principle, the lack of an influence of the organic groups on the CED of the copolymers could be logic in the light that the two POSS used have very similar chemical structure, hence they give rise to very similar interactions. This reduction of the Pseudo Young-moduli is proportional to the value of the calculated CED for all the copolymers, as displayed in figure 4-34:
Figure 4-34  Pseudo Young-moduli normalized as a function of the calculated cohesive energy density CED for MMA-co-CyPOSS-INSA (■ — ■), MMA-co-iBuPOSS-INSA (● — ■) and MMA-co-iBuPOSS-Aldrich (▲ — ■). This is indirectly a good proof that the pseudo E for MMA-POSS copolymers can be foreseen by the calculation of the CED.

The pseudo-hardness of the copolymers normalized with respect to PMMA-INSA has been calculated as well. The results are reported in table 4-3:

**Table 4-3** Pseudo-H normalized with respect to the PMMA-INSA as a function of POSS type and concentration.

<table>
<thead>
<tr>
<th>POSS molar percentage in the copolymers</th>
<th>POSS mass fraction in the copolymers</th>
<th>Pseudo-H normalized that of the corresponding matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA-co-CyPOSS-INSA</td>
<td>1.8</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>31.3</td>
</tr>
<tr>
<td>MMA-co-iBuPOSS-INSA</td>
<td>1.9</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td>8.9</td>
<td>48.0</td>
</tr>
<tr>
<td>MMA-co-iBuPOSS-Aldrich</td>
<td>1.5</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>2.9</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>50.0</td>
</tr>
</tbody>
</table>
Like the pseudo-Young Moduli, the POSS decrease in a similar fashion also the pseudo-hardness. This decrease is not linear with the POSS content but its magnitude is similar for all the three families of hybrid copolymers, as it happens for the pseudo-E. This is not particularly surprising in the light that, in principle, the hardness of a polymer-based system is mainly related to the value of E [Van97]. Therefore, any reduction in the pseudo-E should reduce also the hardness, which is the case for this study.

The apparent increase of the hardness, after the lowest value corresponding to ~2% POSS, is not statistically important, and it is probably a “fake” increase due to the high scattering of the hardness experimental values, a re-occurring situation in nanoindentation analysis [Kla01,Mam05a,Mam05b].

It should be remembered that, more than the values of pseudo-E, the pseudo-hardness found have only an indicative character. In fact, despite all the possible precautions taken during the experiments, the determination of the hardness involves an array of details not fully controllable, like the strain-recovery after the indentation [Bri89].

4.5 Conclusions

Two groups of random copolymers based on MMA and two types of monofunctional-POSS, CyPOSS and iBuPOSS, have been synthesized by free radical polymerization and characterized. These two groups of copolymers have been compared with commercially available POSS-MMA random copolymers. POSS molar fraction ranged from 0 to 10% of the total system, hence POSS mass fraction was varying from 0 to ~50%. All the following considerations will be done with respect to the neat PMMA.

CyPOSS based copolymers presented an increase of the molar masses and of the degree of polymerization due probably to the decrease of the termination rate. In the systems based on iBuPOSS the molar masses are only slightly changed and the degree of polymerization increased. It could be that the isobutyl groups do not cause a great diminution of the termination rate because of their lower steric hindrance. The tacticity of POSS copolymers was not varied by the POSS presence. MMA-co-CyPOSS copolymers show generally tri-regions morphology, with the peculiarity of a needle-raftlike morphology. These morphologies change with the POSS content, and the presence of lamellar nanostructures is
maximum for a CyPOSS molar percentage of 3.9 %, as shown by WAXS, TEM, AFM and DSC. The CyPOSS phase separation-aggregation is likely driven by the POSS miscibility in the MMA-POSS copolymers. On the other hand, MMA-co-iBuPOSS-INSA copolymers show a very homogeneous morphology at the resolution of TEM analysis. MMA-co-iBuPOSS-Aldrich copolymers have salami morphology, with features in the range of hundreds of nm, and the nanostructuration of these materials increase with increasing the POSS content.

This phenomenon of self assembling/crystallization of the CyPOSS in the MMA-co-CyPOSS-INSA, which does not happen for the iBuPOSS in the MMA-co-iBuPOSS-INSA copolymers, could be driven by cage-cage association or polymer-POSS phase separation which can be evaluated from the difference between the solubility parameters, δ, of the PMMA, having a polar character, with the non-polar isobutyl and the cyclohexyl groups [Van97] and from cage-cage interactions, which cannot be taken into account in Van Krevelen model [Sta02, Str05].

The presence of CyPOSS in the copolymers increases linearly the Tg’s with respect to the PMMA, up to ~25°C for the MMA-co-8.8% CyPOSS-INSA system. This increase is due to the combined effect of the bulkiness of the cubic cage and the rigidity of the cyclohexyl groups, which, along with the presence of polymer chains bound to the nanostructured needle-raftlike features, hinder the movement of the polymer chains. The effect of iBuPOSS on the Tg’s is very different in between the MMA-co-iBuPOSS-INSA systems (where the Tg was not particularly affected by the POSS presence) and the great drop in commercially available MMA-co-iBuPOSS-Aldrich systems. This decrease can be due both the flexibility of the peripheral isobutyl groups on the POSS cage along with the POSS arrangement in salami features.

Both in degradation and oxidation experiments, the T₅ were increased by the POSS presence, even if not linearly with the POSS content. Analysis of the char yield in the TGA experiments suggests the presence of polymer entrapped by the POSS in the copolymers, both for degradation under inert and oxidizing atmosphere.
Chapter IV MMA-co-POSS copolymers

The mechanical properties pseudo-E and pseudo-Hardness, as seen by nanoindentation measurements, are decreased by the presence of the POSS in the copolymers. Furthermore, the organic groups borne by the POSS do not have any influence in this reduction. The origin of this phenomenon is to be sought after the reduction of the intermolecular interactions inside the copolymers due to the presence of the POSS objects. The decrease in the CED, (calculated by molecular modelling), and hence in the pseudo-E, are in good agreement with molecular simulation studies.

The CyPOSS, copolymerised with the MMA via free radical polymerizations have been nanostructured in a raftlike morphology. This nanostructure can be addressed to be one of the responsible of the increase of the thermal properties noticed in the MMA-co-CyPOSS-INSa with respect to the PMMA-INSa. The reason can be found in the polymer entrapped and constrained in the nearby of the raftlike features. It could be that a higher ordering of the POSS nanoobjects inside the polymer system would lead to a further improvement of the thermal properties. This higher ordering is in principle attainable in an easy way changing the conditions (solvent, concentration, temperature) of the film preparation. Another possibility could be the annealing of the CyPOSS-copolymers films at a temperature slightly above the Tg. In both cases (by solution or by annealing), the idea is to leave higher freedom to the CyPOSS nanoobjects to rearrange to form a more ordered nanostructure by self-assembling/crystallisation.