

ϵ -Caprolactam polymerization in presence of polyhedral oligomeric silsesquioxanes (POSS)

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Abstract

Polyhedral oligomeric silsesquioxanes (POSS) have been covalently linked to polyamide 6 (PA6) chains with the aim of synthesizing hybrid organic/inorganic polymer materials. The synthesis has been achieved by in situ polymerization of ϵ -caprolactam (CL) in presence of increasing amounts of POSS molecules, using two polymerization mechanisms (hydrolytic and anionic). The latter method has been carried out by three different approaches, in order to get PA6 samples characterized by various morphologies and content of structural defects: (i) quasi-adiabatic bulk polymerization; (ii) isothermal bulk polymerization; (iii) quasi-isothermal suspension polymerization. The products obtained have been characterized in term of structure, morphology, thermal properties and molecular mass.

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1. Introduction

Quite recently, polyhedral oligomeric silsesquioxanes have received a great deal of attention [1,2] as reinforcing nanofillers characterized by a nanostructured 3D cage structure to be incorporated in suitable polymer matrices, thus giving rise to either nanocomposites or hybrids. The interest for POSS-based nanostructures has been most often linked to the dramatic improvement of several properties of the polymer matrix, leading to much better performances of the resultant material. If compared to the neat polymer and as a function of POSS type and content, POSS-based polymer materials are characterized by increased glass transition, improved heat distortion and melt strength, significantly increased moduli, decreased thermal conductivity, improved oxidation resistance, reduced flammability, increased permeability to gases.

As is well known, most POSS molecules are characterized by a peculiar cage structure, i.e. by a polyhedral Si–O nanostructured skeleton (general formula $(\text{SiO}_{3/2})_n$), surrounded by several organic groups linked to silicon atoms

by covalent bonds. The interactions of these side groups, which can be either unreactive or chemically reactive, with an organic polymer may result in the nanometric dispersion of POSS into the polymer matrix. Thus, in order to obtain POSS-polymer nanocomposites and hybrids, respectively, POSS molecules can be either physically dispersed in polymer matrices using traditional processing techniques or linked to the polymer chains by direct (co)polymerization (including grafting), via suitably reactive side groups of POSS.

In recent years, POSS molecules have been successfully dispersed or incorporated in various polymers, such as polystyrenics [3], polyacrylics [4], polyurethanes [5], polysiloxanes [6], polyolefins [7], polynorbornenes [8], epoxies [9], etc. while, at least to our knowledge, no attention has been paid so far to aliphatic polyamides as matrices with the exception of a preliminary report by Schiraldi et al. [10]. Our research group, on the basis of the years-long activity in the field of polyamide 6 synthesis and characterization [11,12] has focused the attention on the preparation of polymer nanocomposites and hybrids made of various POSS molecules and polyamide 6 by in situ polymerization of ϵ -caprolactam. The approach we considered was either the dispersion of unreactive POSS molecules in CL or the direct link formation of reactive POSS molecules to PA6 growing chains. CL polymerization

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by two different mechanisms has been carried out. The first one is the well-known hydrolytic polymerization of CL, and has been chosen at first in order to study the physical interactions between several POSS molecules and PA6 in the absence of any chemical reaction between them. Five POSS molecules with different side groups have been finely dispersed in the polyamide matrix by CL mixing with the chosen silsesquioxane followed by lactam polymerization. Scanning electron microscopy (SEM) on the resultant material has investigated the level of dispersion of silsesquioxane in the PA6 matrix, as well as the adhesion between the two phases. Subsequently, the hydrolytic polymerization reaction of CL has also been carried out in the presence of a pre-mixed POSS molecule containing a reactive side group. Aminopropylheptaisobutyl-POSS (POSS-NH₂) has been chosen in this respect, on the basis of the well-known active role of amino groups as chain terminators in CL hydrolytic polymerization.

The second polymerization mechanism considered in the present work has been the anionic polymerization of CL in presence of a reactive POSS molecule. Advantages and disadvantages of CL anionic polymerization have been extensively examined in the aforementioned works of ours [11,12]. Namely, we have found that side reactions, erroneously believed as intrinsically linked to the anionic mechanism and unavoidable, can be minimized by both a careful control of isothermal reaction conditions and very fast polymerization kinetics, thus synthesizing defect-free, high molecular mass PA6 in a few minutes and at relatively low temperatures. Therefore, the aforementioned POSS-NH₂ has been suitably modified to act as the activator (chain initiator) of CL anionic polymerization, resulting in POSS incorporation at one end of each PA6 chain.

A detailed comparison of both polymerization mechanisms in terms of properties of the resultant nanocomposite/hybrid material has been carried out as a function of POSS type and content, also in relation to the operational synthetic parameters. In particular, anionic polymerization of CL has been carried out by three different methods, widely studied by our research group [11,12]: quasi-adiabatic bulk polymerization, isothermal bulk polymerization and quasi-isothermal suspension polymerization. All products have been characterized in terms of polymer molecular mass, crystalline structure and content, thermal stability and solubility parameters.

2. Experimental section

2.1. Materials

ϵ -Caprolactam was kindly supplied by DSM Research, Geleen, The Netherlands; ϵ -aminocaproic acid (ACA, from Fluka), and aminopropylheptaisobutyl-POSS (POSS-NH₂, from Hybrid Plastics) were used as received. A 60% dispersion of sodium hydride (NaH, Aldrich) in mineral oil

was used without further purification. Sodium caprolactamate (NaCL) was prepared in situ by reaction of NaH and CL. Cyclohexylcarbamoilcaprolactam (CCCL) was a laboratory preparation obtained by blocking cyclohexylisocyanate (Fluka) with CL, as previously reported [10]. Heptaisobutyl-propylcarbamoilcaprolactam-POSS (POSS-CL) was a laboratory preparation obtained by the reaction between POSS-NH₂ and carbonylbiscaprolactam (CBC[®], from DSM), as reported below. Polyisobutene 200 (PIB200, from BP Company) was used as received. Octamethyl-POSS, octaphenyl-POSS, octacyclopentyl-POSS, octaisooctyl-POSS, octaisobutyl-POSS (Aldrich) were used as received.

Methanol (Riedel) and petroleum benzene 40–60 (Riedel) were used without further purification. Sulphuric acid 95–97% (Fluka) and 2,2,2 trifluoroethanol (Fluka) were used as received.

2.2. Synthesis of POSS-CL

POSS-CL was synthesized by reacting POSS-NH₂ with excess CBC[®] (Fig. 1) in boiling toluene followed by solvent removal by vacuum distillation. Unreacted CBC and CL were removed by washing with acetonitrile, while POSS-CL and unreacted POSS-NH₂ were separated by extracting POSS-CL with acetone and removing the solvent by vacuum distillation.

2.3. Polymerization runs

2.3.1. Hydrolytic polymerization

Hydrolytic polyamide samples were synthesized at high temperature (270 °C) using an aluminium block heated by electric resistors connected to a rheostat. Mixtures of CL, ACA (initiator) and POSS were introduced into a glass polymerization vessel at room temperature and heated at the polymerization temperature (T_p) by placing the vessel in the aluminium block; typical polymerization time (t_p) was 4 h. At the end of the reaction, the vessel was rapidly cooled to room temperature under a continuous stream of nitrogen. A typical polymerization run (sample BK12) was as follows: 9.70 g of CL, 0.40 g of ACA, 0.50 g of H₂O and 0.485 g of octaisobutyl-POSS were introduced in a 200-ml reactor at room T . Temperature was raised to 100 °C in ca. 1 h under mild N₂ stream. After 1 h at the above T , the reacting system was brought to T_p (270 °C) and kept for 4 h.

2.3.2. Quasi-adiabatic anionic polymerization in bulk

A double walled glass reactor, equipped with mechanical stirrer, inert gas inlet and outlet and thermocouple lodging, was filled with CL and immersed in an oil bath kept at the temperature of 155 °C. NaCL (initiator) was formed in situ by addition of NaH when CL temperature was around 100 °C. Finally, when the temperature of 155 °C was reached, from a reservoir either POSS-CL or CCCL was added as the activator (chain initiator); after a few seconds,

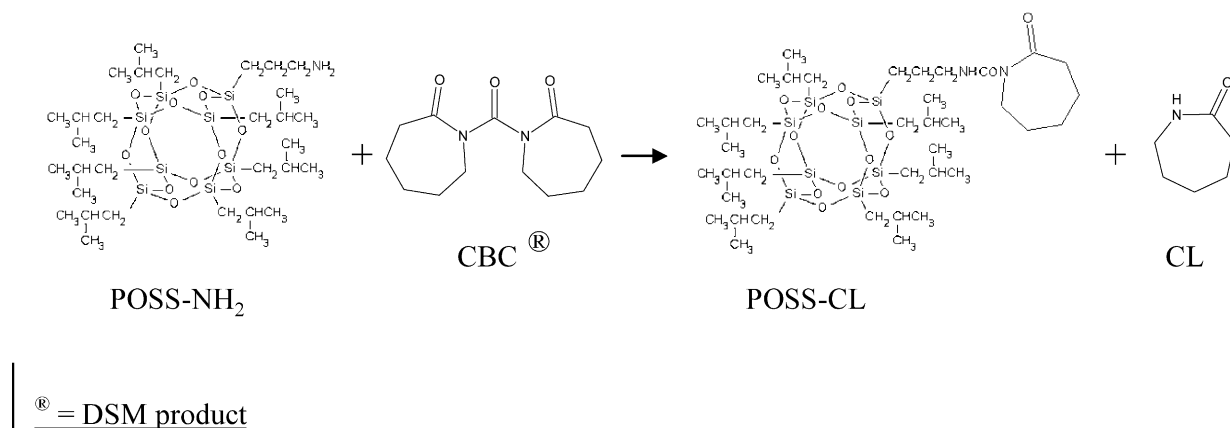


Fig. 1. Scheme for the synthesis of POSS-CL activator.

the temperature raise proved that polymerization started. After reaction completion, generally reached in less than two minutes, the glass vessel was removed from the oil bath and quickly cooled at room temperature. A typical run (AB24) was as follows: 10 g of CL were melt (ca. 70 °C) under vigorous N₂ flux and *T* raised to 95 °C. Then, 0.0212 g of NaH were introduced in the reaction vessel to form NaCl in situ. At 155 °C, 0.54 g of POSS-CL were added. Nitrogen flux enabled to obtain an effective mixing. Almost instantaneously the polymerization started, as evidenced by the sharp *T* raise. After ca. 40 s *T*_{max} was reached (190 °C) and quenching of the reaction mixture was carried out immediately after.

2.3.3. Isothermal anionic polymerization in bulk

Polymerization reactions were carried out in a stainless steel mold, with a disk-shaped die (inner diameter 83 mm; thickness 0.8 mm). The mold, immersed in an oil bath kept at the polymerization temperature of 155 °C, was previously connected with a vacuum pump by using a three-way valve and then filled with the molten reaction mixture (CL + NaCl + CCCL or POSS-CL) under a pressure of dry nitrogen. After 600 s, which is a time more than adequate to reach reaction completion under all chosen conditions [10], the mold was quickly cooled by immersion in a cold water bath. A typical run (AB27) was as follows: the same procedure and amounts described in the quasi-adiabatic run were adopted. Only *T* was kept constant in the reservoir at 95 °C, instead of raising up to 155 °C. The mold was then filled with the above mixture through a 3-way valve connecting mold, reservoir and vacuum pump. After 600 s quenching of the mold was performed.

2.3.4. Anionic suspension polymerization in quasi-isothermal conditions

The polymerization reactions were carried out in a cylindrical glass reactor (volume 250 ml), provided with mechanical stirrer, dry nitrogen inlet and outlet, temperature measurement device and injecting system for the introduction of the reactant mixture (CL + NaCl + CCCL or POSS-

CL). The reactor, filled with 160 g of PIB 200, was immersed in an oil bath thermostated at the polymerization temperature (155 °C). The reactant mixture was prepared in another glass vessel kept at 95 °C (temperature adequate to reach homogeneity of the molten system, but too low to make the polymerization reaction to begin in the time scale used) and injected into the reactor with the aid of a dry nitrogen stream under moderate pressure. After 600 s, the mixture of PIB and PA6 (plus catalytic residues, unreacted CL and low-molecular mass species) was carefully added with petroleum benzine in order to ensure a quick cooling, as well as to dilute the highly viscous suspending medium. A typical run (AB30) was based on: the same procedure and amounts given for the bulk isothermal polymerization.

2.4. Product purification

All solid samples were broken in small pieces and unreacted caprolactam, higher oligomers and other low mass species were removed by Soxhlet extraction with methanol for 48 h. PA6 samples synthesized by suspension polymerization were previously purified from PIB by three subsequent washings with petroleum benzine, followed by Soxhlet extractions with the same solvent for 24 h and with methanol as described above.

2.5. Product characterization

The evaluation of high polymer yield was performed by weighting the samples before and after Soxhlet extraction with methanol. Proper reference to the initial POSS content was made. A Ubbelohde viscometer was used to determine PA6 solution viscosities and evaluate weight average molar masses. The measurements were performed on polymer solutions in H₂SO₄ (*c* = 0.5–1 g/dl) at 20 °C. Crystalline melting temperatures (*T*_m) and degree of crystallinity (*x*_c) of PCL samples were determined by a Mettler differential scanning calorimeter (DSC) Mod. TC 10A. All samples were subjected to the following cycle of three scanning runs: first heating from 0 to 270 °C (at 20 °C/min); cooling

from 270 to 0 °C (at 10 °C/min or at 1 °C/min); second heating from 0 to 270 °C (at 20 °C/min). WAXS intensity profiles were collected by a Philips powder diffractometer Mod. PW1050 (Ni-filtered Cu $K_{\alpha 1}$ radiation). Micrographs of the particles were obtained by a LEO scanning electron microscope (SEM) Mod. stereoscan 440, and by a high resolution JEOL transmission electron microscope (TEM) Mod. JEM-2010.

3. Results and discussion

As mentioned in the Introduction, the first step of the present work consisted in the in situ dispersion of POSS molecules, exempt of reactive side groups, in the PA6 matrix by hydrolytic polymerization of CL. POSS molecules were chosen among the different structures made by Hybrid Plastics Inc. with specific attention to both their solubility parameters and thermal stability. Accordingly, octamethyl-POSS and octaphenyl-POSS were taken in account because of their high T stability (up to 350 °C), while octacyclopentyl-POSS, octaisobutyl-POSS and octaisooctyl-POSS were chosen for their better solubility in some organic solvents (i.e. tetrahydrofuran, chloroform, hexane), thus foreshadowing the possible formation of a homogeneous phase in the reacting mixture during CL polymerization.

Several syntheses have been carried out by introducing different amounts of the above POSS molecules in CL, in order to evaluate the level of filler dispersion in molten caprolactam and in polyamide 6 at the end of polymerization. CL has always been polymerized in the same experimental conditions ($T_p = 280$ °C, $t_p = 4$ h, $p = 1$ atm), using 5% (w/w) of POSS, 4% (w/w) of ACA and 5% (w/w) of water (% referred to CL). All the above POSS molecules have shown no appreciable solubility in the reacting mixture; in particular, octacyclopentyl-POSS and octaisooctyl-POSS gave coarse separation, while octamethyl-POSS, octaphenyl-POSS and octaisobutyl-POSS formed fine and more homogeneous dispersions. Accordingly, only the latter ones, after CL polymerization, were characterized by SEM in order to investigate on dispersion, domain size and adhesion of POSS particles to polymer matrix. Micrographies of the above samples have shown that the particles were homogeneously dispersed in the PA6 matrix, but retained dimensions between 1 and 20 μm with rather poor adhesion to PA6, as evidenced in Fig. 2 for the octaphenyl-POSS/PA6 system. Only the PA6 sample synthesized in presence of octaisobutyl-POSS showed a better dispersion, with smaller POSS domains (ca. 500 nm), as shown in Fig. 3, but no improved adhesion to the PA and matrix.

For comparison, an alternative method of preparation, based on octaisobutyl-POSS/PA6 coprecipitation from a dilute solution in TFE/ CH_2Cl_2 mixture (1:1, v/v) has been tested. SEM micrographies (not shown in the present paper)

evidenced that no reduction in size of the POSS grains was achieved and no better adhesion to PA6 found. Moreover, a less homogeneous dispersion of the silsesquioxane has been observed, as compared to in situ polymerized samples.

These preliminary results suggest that, as expected, for the above systems the interactions between POSS cages and polyamide chains are too weak to favour efficient silsesquioxane dispersion in the polyamide matrix. This effect is obviously related to the highly apolar character of POSS side groups, as compared to the high polarity of PA6 amide groups interlinked by hydrogen bonds.

On this basis, our efforts have been focused on the formation of covalent links between POSS molecules and PA6, i.e. on the preparation of hybrid polymer systems originated from POSS bearing a reactive side group, able to act as either a chain initiator or a chain terminator in PA6 synthesis.

At first, the hydrolytic mechanism of CL polymerization has been attempted in order to make a comparison with the above results. Aminopropylheptaisobutyl-POSS has been chosen among the available POSS structures on the basis of the following considerations: (i) octaisobutyl-POSS already gave better results in terms of its dispersion in PA6, as compared to the other POSS molecules, and (ii) the amino group easily reacts with carboxy end groups during CL polycondensation. Preliminary tests on POSS-NH₂ showed its good solubility in molten caprolactam. The hydrolytic polymerization of CL was carried out as previously described and it is remarkable that the reacting system remained fully homogeneous to the end of polymerization.

Table 1 shows high polymer yield and molecular mass data referred to PA6 hybrids obtained by introducing ca. 5 and 10% (w/w) of POSS-NH₂ as chain terminator. Neat PA6 values are given for comparison. M_w has been calculated by the following equation [13]:

$$[\eta] = 0.51 \times 10^{-3} M_w^{0.74} \quad (1)$$

As can be easily foreseen, the introduction of POSS-NH₂ as chain terminator causes a sharp reduction of PA6 molecular mass and prevents the introduction of higher amounts of POSS-NH₂. Conversely, high polymer yield is unaffected by POSS-NH₂.

On the basis of the above results, activated anionic polymerization of CL has been considered as an alternative

Table 1
Hydrolytic CL polymerization in presence of POSS-NH₂

Sample	POSS-NH ₂ content		High polymer yield% (wt/wt)	$M_w \times 10^{-3}$
	wt%	mol%		
BK1	0	0	87	44
BK12	5	0.6	88	21
BK23	10	1.2	87	11



Fig. 2. Particles of octaphenyl-POSS in PA6 matrix after the in situ hydrolytic polymerization of CL (back scattering image).

synthetic route, with POSS-CL used as fast activator (chain initiator).

As described in Section 2, three different approaches have been tested: quasi-adiabatic bulk polymerization,

isothermal bulk polymerization and quasi-isothermal suspension polymerization.

Quasi-adiabatic bulk polymerization is the most usual technique to carry out anionic CL polymerization [14] as it

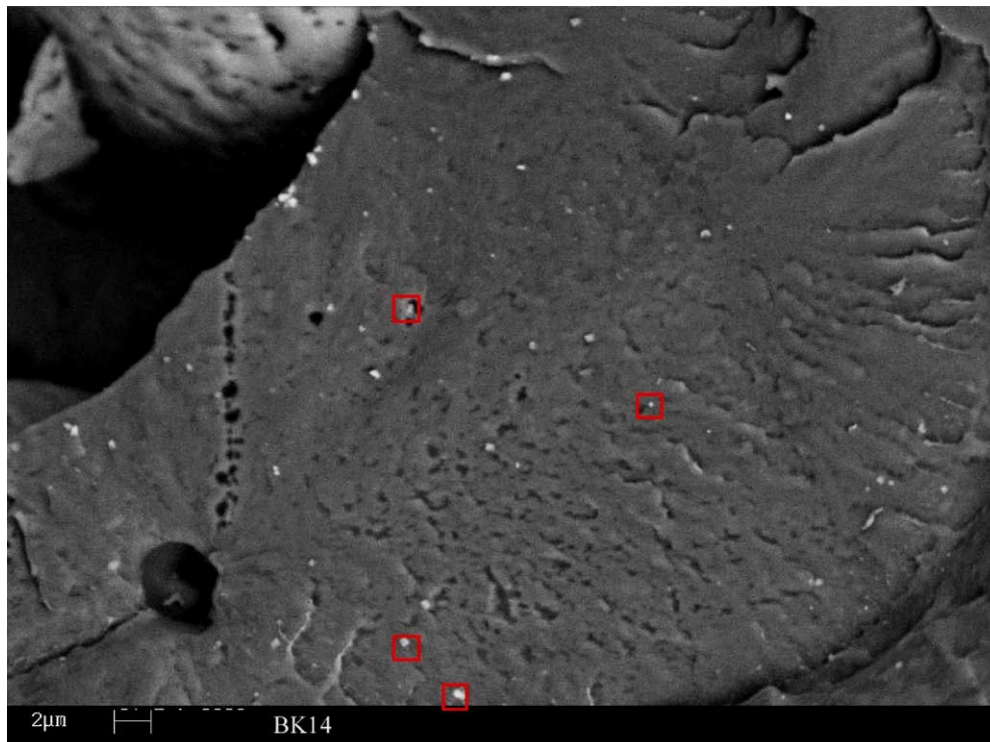


Fig. 3. Particles of octaisobutyl-POSS in PA6 matrix after the in situ hydrolytic polymerization of CL (back scattering image).

is fast and easy to realize; however, it does not allow to easily remove the polymerization heat which is responsible, together with the high basicity of the reaction mixture, for the extensive development of many side reactions [15] causing the introduction of irregular structures in the polyamide chain, a sharp reduction of crystallinity, intensive yellow colour.

As already reported in previous works of ours [11,12], isothermal bulk polymerization and quasi-isothermal suspension polymerization are alternative methods able to effectively dissipate the reaction heat and produce PA6 characterized by a very high structural regularity, because of the complete absence of side reactions.

Table 2 shows high polymer yields and M_w values of anionic PA6 samples synthesized using 0.6, 1.2 and 1.8 mol% of POSS-CL and, as a comparison, the corresponding values of samples made from the same molar concentrations of a classical ultra-fast activator (CCCL). For suspension polymerization high polymer yields are not given, as they could not be accurately evaluated due to the fact that the first Soxhlet extraction with petroleum benzene (in order to remove PIB) also solubilizes a considerable amount of unreacted ϵ -caprolactam.

It can be noticed that the values of high polymer yields are always much higher than those pertaining to the hydrolytic polymerization, although the POSS-CL activator generally gives slightly lower yields than CCCL, in particular in the case of quasi-adiabatic polymerization.

Moreover, no relevant differences in terms of high polymer yield as functions of activator content for both systems can be observed. When using CCCL as activator the above values are also independent of the polymerization technique, while POSS-CL gives more scattered and

generally lower yields when quasi-adiabatic polymerization is adopted.

More relevant differences can be found by comparing the values of molecular mass, obviously affected by the activator content: a higher concentration of activator in the reacting medium leads to a corresponding decrease of PA6 molecular mass. However, even at the highest activator concentration, M_w values can be considered quite acceptable, in particular if compared with the hydrolytic polymerization ones.

Interesting considerations can be done on the M_w data as functions of the polymerization method. The occurrence of side reactions during the quasi-adiabatic polymerization (as said, in the absence of any control on polymerization heat dissipation) is responsible of the many branching points along the polymer chains and justifies the rather high M_w values found, independently of the activator used. Conversely, lower M_w values have been obtained when the removal of the polymerization heat was effective. By comparing isothermal bulk and quasi-isothermal suspension polymerization, a general increase of molecular mass from the bulk to the suspension method is evident and, in our opinion, can be only explained by some partial solubility of activators in the PIB continuous phase, thus causing a change in the relative amounts of initiator, activator and monomer in the suspended particles.

Coming back to the differences in M_w values due to the nature of activator, a few conclusions can be drawn. In fact, higher M_w values coming from POSS-CL suggest, at a first look, a less efficient role of the latter as ultra-fast activator, possibly linked to its size and shape that makes its diffusion in the reacting medium more difficult. However, a more careful consideration of the polymer chain structure and organization, taking in account that each PA6 chains is

Table 2
Fast activated anionic CL polymerization: high polymer yields and molecular masses

Sample	Polymerization method	Activator	Activator content		High polymer yield% (wt/wt)	$M_w \times 10^{-3}$
			wt%	mol%		
AB24	Quasi-adiabatic	POSS-CL	5.4	0.6	93	176
AB25	Quasi-adiabatic	POSS-CL	10.8	1.2	94	58
AB26	Quasi-adiabatic	POSS-CL	16.2	1.8	99	54
AB24b	Quasi-adiabatic	CCCL	1.3	0.6	97	99
AB25b	Quasi-adiabatic	CCCL	2.6	1.2	98	39
AB26b	Quasi-adiabatic	CCCL	3.9	1.8	97	43
AB27	Bulk isothermal	POSS-CL	5.4	0.6	96	82
AB28	Bulk isothermal	POSS-CL	10.8	1.2	96	43
AB29	Bulk isothermal	POSS-CL	16.2	1.8	96	24
AB27b	Bulk isothermal	CCCL	1.3	0.6	98	43
AB28b	Bulk isothermal	CCCL	2.6	1.2	98	20
AB29b	Bulk isothermal	CCCL	3.9	1.8	97	13
AB30	Suspension	POSS-CL	5.4	0.6	–	88
AB31	Suspension	POSS-CL	10.8	1.2	–	60
AB32	Suspension	POSS-CL	16.2	1.8	–	58
AB30b	Suspension	CCCL	1.3	0.6	–	48
AB31b	Suspension	CCCL	2.6	1.2	–	34
AB32b	Suspension	CCCL	3.9	1.8	–	22

characterized by an organic/inorganic end group, suggests the formation of crystalline micro- or nano-aggregates of silsesquioxane as the core and polyamide chains as airy arms. These organizations could partially persist also when the samples apparently seem to be fully solubilized in sulphuric acid, a good solvent for neat polyamide 6 only, not for POSS molecules; aggregation phenomena lead to higher viscosity values. This hypothesis seems to be supported by solubility test performed with both formic acid and trifluoroethanol, each of them a good solvent of PA6. Only partial solubility together with extensive gel formation has been detected, as a proof of the presence of micro-aggregates. A further confirmation is given by the successful use of systems based on two different solvents: dichloromethane, a good solvent of POSS molecules, and trifluoroethanol, a good solvent of neat PA6. When dichloromethane is added to trifluoroethanol in the composition range between 20 and 40% (vol/vol) on the total, the solubility of the POSS-PA6 system notably improves. Indeed, when PA6 samples containing 5 wt% of POSS are tested, a full solubilization is reached, as no gel formation is evident.

X-ray measurements have been performed in order to study the influence of POSS insertion on solid state PA6 organization. For the PA6 samples polymerized in presence of POSS-CL, a general trend has been noticed independently of the polymerization method: the increase of silsesquioxane content always causes a decrease of PA6 crystallinity, as shown in Fig. 4 where WAXD spectra of hybrid samples from CL isothermal bulk polymerization are

given. This effect is not found for PA6 samples made from CCCL, as evidenced by comparing the samples AB27b, AB28b and AB29b in Fig. 5. Moreover, a crystalline peak at 8.2° of 2θ can be noticed in Fig. 4 and attributed to a typical POSS signal. The above observations give further confirmation of the hypothesis that silsesquioxane end groups are prone to organize themselves in crystalline entities and, accordingly, to influence the arrangement of PA6 chains, favouring the formation of more amorphous regions.

A similar crystalline organization of POSS was found in other nanocomposites, such as PE-based copolymers [7]. In the above system, POSS units, incorporated as pendant groups to PE backbone, turned out to aggregate and crystallize as nanocrystals. As found in our case, the presence of POSS nanoparticles lowered the crystallinity of the polymer component.

Semi-quantitative values of the hybrid PA6 crystallinity vs. neat PA6 have been obtained by DSC measurements. The evaluation of both the degree of PA6 crystallinity and the melting point of as-polymerized samples have been obtained from the DSC first heating traces. The experimental data are given in Table 3. The results are in good agreement with the trends of the above X-ray diffractograms: in general, PA6 chains synthesized from the classical fast activator (CCCL) are almost always characterized by higher values of x_c , as compared to samples originated from the new activator (POSS-CL), which show a lower degree of crystallinity, slightly decreasing by increasing POSS content. On the contrary, the polymerization method (adiabatic or isothermal) does not seem to appreciably

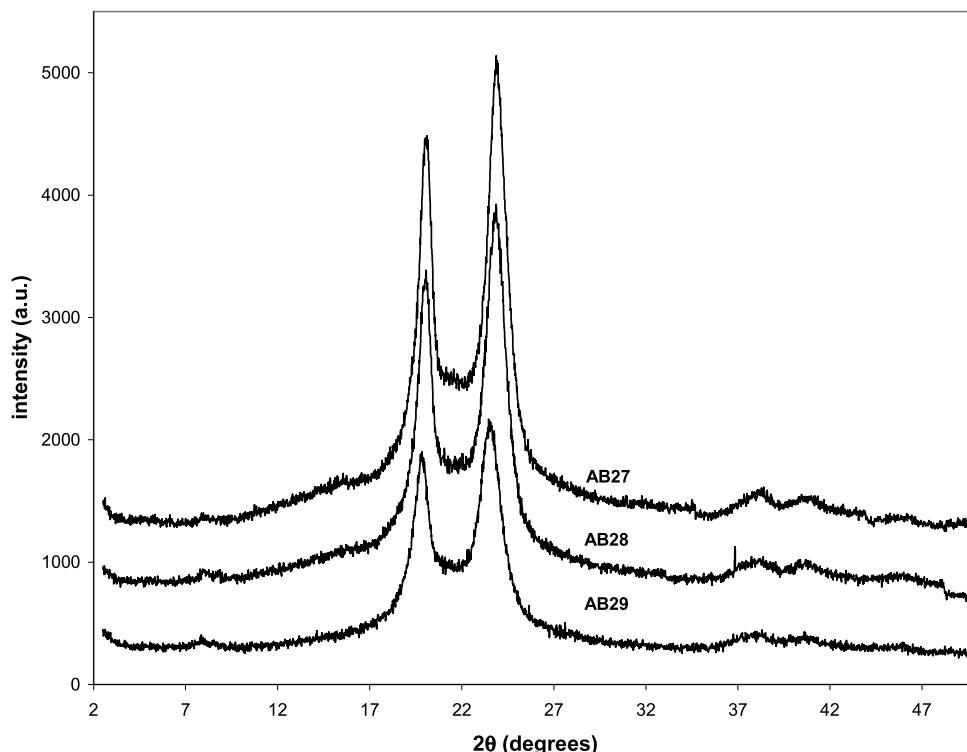


Fig. 4. WAXD intensity profiles of hybrid PA6 samples synthesized from 0.6, 1.2 and 1.8 mol% of POSS-CL (AB27, AB28, AB29, respectively).

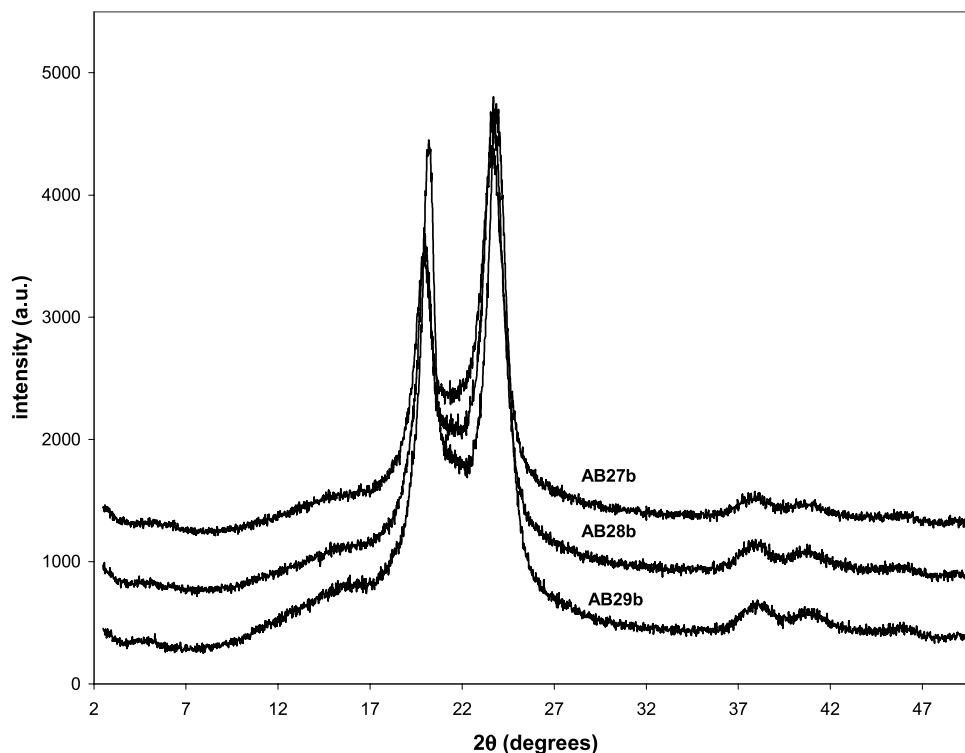


Fig. 5. WAXD intensity profiles of neat PA6 samples synthesized from 0.6, 1.2 and 1.8 mol% of CCCL (AB27b, AB28b, AB29b, respectively).

affect the solid state organization both in the case of CCCL and of POSS-CL as activators.

With reference to the melting temperature of as-polymerized samples, the values given in Table 3 show a very slight decrease (almost within the experimental error) when the activator concentration increases: this effect is evident for both activators and could be linked to the sharp decrease of PA6 molecular masses.

As is well known, the degree of crystallinity is determined by two main contributions: (i) the thermal history during (and after) polymerization; (ii) the molecular and structural characteristics of polymers.

In order to evaluate the relevance of the different contributions, samples have been re-analyzed after the same thermal history, i.e. x_c has been recalculated on the second heating trace after fast cooling (10 °C/min). These

Table 3
Activated anionic polymerization of CL: melting temperatures and degrees of crystallinity

Sample	Polymerization method	Activator	Activator content (mol%)	T_m (I heating) (°C)	x_c (I heating)	T_m (II heating) after fast cooling (°C)	x_c (II heating) after fast cooling
AB24	Quasi-adiabatic	POSS-CL	0.6	224	0.41	214	0.22
AB25	Quasi-adiabatic	POSS-CL	1.2	222	0.38	215	0.19
AB26	Quasi-adiabatic	POSS-CL	1.8	217	0.35	207	0.16
AB24b	Quasi-adiabatic	CCCL	0.6	219	0.46	217	0.27
AB25b	Quasi-adiabatic	CCCL	1.2	216	0.42	216	0.29
AB26b	Quasi-adiabatic	CCCL	1.8	216	0.45	214	0.26
AB27	Bulk isothermal	POSS-CL	0.6	224	0.36	212	0.21
AB28	Bulk isothermal	POSS-CL	1.2	219	0.40	212	0.19
AB29	Bulk isothermal	POSS-CL	1.8	224	0.37	208	0.16
AB27b	Bulk isothermal	CCCL	0.6	224	0.44	216	0.26
AB28b	Bulk isothermal	CCCL	1.2	223	0.51	217	0.31
AB29b	Bulk isothermal	CCCL	1.8	219	0.39	216	0.26
AB30	Suspension	POSS-CL	0.6	219	0.40	215	0.26
AB31	Suspension	POSS-CL	1.2	217	0.37	211	0.20
AB32	Suspension	POSS-CL	1.8	216	0.37	209	0.19
AB30b	Suspension	CCCL	0.6	219	0.42	216	0.28
AB31b	Suspension	CCCL	1.2	217	0.47	217	0.30
AB32b	Suspension	CCCL	1.8	216	0.45	216	0.31

results are also shown in Table 3 (last two columns). It can be seen that the decrease of crystalline content from the first to the second heating is rather relevant and easily explained when the high cooling rate of the thermal cycle is considered. With reference to the influence of the activator on crystallinity degree, it can be observed that POSS-CL leads to more amorphous structures and the decrease of PA6 crystallinity is higher when higher is the POSS content. The T_m trend is the same as in the case of first heating, although the values are lower when lower is the degree of crystallinity. Accordingly, all the above considerations on first heating data can be reaffirmed when homogeneous thermal history of the samples is imposed.

Much slower cooling rates (1 °C/min) modify T_m and x_c values in the second heating scan, as shown in Table 4, where data of PA6 samples prepared by the bulk isothermal polymerization method are compared (slow vs. fast cooling rate). It can be noticed that slow cooling vs. fast cooling allows a much greater increase of both T_m and x_c for POSS-containing hybrids, as compared to neat PA6 samples. From the above data, it is evident that the polyamide chain dynamics are slowed down to a greater extent by the bulky POSS moiety at the end of the chain.

SEM and TEM characterizations have been carried out in order to show the presence of POSS crystalline aggregates, as they are believed responsible of the above results in terms of apparent molecular mass and crystallinity degree of hybrid PA6.

Unfortunately, no evidence of crystalline aggregate formation has been found, probably because of the size of the aggregates which is lower than both the detectability limit of SEM microscope and the thickness of the slices prepared for TEM characterization by ultramicrotome.

4. Conclusions

We have seen that polyhedral oligomeric silsesquioxanes can be inserted in the polyamide 6 matrix by different synthetic methods. At first, POSS molecules with no reactive side groups have been taken in account and hydrolytic in situ polymerization of ϵ -caprolactam has

been used, in order to obtain PA6 nanocomposites. As foreseen, the interactions between highly polar PA6 chains and apolar siloxane cages were found too weak to cause a good POSS dispersion in (and adhesion to) the polymer matrix, so that unsatisfactory results have been obtained and only microcomposites at the best were produced.

As a second step, hybrid PA6 has been synthesized by using POSS with a reactive side group able to form a covalent link with the polyamide. Hydrolytic polymerization of ϵ -caprolactam has been carried out in presence of POSS-NH₂ as chain terminator: 5 and 10 wt% of POSS-NH₂ have been linked at one end of PA6 chains, causing a large decrease of PA6 molecular mass as a function of silsesquioxane content.

Much better results have been obtained when the activated anionic polymerization of ϵ -caprolactam has been considered: POSS-CL, a laboratory-made modification of POSS-NH₂, has been used as fast activator and covalently linked to PA6 at various contents. Quasi-adiabatic bulk polymerization, isothermal bulk polymerization and quasi-isothermal suspension polymerization have been performed and compared, with the aim to produce hybrid PA6 characterized by different chain regularity and morphology. PA6 hybrids have been characterized in term of both structure and molecular mass, and compared also to neat PA6, synthesized in the same conditions but from CCCL, a classical ultra-fast activator. In general, anionic polymerization allows to introducing rather high amounts of silsesquioxane as chain initiator, still yielding sufficiently high molecular masses of PA6. The hybrid polyamide 6 is semicrystalline, with a degree of crystallinity only slightly lower than neat PA6 although decreasing when POSS content increases. DSC, WAXS and solubility data suggest that silsesquioxane end groups form nanometric crystalline aggregates, influencing solid-state PA6 chain organization and acting as physical crosslinking points. Accordingly, solubility in some classical PA6 solvents decreases and only mixed systems, such as trifluoroethanol/dichloromethane, could be used to get real dissolution at molecular level.

In terms of polymerization methods, the anionic approach supports the arguments already presented in the case of neat PA6 [11,12]. With the POSS-CL activator too, a better chain regularity, without branching points and UV-absorbing groups, can be obtained when isothermal bulk and suspension methods are considered. Moreover, suspension CL polymerization provides particulated products, suitable for many technological applications: the production of finely powdered, POSS-containing PA6 make it easy to utilize it as a compatibilizer or interfacial modifier, etc. with improved tailorability and versatility. Mechanical and rheological properties of the above hybrid will be given in a subsequent paper [16]. In the near future, H₂N-POSS-NH₂ will be synthesized and copolymerized with CL [17] in order to obtain PA6 with several POSS moieties distributed in the main chain.

Table 4
Melting temperatures and degrees of crystallinity of bulk isothermal polymerization samples. Comparison between second heating data after fast and slow cooling

Sample	Fast cooling		Slow cooling	
	T_m (°C)	x_c	T_m (°C)	x_c
AB27	212	0.21	222	0.29
AB28	212	0.19	217	0.26
AB29	208	0.16	219	0.31
AB27b	216	0.26	222	0.31
AB28b	217	0.31	219	0.34
AB29b	216	0.26	219	0.33

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