Volume 43, Issue 10, October 2007
ISSN 0014-3057

EUROPEAN
POLYMER
JOURNAL

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Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 43 (2007) 4103–4113
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

New organic–inorganic nanohybrids *via* ring opening polymerization of (di)lactones initiated by functionalized polyhedral oligomeric silsesquioxane

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Received 4 June 2007; received in revised form 21 July 2007; accepted 22 July 2007
Available online 10 August 2007

Abstract

The synthesis of new organic–inorganic materials were investigated. Poly(ε-caprolactone) and poly(L, L-lactide) covalently end-capped by a polyhedral oligomeric silsesquioxane (POSS) moiety, leading to new nanohybrid materials, were successfully prepared by coordination–insertion ring opening polymerization (ROP) of ε-caprolactone (ε-CL) and L,L-lactide (L,L-LA) respectively. The reaction was initiated from the primary amine available on aminopropylheptakis(isobutyl)POSS nanoparticles and catalyzed by tin(II) 2-ethylhexanoate (tin octoate, $Sn(oct)_2$). The covalent grafting of the polyester chains onto the POSS "nanocages" was assessed by selective fractionation experiment, Fourier transform infrared spectroscopy (FTIR) and further confirmed by proton nuclear magnetic resonance (^{1}H NMR). The polymerization proved to be well controlled as attested by the quite narrow polydispersity indices as determined by size exclusion chromatography (SEC). Furthermore, well-defined semi-crystalline poly(ε-caprolactone)-b-polylactide block copolymer carrying such POSS nanoparticle at one end was successfully synthesized attesting for the very efficient control over the polymerization reaction.

Keywords: Nanohybrids; Nanocomposites; POSS; Polyesters; Ring opening polymerization

1. Introduction

Since the emergence of nanotechnologies, a strong demand exists to continuously improve the properties of the so-called nanomaterials. Thus, the introduction of nano-sized inorganic reinforcements has appeared to be a very efficient way to modify polymer-based materials. By means of a good choice of the blended partners and an efficient

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doi:10.1016/j.eurpolymj.2007.07.041

compounding process, this technique can lead to the production of new materials with improved properties. Indeed, it is now well known that the introduction of rigid filler into thermoplastic or thermoset matrices may lead to some improvement of their mechanical, thermal, barrier, electrical or fire resistance properties [1–4], depending on the nature of the chosen filler. Compared to micrometric size fillers for which a high amount of filler content is required for a real improvement of the composite properties, only a few percents of nanofillers (1–5 wt%) are usually sufficient to obtain a nanocomposite showing the same behaviors, if not better [5].

Among all the nanofillers, layered silicates have been indubitably the most reported in the literature [6–8]. Even if they have drawn less attention than layered silicates, polyhedral oligomeric silsesquioxane (POSS) have been more and more studied in the past decade [9,10]. Indeed, they have proved to influence the thermal, mechanical [5] and particularly fire resistance [2,3,11] properties of polymer materials. Typically POSS nanoparticle is a 3D cage like siloxane structure surrounded by eight organic R groups ($RSiO_{1.5}$). These organic groups can be hydrocarbon species, which allow compatibilization and solubility of the particles into polymer matrices, or they can embody a large range of functional groups suitable for the preparation of nanohybrids by copolymerization or grafting [12]. The structure–property relationship of polymer incorporating POSS has been recently reviewed [9,13] and interestingly, several recent publications reported on the use of these new nanomaterials in many different applications [5,14–21] including the potential of POSS-based nanocomposites in the biomedical field [22,23]. However, as depicted in the literature, in most of the cases, such nanofillers tend to aggregate when they are simply melt blended within polymer matrices, mainly due to the existence of numerous nanofiller–nanofiller interactions [24,25]. In order to improve the dispersion, the nanofiller and the matrix need to be compatibilized. For instance, the nanofiller can be organo-modified in order to promote more favorable nanofiller–polymer interactions, leading to a reduction of the interfacial energy. The creation of a strong chemical bond between the filler and the polymer matrix allows for a complementary enhancement of the material properties compared to the simple blends. Indeed, the presence of a covalent bond can improve the interfacial adhesion between the organic and the inorganic part of the composition, leading consequently to a material with better mechanical properties for instance, as nicely reviewed by Pittman in 2001 [26].

The synthesis of POSS-based nanohybrids, i.e., polymer grafted POSS nanoparticles has drawn a lot of attention over the last decade. For instance, Mather and et al. reported the preparation of amphiphilic telechelic incorporating POSS copolymers. Indeed, α, ω diol end-capped PEG homopolymers of various molecular weights were reacted with monoisocyanate functionalized POSS nanoparticles [27]. They evidenced a strong modification of the thermal and morphological properties of the amphiphilic telechelics by controlling the hydrophilic–hydrophobic balance. Later, the group of Coughlin has used the same monoisocyanate–POSS to synthesize hemi-telechelic polystyrene–POSS copolymer [28]. Authors have developed a synthetic protocol that can act as an experimental model to probe the ordering or aggregation behavior of inorganic nanoparticles within polymeric matrices.

In this contribution, we report on the synthesis of well-defined POSS–poly(ε-caprolactone) (POSS–PCL) and POSS–poly(L,L-lactide) (POSS–PLA) nanohybrids prepared by ring opening polymerization (ROP) of ε-caprolactone (CL) and L,L-lactide (LA) catalyzed by tin(II) 2-ethylhexanoate (tin octoate, $Sn(oct)_2$). Purposely, the ROP is initiated by the primary amine group made available onto an aminopropylheptakis(isobutyl)POSS ($POSS\text{-}NH_2$). PCL and PLA have been chosen as the organic counterpart of these novel nanohybrids owing to their biodegradability and biocompatibility, which can be consequently useful as environmentally friendly material or for biomedical applications. Moreover, PCL is well known to be miscible or at least mechanically compatible with a large variety of polymers, e.g., SAN, PVC, chlorinated polyethylene... [29]. Therefore, the as-synthesized POSS–PCL nanohybrids could then be used as surface-compatibilized POSS for further dispersion in polymeric matrices known to be miscible (or simply mechanically compatible) with the PCL segment. It is worth pointing out that very recently Zheng et al. have interestingly reported about the synthesis of octaarmed star PCL with a POSS core. Accordingly a octa(3-hydroxypropyl)POSS was considered as an octafunctional initiator for promoting the CL ring opening polymerization [32]. Even more recently (while this contribution was submitted for publication), Ni and Zheng extrapolated the CL polymerization using 3-hydroxypropylheptaphenyl

POSS as a monofunctional intiator and allowing for supramolecular inclusion complexes between the resulting POSS-b-PCL and alpha-cyclodextrin [33].

2. Experimental section

2.1. Materials

ε-Caprolactone (CL) (99%, Acros) was dried 48 h over calcium hydride and distilled under reduced pressure. Toluene (p.a., Labscan) was dried over calcium hydride and distilled. L,L-Lactide (LA) (99%, Galactic) was recristallized in toluene at 0 °C and dried under vacuum at ambient temperature. Tin(II) ethylhexanoate ($Sn(Oct)_2$) (95%, Aldrich) was used as received without further purification. Aminopropylheptakis(isobutyl)POSS ($POSS\text{-}NH_2$, 97%) was purchased from Hybrid Plastics. Note that the purity (i.e., amino functionalization) of the received sample was actually estimated to 83% by multinuclear NMR, the impurities proved to be "open" POSS deprived of amino-functionalization. Since such impurities did not participate in the polymerization reaction (and the resulting polyester grafting) and furthermore they were readily eliminated at the end of the polymerization by simple selective precipitation step (see polymerization procedure hereafter), the $POSS\text{-}NH_2$ sample was used as received.

2.2. Polymerization procedure

Typically, 0.2 g ($n_{NH_2} = 2.26 \times 10^{-4}$ mol) of aminopropylheptakis(isobutyl)POSS ($POSS\text{-}NH_2$) was introduced under nitrogen flow in a two-neck flask equipped with a three-way stopcock and a magnetic stirring bar. Then, toluene (7 mL), $Sn(Oct)_2$ (0.2 mL of a 0.09 M toluene solution) and ε-caprolactone ($V_{CL} = 2$ mL; $m_{CL} = 2.06$ g; $n_{CL} = 0.018$ mol) were added successively under nitrogen using previously flame-dried syringes. The mixture was then heated at 100 °C under stirring. After the desired reaction time, the polymerization was stopped by adding of a few drops of diluted hydrochloric acid (1 M). The POSS end-capped PCL was recovered from heptane precipitation, filtered and dried until constant weight at 40 °C under vacuum. As far as L,L-lactide (LA) (co)polymerization was concerned, a determined amount of purified LA (previously dissolved in hot dry toluene) was added to the reaction medium (after CL polymerization in the case of POSS-P(CL-b-LA) synthesis) and the (co)polymerization allowed to proceed at 100 °C (80 °C for POSS-b-PLA) before addition of a few drops of diluted hydrochloric acid (0.1 M) and further precipitation, filtration and drying as reported above.

2.3. Characterization

Proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded on solutions prepared in $CDCl_3$ using a Bruker AMX-300 apparatus at a frequency of 300 MHz. Fourier transform infrared (FTIR) spectra were recorded using a BIO-RAD Excalibur spectrometer equipped with an ATR Harrick Split Pea™. Size exclusion chromatography (SEC) was performed in THF (sample concentration: 1 wt%) at 35 °C using a polymer laboratories (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocratic HPLC pump LC1120 (flow rate: 1 mL/min), a Basic-Marathon Autosampler, a PL-RI refractive index detector and four columns: a guard column PLgel 10 μm (50 × 7.5 mm) and three columns PLgel mixed-B 10 μm (300 × 7.5 mm). Molecular weight and molecular weight distribution were calculated by reference to a calibration curve built up by using polystyrene standards. The thermal behavior of the copolymer was analyzed by differential scanning calorimetry (DSC) using a DSC Q100 from TA Instrument at a heating and cooling rates of 10 K/min under nitrogen flow.

3. Results and discussion

3.1. Synthesis of POSS–PCL nanohybrids

In a first series of experiments, the polymerization/grafting of polyesters chains has been performed using commercially available $POSS\text{-}NH_2$ nanofillers (from Hybrid Plastics) in toluene in a relatively diluted medium ($[CL]_0 = 2$ M) at high temperature ($T = 100$ °C). The monomer conversion has been recorded in function of time and the molecular parameters of the as-synthesized POSS end-capped PCL chains characterized by ^1H NMR and SEC. The experimental conditions and results are reported in Table 1. The mechanism of the ROP of cyclic esters initiated by tin octoate and primary amines has been deeply studied and recently reported in the literature [30]. Accordingly, the polymerization reaction proved to take place through a coordination–insertion mechanism

Table 1
Characterization of the POSS–PCL and POSS–PLA nanohybrids as synthesized by ROP of CL and L,L-LA, respectively

Entry	Monomer	Time (h)	Conv.[a] (%)	DP_{th} [b]	DP_{NMR} [c]	$M_{n\ SEC}$ [d] (g/mol)	M_w/M_n [d]
1	CL	2	24	23	40	6500	1.22
2	CL	3	42	40	50	9400	1.17
3	CL	4	86	83	85	14,300	1.27
4	CL	5	81	78	85	14,800	1.31
5	CL	6	89	85	75	13,700	1.33
6	CL	7	99	95	100	18,600	1.38
7	LA	1	53	48	42	5000	1.07
8	LA	2	71	64	57	6700	1.08
9	LA	3	79	71	66	7900	1.08
10	LA	4	86	78	72	8200	1.09
11	LA	5	90	82	75	8300	1.09

($[CL]_0[NH_2]_0 = 95$; $[NH_2]_0/[Sn(oct)_2]_0 = 2.5$; $[CL]_0 = 2$ M; $T = 100$ °C) ($[LA]_0/[NH_2]_0 = 90$; $[NH_2]_0/[Sn(oct)_2]_0 = 2.5$; $[LA]_0 = 1$ M; $T = 80$ °C).

[a] As measured by gravimetry.

[b] $DP_{th} = ([Monomer]_0/[NH_2]_0) \times conv.$

[c] As measured by ^1H NMR in $CDCl_3$; $DP(PCL)_{NMR} = [(I_d/2)/(I_{h,f+g}/58)]$ (cf. Fig. 1). $DP(PLA)_{NMR} = [(I_a)/(I_{h,f+g}/58)]$ (cf. Fig. 5).

[d] As measured by SEC (relative to polystyrene standards).

involving the *O*-acyl cleavage of the cyclic monomer.

After one hour of polymerization time, no polymer is recovered from tentative precipitation in heptane. This observation can be explained by the solubility of POSS-NH_2 in this solvent. Indeed, the POSS grafted with short polyester oligomer are soluble enough to lead to a partial fractionation of the sample. After 2 h, the grafted PCL chain gets sufficiently long to promote the POSS–PCL nanohybrid precipitation allowing the monomer conversion measurement. A typical ^1H NMR spectrum is depicted in Fig. 1. This spectrum attests for the covalent grafting of the PCL chains onto the POSS

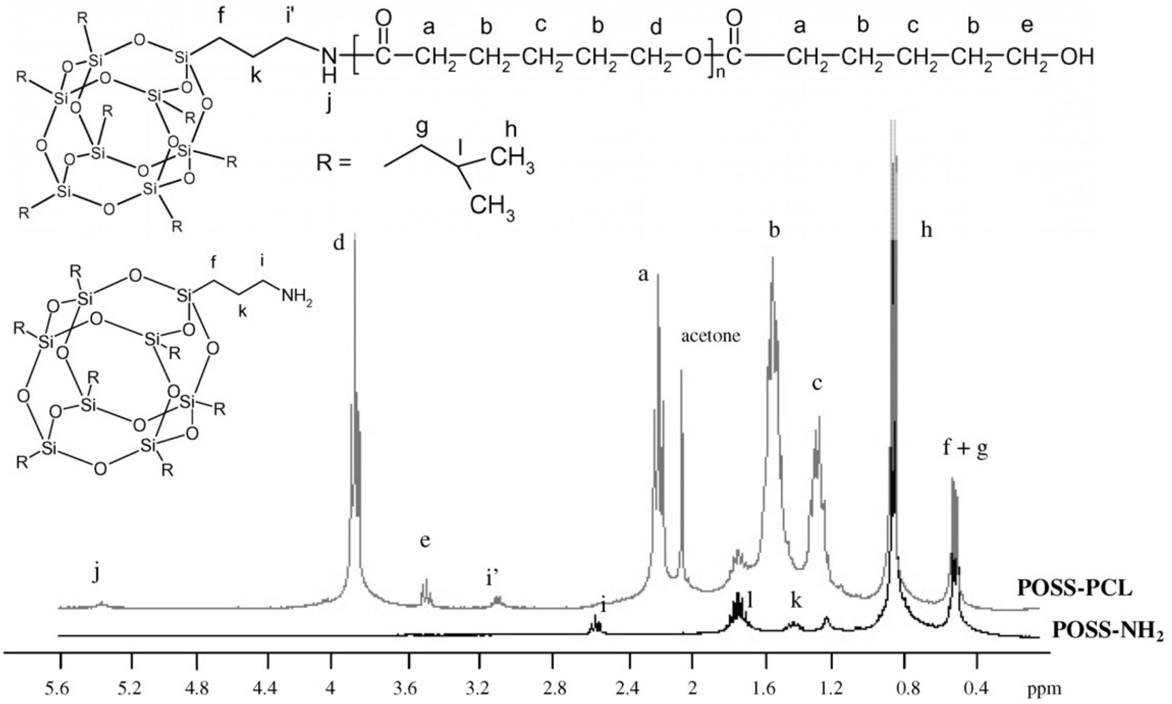


Fig. 1. ^1H NMR spectrum of the POSS-NH_2 and a POSS–PCL nanohybrid in $CDCl_3$ (entry 2, Table 1).

cages by the quantitative shift of the signal –CH_2–NH_2 from 2.6 ppm (signal i in Fig. 1) to a new signal –CH_2–NH–C(O)– at 3.2 ppm (signal i′ in Fig. 1). Moreover, one can note the presence of a signal characteristic of an amide proton around 5.5 ppm. These observations have been confirmed by FTIR analysis. Indeed, the FTIR spectrum in Fig. 2. evidences the presence of both POSS and PCL by the appearance of the siloxane and carbonyl characteristic absorption bands at 1099 and 1720 cm^{-1}, respectively. Moreover, the presence of a weak band around 1648 cm^{-1} characteristic of an amide linkage is again in favor for the covalent grafting of the polyester chains.

In Table 1, one can note a gradual increase of the monomer conversion in function of reaction time. This evolution goes with a continuous growth of the grafted polyester chains as attested by the polymerization degree (DP) measured by ^{1}H NMR. Interestingly enough, this chain growth is clearly evidenced by SEC (Fig. 3). Fig. 3 displays the evolution of the SEC signal towards lower elution volumes, i.e., higher molecular weights, with increasing monomer conversion. Moreover, a good control

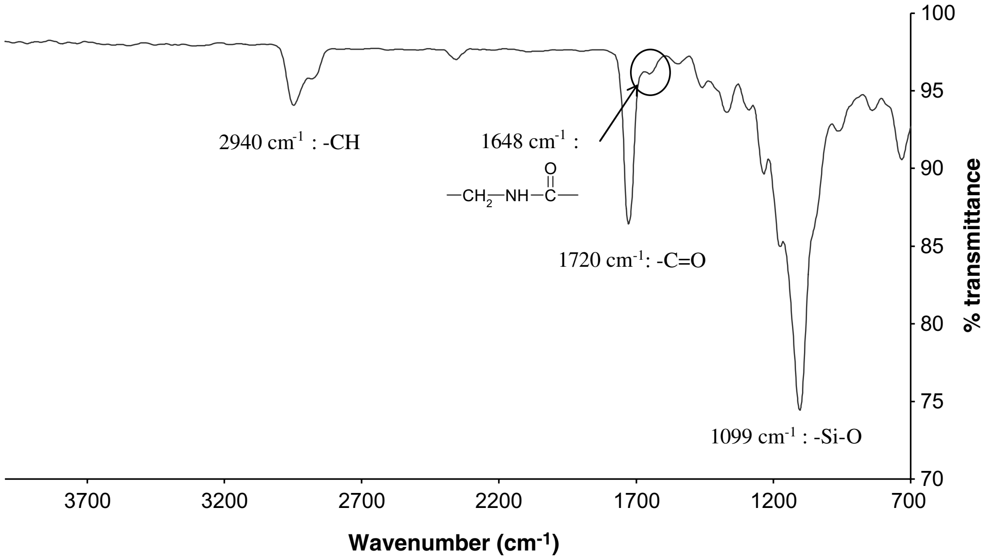


Fig. 2. FTIR spectrum of a POSS–PCL nanohybrid (entry 2, Table 1).

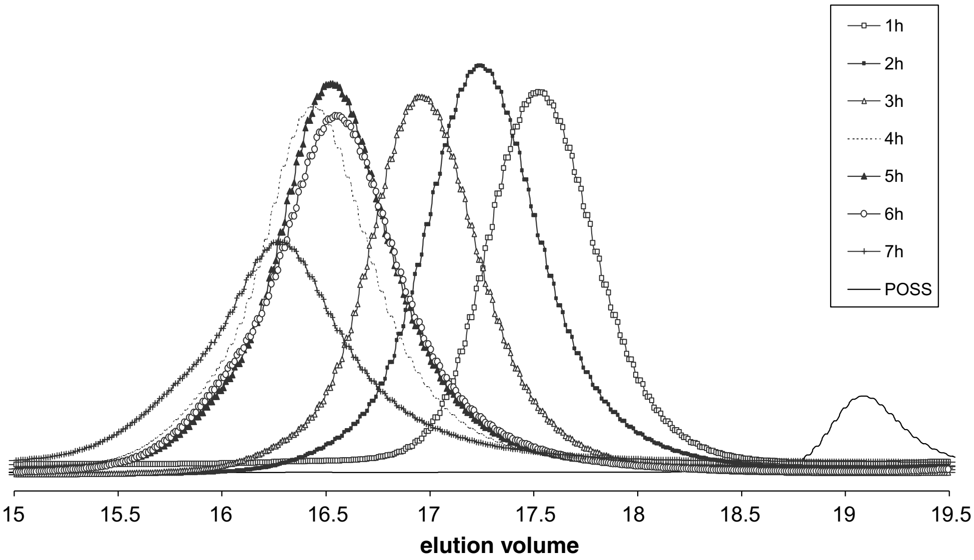


Fig. 3. Size exclusion chromatograms of POSS–PCL nanohybrids (effect of reaction time, see Table 1).

over the polymerization reaction can be observed as attested by the rather narrow molecular weight distributions ($M_w/M_n = 1.2-1.4$), at least for such a particular inorganic initiator.

3.2. Synthesis of POSS–PLA nanohybrids

Concerning the polymerization of L,L-LA, it comes out from Table 1 that the reaction kinetics is enhanced compared to CL. Indeed, even in a more diluted medium than for ROP of ε-caprolactone ($[LA]_0 = 1$ M) as well as and a lower temperature (80 °C against 100 °C for CL), the monomer conversion reaches ca. 50% after only one hour of reaction. However, in spite of this dramatic increase of the polymerization rate, the control over the molecular parameters of the synthesized POSS–PLA copolymer remains effective. Indeed an excellent control is observed all along the polymerization reaction as attested by the experimental DP's (measured by ^{1}H NMR) close to the theoretical values as well as the remarkably narrow polydispersity indices ($M_w/M_n < 1.1$). This is clearly evidenced in the SEC chromatograms where the total shift of the signal towards higher molecular weight (without any remaining traces of homopolymer) can be observed while maintaining very narrow molecular weight distribution (Fig. 4). The composition of the copolymers has been attested by ^{1}H NMR and is depicted in Fig. 4. The characteristic signals of the PLA segments can be assigned at 1.6 and 5.2 ppm for the protons –C(O)– CH(CH_3)– O– and –C(O)– CH(CH$_3$)– O–, respectively. Moreover, one can note the presence of the signal CH_2–NH–C(O)– at 3.3 ppm (signal i′ in Fig. 5) as well as the characteristic signal of an amide proton around 5.5 ppm. Once again, these observations have been confirmed by FTIR (Fig. 6). The band characteristic of the siloxane bonds appears around 1095 cm^{-1} and the carbonyl band around 1720 cm^{-1}. Finally, the weak band around 1680 cm^{-1} can be assessed to an amide linkage attesting the covalent grafting of the polylactide chains.

3.3. Synthesis of POSS-P(CL-b-LA) block copolymer

The POSS-NH$_2$ proved to be very efficient as initiator for the ROP of ε-CL as well as L,L-LA catalyzed by tin octoate. Accordingly, a novel POSS-end functionalized diblock copolyester has been studied by the introduction of l,L-lactide in the polymerization medium right after POSS–PCL synthesis. That leads not only to the synthesis of POSS-P(CL-b-LA) block copolymer but gives some more evidence for the effective controlled character of the ROP of lactones as initiated from POSS-NH$_2$. In order to prepare such diblock copolyesters by

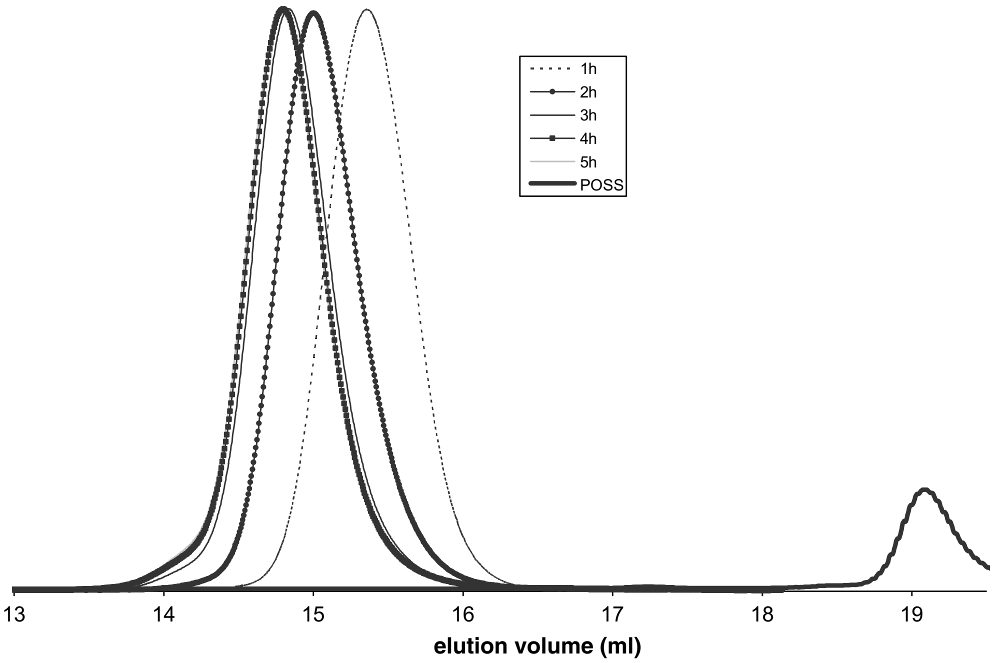


Fig. 4. Size exclusion chromatograms of POSS–PLA nanohybrids (effect of reaction time, see Table 1).

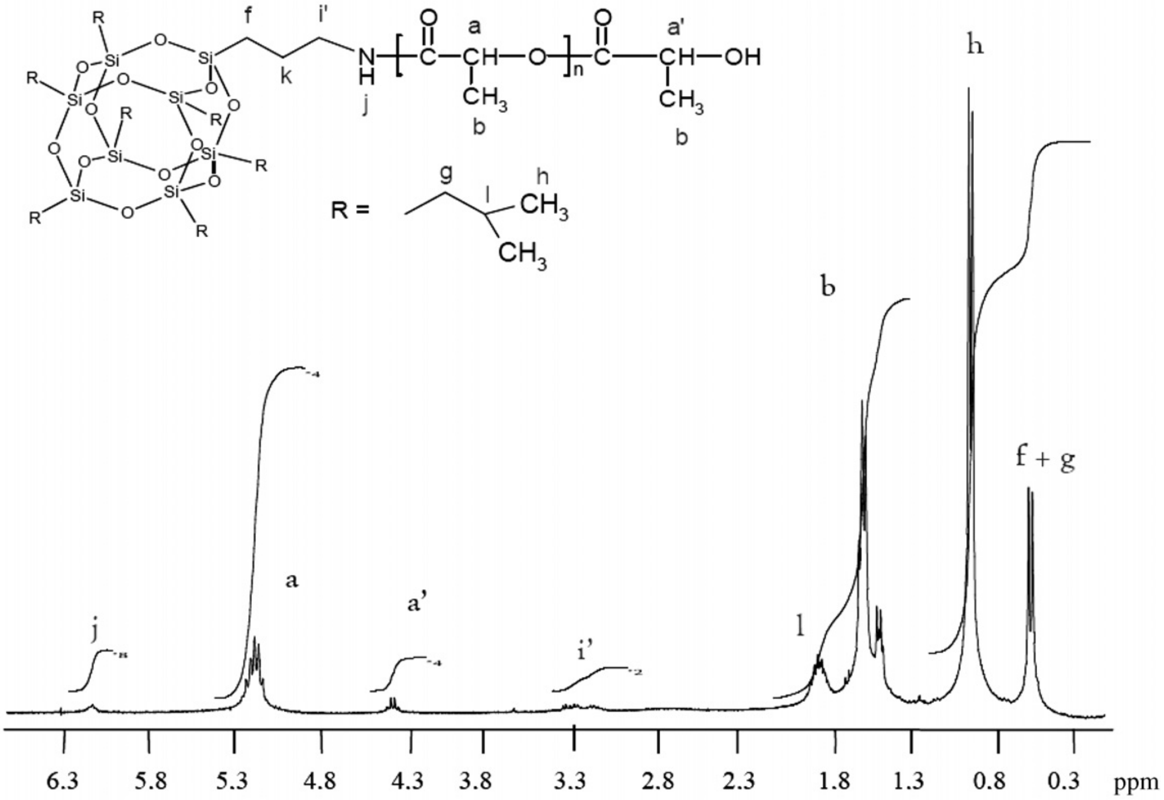


Fig. 5. ^{1}H NMR spectrum of POSS–PLA nanohybrid in $CDCl_3$ (entry 7, Table 1).

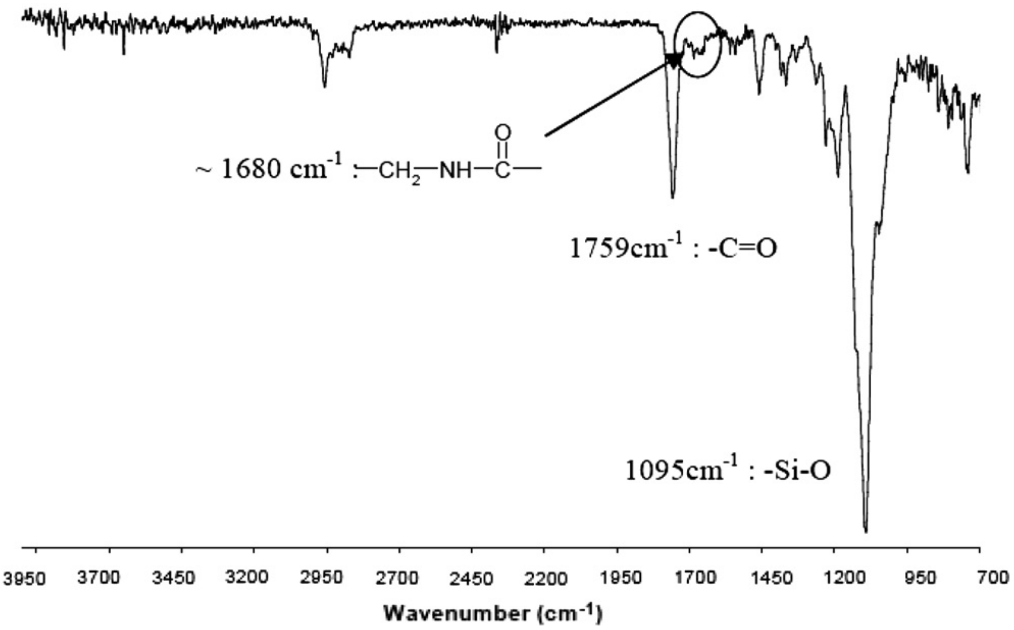
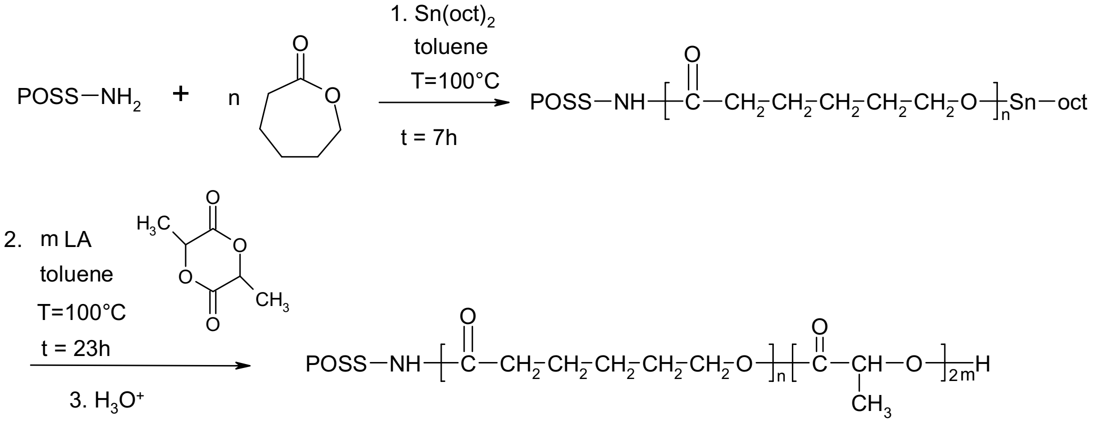


Fig. 6. FTIR spectrum of a POSS–PLA nanohybrid (entry 7, Table 1).

sequential polymerization, CL was first polymerized for 7 h to ensure almost complete conversion. An aliquot was picked out for characterization just before adding L,L-lactide in the reaction medium. The synthesis strategy is depicted in Scheme 1. After 30 h of reaction time, the copolymer was recovered



Scheme 1. Synthesis of POSS-P(CL-b-LA) block copolymer.

by precipitation from heptane to remove unreacted CL, in any, and non-functionalized POSS. Then, the copolymer was dissolved in THF and precipitated from methanol at 0 °C to remove residual lactide (soluble in methanol while the copolyester is insoluble). The lactide conversion of 86% has been determined by gravimetry. The as-synthesized copolymer has then been characterized by SEC and NMR. Table 2 shows the experimental conditions and molecular parameters of the recovered POSS-P(CL-b-LA) block copolyester. The controlled behavior of the copolymerization reaction is clearly attested by SEC. Fig. 7 gives evidence for the complete shift of the POSS–PCL nanohybrid signal through higher molar masses after lactide copolymerization, and the appearance of a monomodal signal corresponding to the copolymer. No termination side-reaction can be detected since there is no trace of POSS–PCL species in the chromatogram. ^{1}H and ^{13}C NMR analyses were performed on the recovered polymeric chains in order to determine the copolymer structure. Fig. 8 presents the ^{1}H NMR spectrum of the POSS–PCL nanohybrid and the corresponding POSS-P(CL-b-LA) block copolymer. The characteristic signals of POSS, PCL and PLA segments have been assigned and the composition can be determined from the ratio

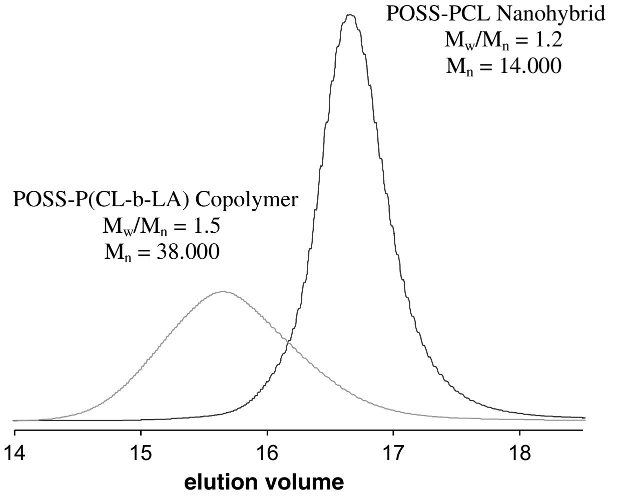


Fig. 7. SEC traces of POSS–PCL nanohybrid and POSS-P(CL-b-LA) block copolymer (see Table 2).

Table 2
Characterization of the POSS-P(CL-b-LA) copolymer as synthesized by ROP

Conv. (%)		DP_{th} [c]		DP_{NMR} [d]		M_w/M_n [e]	
CL [a]	LA [b]	CL	LA	CL	LA	POSS-CL	POSS-P(CL-b-LA)
~100	86	96	258	94	336	1.2	1.5

$[CL]_0/[NH_2]_0 = 96$; $[LA]_0/[NH_2]_0 = 300$); $[NH_2]_0/[Sn(oct)_2]_0 = 2.5$; $T = 100$ °C.

[a] Estimated based on previous experiments (see Table 1).

[b] Determined by gravimetry.

[c] $DP_{th\ monomer} = ([M]_0/[NH_2]_0) \times$ conv. where M = CL or LA.

[d] As measured by ^{1}H NMR in $CDCl_3$; $DP_{NMR\ PCL} = [(I_d/2)/(I_{h,f+g}/58)]$ and $DP_{NMR\ PLA} = [(I_m)/(I_{h,f}/58)]$ (cf. Fig. 8).

[e] As measured by SEC (relative to polystyrene standards).

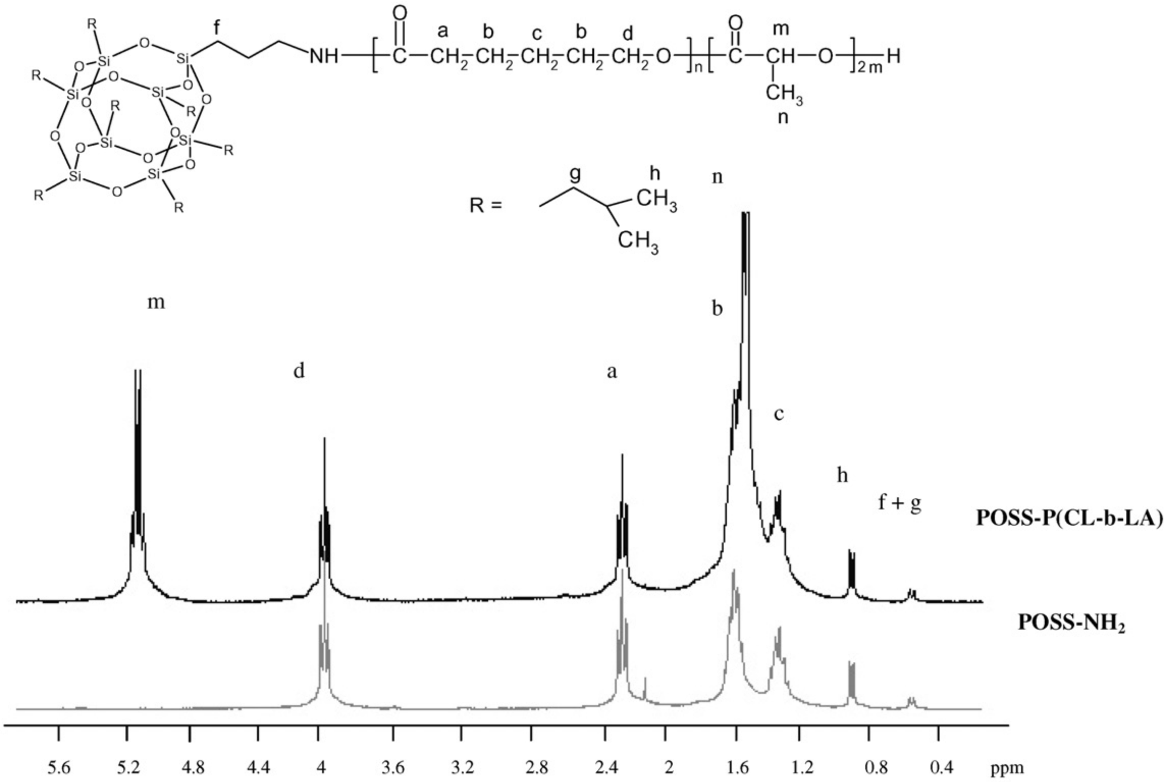


Fig. 8. ^{1}H NMR spectra of POSS–PCL nanohybrid and POSS-P(CL-b-LA) block copolymer.

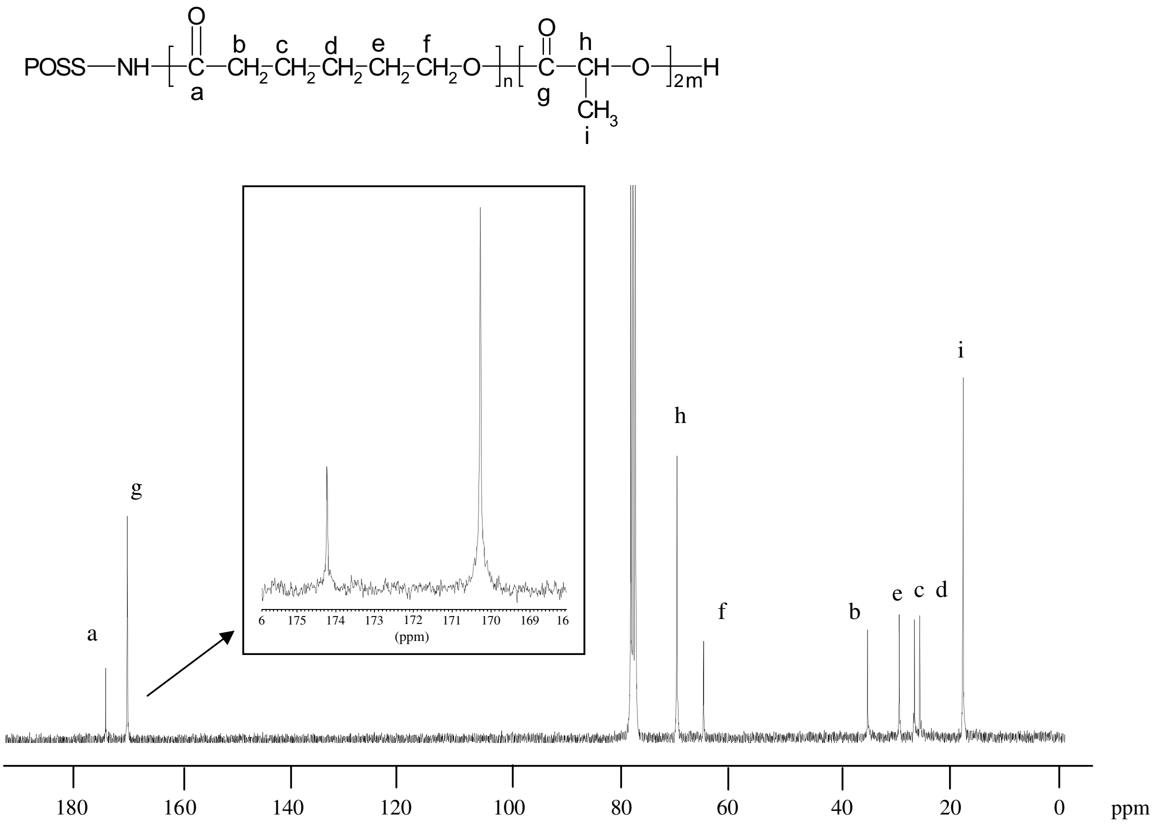


Fig. 9. ^{13}C NMR spectrum of POSS-P(CL-b-LA) block copolymer in CDCl$_3$.

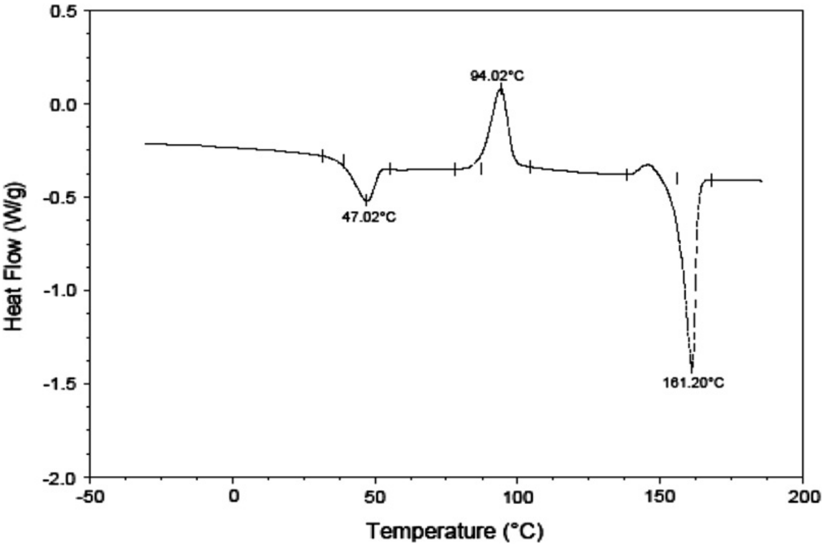


Fig. 10. DSC curve of POSS-P(CL-b-LA) block copolymer (see Table 2).

of their respective intensities as referenced in Table 2. The ^{1}H NMR spectrum highlights a good agreement between the relative comonomer experimental composition and the expected values based on the starting composition and the respective monomer conversion (see Table 2). It is worth noting that the small difference between theoretical and experimental DP as well as the polydispersity index for such a ROP are quite acceptable for conversions near 100% (see Table 1 for the sake of comparison). A ^{13}C NMR analysis, by focusing on the carbonyl region of the spectrum, brought additional evidence for the diblock structure of the copolymer and confirms that no side-reactions, such as transesterification, have occurred (Fig. 9). Indeed, only two types of carbonyl groups are observed (CL: 174 ppm and LA: 170 ppm) without any signals detectable in-between these two main resonance peaks. Such intermediate signals would have been the signature of some more randomly distributed comonomers resulting from transesterification reactions [31]. The POSS-P(CL-b-LA) diblock copolymer has been further analyzed by DSC. Interestingly enough, both blocks can crystallize and the melting endotherms of each block are clearly observed (Fig. 10). On one hand, a crystallization exotherm is centered on 94 °C followed by the melting endotherm at 161 °C typical of the PLA segment. On the other hand, a more complex transition is observed at ca. 47 °C, more likely superposing the T_g of the PLA block (around 50–55 °C) and the melting endotherm of the PCL block (around 50–60 °C).

4. Conclusion

In this work, novel organic–inorganic nanohybrids were synthesized by grafting polyesters chains from amino-functionalized POSS nanocages. Such nanohybrids were obtained via ROP of lactones initiated by the primary amine groups available onto the inorganic nanofillers and catalyzed by tin octoate. Firstly, the ROP of ε-CL and L,L-LA were investigated. The formation of a covalent amide link between the nanofiller and the growing polyester chains was evidenced by fractionation experiment, ^{1}H NMR and FTIR. Then, the growth of the polymer chains has been followed in function of time. This study has evidenced a very good correlation with the theoretical values. Moreover, the molecular weight distribution remained narrow, attesting for a good control over the polymerization. Finally, the synthesis of a POSS-P(CL-b-LA) block copolymer has been carried out. ^{1}H NMR analysis gives credit for the control achievable on the copolymer composition. The quantitative shift of the POSS–PCL nanohybrid SEC trace towards higher molar masses and the observation of a monomodal signal attest for the absence of termination side-reactions. The absence of transesterification reactions has been confirmed by ^{13}C NMR. Indeed, only two carbonyl signals respectively assigned to the ester functions of the CL and LA were detected. Interestingly enough, these POSS–PCL nanohybrids can be considered as "compatibilized" nanofillers to be finely dispersed in either PCL or any polymeric matrices known to be miscible (or at least mechanically compatible) with the PCL chains covalently bonded onto the inorganic nanocages. These results will be the topic of a forthcoming paper.

Acknowledgements

Authors are grateful to the 'Région Wallonne' and European Community (FSE, FEDER) in the frame of Objectif-1 and Phasing Out financing of Materia Nova. This research was carried out in the frame of the STReP European Research program "NANOFIRE" (Contract No. 505637) from the 6th Framework Program. This research was partially performed in the frame of SSTC-PAI 6/27 project of the Belgian Federal Science Policy Office.

References

[1] Blake F. Agence Rhône-Alpes pour la Maîtrise des Matériaux, Les nanocomposites à matrice polymère; 2001.
[2] Bourbigot S, Duquesne S, Jama C. Macromol Symp 2006;233:180.
[3] Bourbigot S, Le Bras M, Flambard X, Rochery M, Devaux E, Lichtenhan JD. In: Le Bras M, Bourbigot S, Duquesne S, Jama C, Wilkie CA, editors. Fire retardancy of polymers: new applications of mineral fillers. Cambridge: Royal Society of Chemistry; 2005. p. 189.
[4] Lu SY, Hamerton I. Prog Polym Sci 2002;27:1661.
[5] Zhao YQ, Schiraldi DA. Polymer 2005;46:11640.
[6] Alexandre M, Dubois Ph. Mater Sci Eng R 2000;28:1.
[7] Ray SS, Okamoto M. Prog Polym Sci 2003;28:1539.
[8] Usuki A, Hasegawa N, Kato M. Adv Polym Sci 2005;179:135.
[9] Phillips SH, Haddad TS, Tomczak SJ. Curr Opin Solid State Mater Sci 2004;8:21.
[10] Baney RH, Itoh M, Sakakibara A, Suzuki T. Chem Rev 1995;95:1409.
[11] Jash P, Wilkie CA. Polym Deg Stab 2005;88:401.
[12] www.hybridplastics.com.
[13] Joshi M, Butola BS. J Macromol Sci Part C: Polym Rev 2004;44:389.
[14] Fina A, Abbenhuis HCL, Tabuani D, Camino G. Polym Degrad Stab 2006;91:2275.
[15] Liu YL, Chang GP, Hsu KY, Chang FC. J Polym Sci Part A Polym Chem 2005;44:3825.
[16] Zeng J, Kumar S, Iyer S, Schiraldi DA, Gonzalez RI. High Perf Polym 2005;17:403.
[17] Jash P, Wilkie CA. Polym Degrad Stab 2005;88:401.
[18] Song XY, Geng HP, Li QF. Polymer 2006;47:3049.
[19] Kopesky ET, McKinley GH, Cohen RE. Polymer 2006;47:299.
[20] Huang JC, He CB, Xiao Y, Mya KY, Dai J, Siow YP. Polymer 2003;44:4491.
[21] Yei DR, Kuo SW, Su YC, Chang FC. Polymer 2004;45:2633.
[22] Kannan RY, Salacinsli HJ, De Groot J, Clatworthy I, Boezc L, Horton M, et al. Biomacromolecules 2006;7:215.
[23] Kannan RY, Salacinski HJ, Butler PE, Seifalian AM. Acc Chem Res 2005;38:879.
[24] Matejka L, Strachota A, Plestil J, Whelan P, Steinhart M, Slouf M. Macromolecules 2004;37:9449.
[25] Strachota A, Kroutilova I, Kovarova J, Matejka L. Macromolecules 2004;37:9457.
[26] Li G, Wang L, Ni H, Pittman Jr CU. J Inorg Org Polym 2001;11(3):123.
[27] Kim BS, Mather PT. Macromolecules 2002;35:8378.
[28] Cardoen G, Coughlin EB. Macromolecules 2004;37:5123.
[29] Heuschen J, Jérôme R, Teyssié Ph. Macromolecules 2006;47:5161.
[30] Kowalski A, Libiszowski J, Biela T, Cypryk M, Duda A, Penczek S. Macromolecules 2005;38(20):8170.
[31] Vanhoorne P, Dubois Ph, Jérôme R, Teyssié Ph. Macromolecules 1992;25:37.
[32] Liu Y, Yang Y, Zhang W, Zheng S. Polymer 2006;47:6814.
[33] Ni Y, Zheng S. J Polym Sci Part A Polym Chem 2007;45:1247. and refs. herein cited.