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Controlled Ring-Opening Polymerization of ϵ-Caprolactone in the Presence of Layered Silicates and Formation of Nanocomposites

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Introduction. Nanocomposites[1] of poly(ϵ-caprolactone) (PCL) deserve interest because of the possible upgrading of a polymer known for biocompatibility, biodegradability, and compatibility with a large range of polymers.[2,3] In previous studies,[4,5] ϵ-caprolactone (ϵ-CL) was polymerized at 170 °C, in the presence of silicates premodified by alkylammonium cations end-capped by a carboxylic acid. No linear dependence of the PCL molecular weight on the carboxylic acid content was observed, which precludes the "in situ" controlled/living growth of the chains in agreement with earlier observations for polymerization initiated by protonic acids.[6] In contrast, control/livingness can be imparted to the ϵ-CL polymerization by alkoxy compounds, either preformed (e.g., Al isopropoxide) or formed "in situ" by reaction of a metal catalyst (e.g., tin octoate) with an alcohol.[7−10] This work aims at initiating the controlled/living polymerization of ϵ-CL in the presence of montmorillonite (MMT) modified by alkylammonium cations able to initiate or not the ϵ-CL polymerization. In the first instance, tin(II) octoate has been combined with hydroxyl-containing alkylammonium cations, and the PCL chains have to grow from the silicate surface as tethered chains. It is no longer the case when dibutltin(IV) dimethoxide is the initiator in conjunction with inactive alkylammonium cations.

Experimental Section. Montmorillonite (9.2×10^{-4} mol of Na^+/g) was modified by standard exchange of Na^+ by *N*,*N*-diethyl-*N*-3-hydroxypropyloctadecylammonium bromide (MMT/OH). The organic (and thus hydroxyl) content was 7.2×10^{-4} mol/g, as determined from the weight loss measured by thermogravimetric analysis (Thermal Analyst 2100, TA Instrument; under N_2 flow, in the temperature range from 25 to 800 °C at 10 °C/min). Only data in the 200−400 °C range were considered in order to exclude contribution of adsorbed water and clay dehydroxylation. Cloisite 25A, *N*,*N*,*N*,*N*-dimethyldodecyloctadecylammonium bromide montmorillonite, was supplied by Southern Clay Products (Gonzales, TX).

Table 1. Bulk Polymerization of ϵ-CL in the Presence of MMT/OH and Tin(II) Octoate[a]

entry	silicate (wt %)	M_n (calc)	M_n[b] (SEC)	M_w/M_n (SEC)
1	2	71 500	43 500	2.1
2	3	42 900	34 000	1.8
3	6	21 500	20 000	1.9
4	10	12 200	15 000	2.1
5	15	7 800	8 500	1.8
6	24	4 300	5 500	1.9

[a] Bulk polymerization at 90 °C for 17 h (7.2×10^{-4} mol of OH/g of silicate). [b] Universal calibration curve.

Organically modified silicate was swollen by ϵ-CL under nitrogen at 50 °C for 1 h. Either the catalyst, tin(II) octoate (monomer/$Sn(Oct)_2$ = 200 mol/mol), or the initiator, dibutyltin(IV) dimethoxide, was then added, and the polymerization mixture was heated at 90 °C for 17 h or at 40 °C for well-known periods of time, respectively. A sample was directly analyzed by wide-angle X-ray diffraction (WAXS). The polymerization product was then diluted with toluene and poured into heptane, and the precipitate was dried at 40 °C in vacuo. PCL was separated from the silicate before analysis by size exclusion chromatography (SEC), as follows. A 2 mL aliquot of the nanocomposite solution in toluene (10 g/L) was added dropwise to 4 mL of 1% LiCl solution in THF. The mixture was stirred for 2 days in order to exchange back the ammonium cations by Li^+ and to make the silicate hydrophilic again and separable from PCL by centrifugation (5 min/5000 rpm). PCL was recovered by precipitation from the supernatant into heptane.[7]

Molecular weight and molecular weight distribution of PCL were analyzed with a Waters 600 chromatograph equipped with a differential refractometer in THF at 40 °C. Polystyrene (PS) standards were used and the Mark−Houwink equations for PS ($K_{PS} = 1.25 \times 10^2$ mL/g; $a_{PS} = 0.717$) and for PCL ($K_{PCL} = 1.09 \times 10^2$ mL/g; $a_{PCL} = 0.6$) as well.

WAXS was carried out with a Powder diffractometer Siemens D 5000, (Cu Kα radiation with $\lambda = 1.54$ Å, 50 kV, 40 mA, Ni filter) at room temperature. Nanocomposite morphology was directly observed by transmission electron microscopy (TEM Philips CM100). Ultrathin sections were prepared with an Ultramicrotome Ultracut FC4E, Reichert-Jung.

Results and Discussion. 1. Bulk Polymerization of ϵ-CL in the Presence of MMT/OH and Tin(II) Octoate. Hydroxyl groups, which are known initiators for the ϵ-CL polymerization in the presence of $Sn(Oct)_2$,[7−10] have been attached to the MMT layers by exchange of the sodium cations by *N*,*N*-diethyl-*N*-3-hydroxypropyloctadecylammonium cations. The hydroxyl content has been calculated from the organic content of MMT/OH determined by thermogravimetric analysis (7.2×10^{-4} mol/g), which allows the molecular weight of PCL to be predicted from the OH/ϵ-CL molar ratio in the case of controlled/living polymerization (Table 1).

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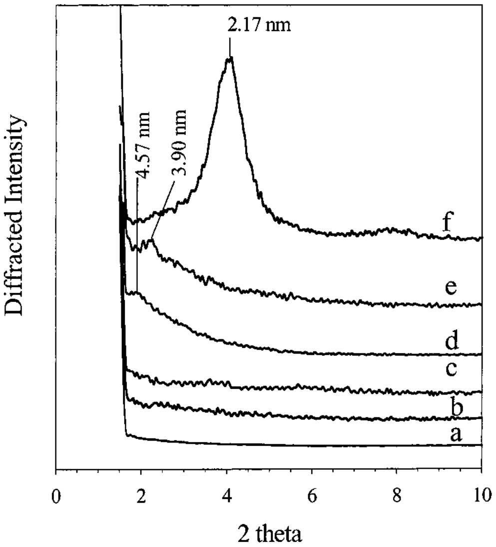

Figure 1. X-ray diffraction patterns for the PCL (MMT/OH) nanocomposites reported in Table 1: (a) 2% MMT/OH; (b) 3% MMT/OH; (c) 6% MMT/OH; (d) 15% MMT/OH; (e) 24% MMT/OH; (f) the original MMT/OH.

The ϵ-CL conversion at 90 °C for 17 h is higher than 95% and PCL shows a monomodal distribution, which is however broader compared to homogeneous bulk polymerization under the same conditions (1.5−1.6). The reason is the slower chain initiation because tin octoate has to diffuse in the clay galleries for reacting with the immobilized hydroxyl groups and forming tin alkoxide, the actual initiator ($\mathrm{R{-}OH} + \mathrm{Sn(Oct)_2} \rightarrow \mathrm{R{-}O{-}SnOct} + \mathrm{OctH}$). When the silicate content is higher than 3% (Table 1, entries 3−6), the agreement between theoretical and experimental M_n is consistent with a controlled polymerization having in mind that tin alkoxide has to be formed within a hardly purified silicate. Whenever the hydroxyl content is too low (entries 1 and 2, in Table 1), the experimental M_n is appreciably smaller than expected, because initiation is dominated by protic impurities more abundant than the hydroxyl groups. This undesirable situation should be improved by more efficient purification of the modified silicate.

Initiated from the hydroxyl groups attached to the inner silicate surface, PCL chains are tethered onto the MMT sheets, and beyond a certain M_n, they must be able to exfoliate the nanofiller. Consistently, Figure 1 shows that reflection peak at $2\theta = 4.21°$ for MMT/OH (d_{001} = of 2.17 nm; curve f) is shifted to lower values and is less intense as M_n is increased, e.g., $d_{001} = 3.9$ and 4.57 nm, for PCL chains of $M_n = 5500$ and 8500, respectively. The constitutive sheets of MMT/OH are thus increasingly separated by tethered PCL chains growing in the interlayer space. Finally, the reflection peak disappears for samples containing less than ca. 10% silicate ($M_n > 15\,000$), which indicates that the layered silicate is highly exfoliated, as confirmed by TEM (Figure 2).

2. Bulk Polymerization of ϵ-CL in the Presence of Cloisite 25A and Dibutyltin(IV) Dimethoxide. In this series of experiments, dibutyltin(IV) dimethoxide is a preformed initiator, and MMT is modified by alkylammonium cations without hydroxyl end groups, i.e., Cloisite 25A (*N*,*N*,*N*,*N*-dimethyldodecyloctadecylammonium montmorillonite). At constant silicate content (3 wt % with respect to ϵ-CL), the monomer/tin alkoxide molar ratio has been changed in order to modulate M_n in the 5000−50 000 range assuming a controlled polymerization.

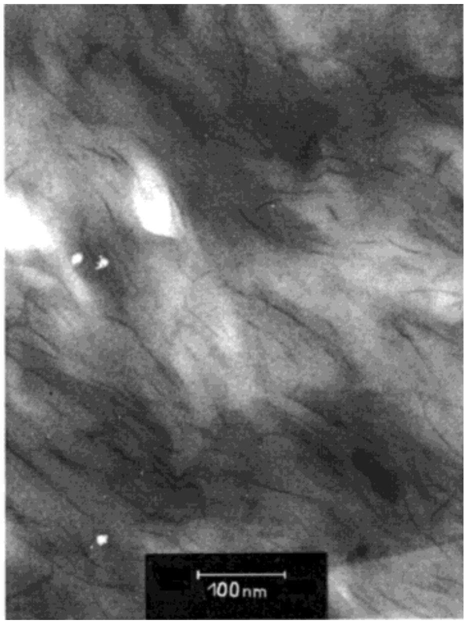

Figure 2. Transmission electron micrograph of the PCL nanocomposite containing 3% MMT/OH.

Table 2. Bulk Polymerization of ϵ-CL in the Presence of Cloisite 25A and Dibutyltin(IV) Dimethoxide[a]

entry	polym time (h)	M_n (calc)	M_n[b] (SEC)	M_w/M_n (SEC)
1	17	50 000	44 500	2.05
2	20	40 000	35 500	1.80
3	20	30 000	28 000	1.80
4	5	10 000	8500	2.15
5	3.5	5 000	4 500	1.90

[a] Bulk polymerization at 40 °C (except for entry 1, where $T = 60$ °C), 3 wt % of Cloisite 25A in ϵ-CL; monomer conversion higher than 95%. [b] Universal calibration curve.

Table 2 shows that the control imparted to the ϵ-CL polymerization by $\mathrm{Bu_2Sn(OCH_3)_2}$[11,12] is maintained in this study. M_n of PCL is indeed consistent with a polymerization basically free from irreversible chain-breaking reactions, i.e., intra- and intermolecular transesterification. M_n (SEC) is systematically smaller than M_n (calc) by 10% as result of a systematic error on the concentration of the initiator solution. Molecular weight distribution is monomodal but broad, more likely because part of the chains are initiated and grow (until silicate exfoliation) in the clay galleries rather than in solution.

The WAXS profile for the nanocomposite that contains chains of $M_n = 35\,500$ (entry 2 in Table 2) shows a peak that corresponds to $d_{001} = 2.65$ nm. PCL is thus merely intercalated, in sharp contrast to the exfoliation observed for chains of the same length initiated from the hydroxyl groups of MMT/OH (entry 2 in Table 1). Therefore, at constant composition (3 wt % of MMT), and quasi-complete conversion of ϵ-CL, the nanocomposite morphology strongly depends on whether all the chains are initiated in the silicate galleries and tethered to the surface or only part of them are formed and confined in the layered structure.

The intermediate situation in which MMT is modified by a mixture of inactive and hydroxyl-capped alkylammonium cations is under current investigation in order to modulate the nanocomposite structure more accurately.

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Supporting Information Available: One figure showing the X-ray diffraction patterns for the PCL/Cloisite25A nanocomposites reported in Table 2: (a) Cloisite 25A; (b) 3% C25A, $M_n = 8500$; (c) 3% C25A, $M_n = 35\,500$; (d) 3% MMT/OH (curve b, in Figure 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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