I. Preparation of PP-t-NH$_2$ and PP-t-NH$_3$$^+$Cl

The ammonium-group terminated isotactic-PP (PP-t-NH$_3$$^+$) was synthesized for previous studies, by Dong, Wang and Nakajima,\textsuperscript{1,4} and used here without further interventions. The synthesis details are summarized here as: The end-terminated polymer PP was prepared by the combination of an Exxon-Hoechst C$_2$-symmetric catalyst (rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO) and silane-protected styrene (4-{2-[N,N-bis (trimethylsilyl) amino]ethyl}styrene) acting as a chain transfer agent (Scheme S-1). First, PP-t-St-NSi$_2$ polymers were prepared by using 4-{2-[N,N-bis (trimethylsilyl) amino]ethyl}styrene as a chain transfer agent in propylene polymerization. In a typical reaction, a Parr 450 mL stainless autoclave reactor equipped with a mechanical stirrer was charged with 50 mL of toluene and 4.5 mL of MAO (10 wt.% in toluene) before purging with hydrogen (20 psi). Then 1.0 mL (0.125) of 4-{2-[N,N-bis (trimethylsilyl) amino]ethyl}styrene was injected into the reactor and 100 psi (3.24 M) of propylene was charged, bringing the total pressure to 120 psi at an ambient temperature (30 °C). About 1.25 × 10$^{-6}$ mol of rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$ catalyst in toluene solution was subsequently syringed into the rapidly stirred solution under propylene pressure to initiate the polymerization reaction. Additional propylene was fed continuously into the reactor to maintain a constant pressure (120 psi) during the course of polymerization. After 15 min of reaction at 30 °C, the reaction solution was quenched with methanol, then filtered and washed extensively with THF, and the resulting polymer was dried under vacuum at 50 °C for 8 hours. PP-t-St-NH$_2$ polymers were prepared from the PP-t-St-NSi$_2$ polymers by treating them with hydrogen chloride: PP-t-St-NSi$_2$ (2 g) was suspended in 50 mL of toluene at 50 °C before adding
dropwise 2 N hydrogen chloride ether solution. The mixture was stirred for 5 hours at 50 °C, and then poured into a 1 N methanolic NaOH solution. The polymer was collected by filtration, and washed with 1 M aqueous ammonia and water under a nitrogen atmosphere. The polymer was dried overnight at 50 °C under vacuum. The polymer yield was quantitative. The protonation of the terminal NH$_2$ towards PP-$\tau$-St-NH$_3^+$ was achieved simply by using excess HCl reagent in the above described reaction at the work-up step (and skipping the neutralization by NaOH) and was confirmed by titration.

For further details on the syntheses, we refer the interested reader to previous literature for the catalyst structure (pg 62 in ref. 3), the synthesis of the chain transfer agent (pg.56ff. of ref. 3), the $^1$H NMR spectra (of the chain transfer agent are shown in fig 3.1 on pg. 58 of ref. 3, and of the Si and NH$_2$ terminated PPs are given in Fig. 5 of ref. 2 or in Fig. 3.4 of ref. 3), and the detailed characterization of the final and intermediate products of the reaction (Table 2 in ref. 2 or Table 3.1 of ref. 3).
II. Characterization of PP-t-NH$_3^+$ / Montmorillonite Nanocomposite

Static melt intercalation was employed to prepare a PP-t-NH$_3^+$Cl$^-$/Na$^+$- montmorillonite nanocomposites of Series 2. Specifically, PP-t-NH$_3^+$Cl$^-$ (M$_n$ = 58,900, M$_w$ = 135,500 g/mol) dried powder and Na$^+$-mmt were first mixed and ground together, at a 90/10 weight ratio, in a mortar and pestle, at ambient temperature. The XRD pattern of this simple mixture shows a (001) peak at 2θ~7, corresponding to a Na$^+$-mmt interlayer structure with a $d_{001}$-spacing of 1.26 nm (Figure 1). The mixed powder was then heated in a vacuum oven at 180-190 °C for 2 h under a nitrogen atmosphere. The resulting PP-t-NH$_3^+$Cl$^-$/Na$^+$-mmt concentrate shows a featureless XRD pattern$^1$ (Figure S-1), which corresponds, as observed by bright field TEM, to a well-dispersed morphology with some clustering of mmt fillers, which are well separated and without a parallel stacking (Figure S-2). Application of shear, such as blending in an extruder or twin-head kneader, most often results in an intercalated structure with a pronounced $d_{001}$ XRD reflection. This same trend seems also to manifest upon dilution of the PP-t-NH$_3^+$/Na$^+$-montmorillonite by unfunctionalized PP. Finally, static melt heating of PP-t-NH$_3^+$Cl$^-$ with dimethyl-dioctadecyl-ammonium modified mmt also produces a nanocomposite with featureless XRD and similar morphologies –as observed by TEM– with the PP-t-NH$_3^+$Cl$^-$/Na$^+$-mmt systems.$^3$
Figure S-1  Wide angle X-Ray diffraction patterns of the PP-$t$-NH$_3$$^+$Cl$^-$ / Na$^+$ mmt mixture at ambient temperature, after quiescent annealing at 180 °C for 2 h (concentrate, HN188 M/B), and after dilution by quiescent melt-intercalation with unfunctionalized PP (nanocomposites, PP / PP-$t$-NH$_3$$^+$ / 5 wt% mmt , HN191 and HN192).
Figure S-2. Bright field TEM micrographs of the nanocomposite based on the PP-t-NH$_3^+$ / mmt concentrate: (a) At low magnification (scale bar is 250nm) the structure seems mostly exfoliated with a few ‘disordered’ clusters of montmorillonite; adopted with permission from ref. Error! Bookmark not defined., Macromolecules, 2003, 36, 8919, Copyright 2003, American Chemical Society. (b) A higher magnification of one of these ‘disordered’ clusters is also shown (scale bar is 50nm).
References and Notes


   [http://etda.libraries.psu.edu/theses/approved/WorldWideIndex/ETD-988/](http://etda.libraries.psu.edu/theses/approved/WorldWideIndex/ETD-988/)
   
   Chapter III of this thesis, which is quoted above and which describes the synthesis details, was published in part in Macromolecules (see ref. 1, above).


5. The existence of any non protonated end-functionalized PPs (PP-\text{t-NH}_2) between the PP-bearing montmorillonite fillers cannot be excluded, but such “free” PP polymers are not expected to cause any substantial effects in the nanocomposites (which are in most cases further diluted by unfunctionalized PP, cf. HN191 and HN192, Table 1 in this article).