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A Two-Step Reactive Extrusion Process for the Synthesis of Graft Copolymers with Polyamides as Grafts

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1. Introduction. Today polymer blends are an important family of polymer materials. Whether or not an industrial development of a polymer blend is successful depends very often on whether a method is available to make a compatibilizer, i.e., a block or graft copolymer, in large quantities and in an economically feasible way. In practice, such a copolymer is either synthesized separately and then added to the polymer blending system (nonreactive compatibilization) or generated in situ by interfacial reactions between mutually reactive polymers during blending (reactive or in situ compatibilization).[1]

Many chemical routes cannot be followed easily or in an economically feasible fashion to synthesize block or graft copolymers for industrial compatibilization purposes. The one that has been frequently followed consists of reacting two mutually reactive polymers (reactive compatibilization). However, this method hardly leads to the formation of pure copolymers when the reactive polymers are immiscible, unless the chain length of at least one of them is relatively short, or once formed at the interfaces the copolymer chains walk away. Limited amounts of copolymer formed by interfacial reactions can be explained as follows. First, the interfacial volume available for reaction between two immiscible polymers is often very small, even under intense mixing; second, the intrinsic reactivity of two mutually reactive groups attached to polymer backbones can be much smaller than their small-molecule analogues because of steric hindrance effects.

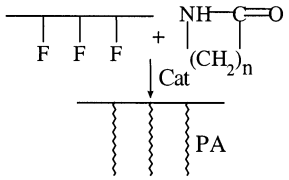

Figure 1. Formation of a graft copolymer with PA as grafts by polymerization of lactam onto a polymer backbone via initiating sites F.

This paper reports on a chemical route that can be of great interest for the compatibilization of polyamide (PA)-based polymer blends, a very important family of commercial materials. The basic idea is that, instead of reacting the terminal functional groups of polyamides with their polymer component partners, the monomers of the polyamides are polymerized onto their partners. This is possible if the latter contain functional groups such as isocyanate capable of initiating the polymerization of lactams in the presence of a catalyst such as sodium caprolactam (NaCL). Such polymers are called macroactivators. Figure 1 shows schematically this chemical route: lactam is polymerized onto a polymer backbone via initiating sites moieties F along its backbone. This grafting polymerization route is expected to generate graft copolymers with very high purity. This is because, unlike reactive compatibilization, both the interfacial area limitation and steric hindrance effects are much reduced or totally absent.

The principle of chemical route in Figure 1 per se is not new. In fact, it was used some 30 years ago to synthesize graft copolymers with polystyrene and polyethylene as backbones and PA6 as grafts.[2,3] To that end, acrylic esters incorporated in polystyrene and polyethylene by free radical copolymerization were used as the macroactivators. However, this type of macroactivator often leads to cross-linking. Moreover, its activation capacity is relatively low. Therefore, the time necessary for the polymerization to go to completion is long

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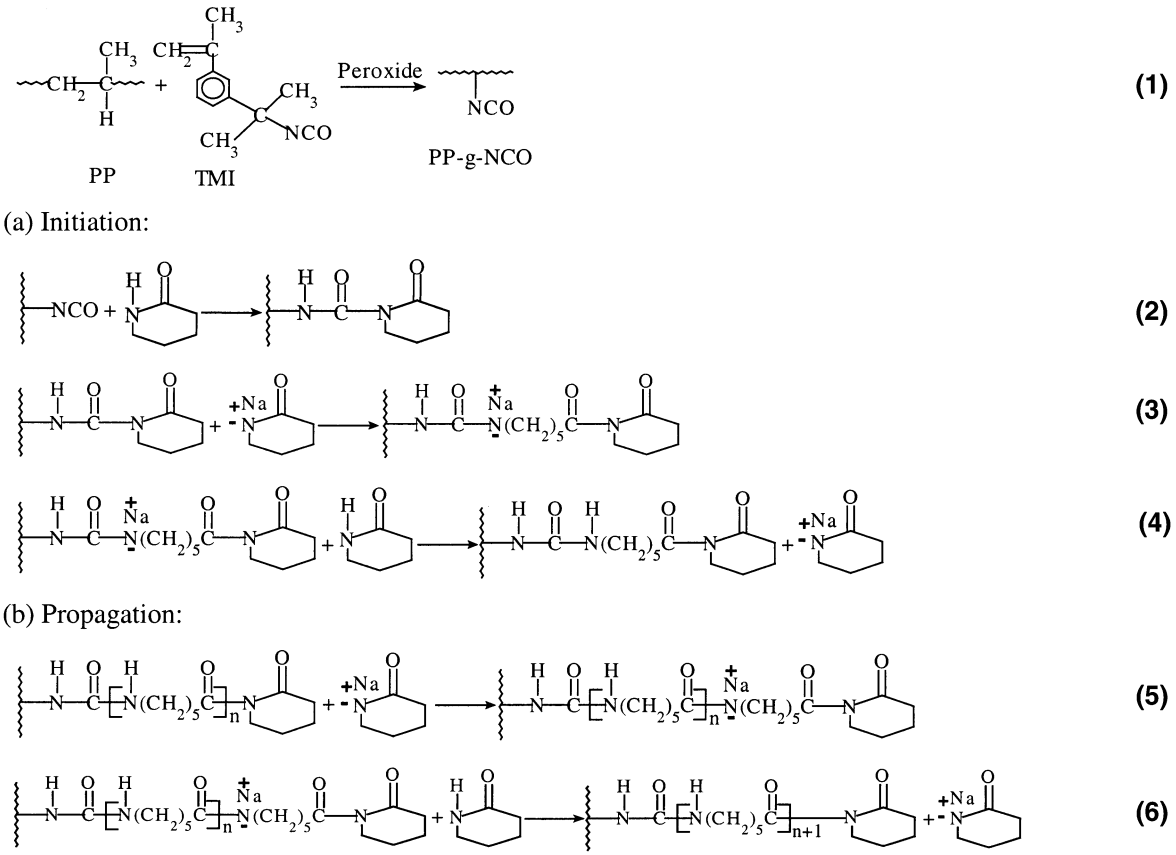

Figure 2. Mechanism of PP-*g*-PA6 graft copolymer formation.

compared to the mean residence time of a typical reactive extrusion process (less than a few minutes). The latter is our ultimate goal. The aim of our study was to replace (meth)acrylic ester-bearing polymers by isocyanate-bearing ones. The latter are expected to have a greater activating capability. Moreover, there would be no cross-linking. The idea of using isocyanate-bearing polymers would not have been feasible some 15 years ago because of the lack of isocyanate-bearing vinyl monomers. In the mid-1980s, a unique monomer of this kind, 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI), became available.[4] It can be either copolymerized with various other vinyl monomers such as styrene[4−6] or attached to polymer backbones by free radical grafting.[7−9] The latter technique is very useful for polyolefins whose monomers could not be copolymerized easily with TMI. This paper reports on a two-step method for the synthesis of pure graft copolymers of polypropylene and polyamide 6 (PA6). Such graft copolymers, denoted as PP-*g*-PA6, are of great industrial potential. The lactam corresponding to PA6 is ϵ-caprolactam (CL). Its chemical basis is shown in Figure 2. This method has two unique features in terms of the control of the molecular architecture of PP-*g*-PA6. The number of PA6 grafts per PP chain should be equal to that of the isocyanate group per PP chain if all isocyanate moieties react with CL. The length of PA6 grafts is dictated by the molar ratio between CL and the NCO group in the system.

2. Experimental Section. a. Materials. Three PP-*g*-NCO macroactivators containing different NCO contents were used in this work. They were made in our laboratory by attaching TMI onto PP through melt free radical grafting according to the procedures described elsewhere.[10] The weight percentages of the NCO group attached onto the PP backbone were measured experimentally. They were 0.27, 0.69, and 1.34 wt %. The corresponding PP-*g*-NCO will be denoted as PP-*g*-NCO0.27, PP-*g*-NCO0.69, and PP-*g*-NCO1.34, respectively. ϵ-Caprolactam (CL) was purchased from Aldrich and was recrystallized from cyclohexane before use. Sodium caprolactam (NaCL) was used as the catalyst. It was actually a mixture of NaCL (15.9 wt %) and CL (84.1 wt %).

b. Synthesis of PP-*g*-PA6 Graft Copolymers. Desired amounts of PP-*g*-NCO, CL, and NaCL were mixed in a cup and then charged to an internal mixer of type Haake Rheocord, which was preheated to 215 °C, unless specified otherwise. The rotation speed of the rollers in the mixing chamber was 64 rpm. Products were taken out from the mixing chamber after 10 min of reaction and quenched immediately in liquid nitrogen in order to stop the reaction and reduce the loss of CL for subsequent polymer yield determination.

c. Determination of Polymer Yield. A known amount of the reaction product, W_0, was pressed into a thin film. The monomer and catalyst residues therein were removed by Soxhlet extraction for 36 h using water as solvent. After exaction, the film was dried in a vacuum oven at 100 °C overnight and then its weight, W, measured. The polymer yield, y, was defined as

$$y\ (\%) = \frac{W}{W_0} \times 100$$

3. Results and Discussion. In what follows, two key questions are to be addressed: (1) Does a mixture of PP-*g*-NCO/CL/NaCL undergo polymerization? If it does, what is the polymer yield? (2) Is the product formed a

Table 1. Polymerizability of Different Systems (Set Temperature, 215 °C; Polymerization Time, 10 min)

trial	polymerization system	composition by weight	polymer yield (%)	remark
1	CL/NaCL	100/4	0	no polymerization detected
2	CL/NaCL/Ph-NCO	100/4/3	95	homo-PA6 expected
3	CL/NaCL/PP-*g*-NCO0.27	25/75/4	87.4	PP-*g*-PA6 expected
4	CL/NaCL/PP-*g*-NCO0.69	25/75/4	89.5	PP-*g*-PA6 expected
5	CL/NaCL/PP-*g*-NCO1.34	25/75/4	92.9	PP-*g*-PA6 expected
6	CL/NaCL/PP-*g*-NCO0.27	50/50/4	92.2	PP-*g*-PA6 expected
7	CL/NaCL/PP-*g*-NCO0.69	50/50/4	94.0	PP-*g*-PA6 expected
8	CL/NaCL/PP-*g*-NCO1.34	50/50/4	95.6	PP-*g*-PA6 expected

pure PP-*g*-PA6 graft copolymer, a homopolyamide 6 (homo-PA6), or a mixture of both?

a. Polymerizability of Different Systems and Their Polymer Yields. Eight trials were carried out at 215 °C for 10 min. Their compositions and polymer yields are shown in Table 1. The following comments can be made: (1) CL did not polymerize in the presence of NaCL as catalyst without activator (trial 1). (2) In the presence of NaCL as catalyst and Ph−NCO (phenyl isocyanate) as activator, CL polymerized with a polymer yield of 95% (trial 2). This shows that an activator was necessary for CL to polymerize under the specified conditions. The final product was expected to be a homopolyamide 6 (homo-PA6). (3) When the microactivator Ph−NCO was replaced by the macroactivator PP-*g*-NCO, the polymerization of CL occurred, too. The polymer yield ranged from 88 to 96%, depending on the composition and the NCO content in the PP-*g*-NCO (trials 3−8). The higher the NCO content in the PP-*g*-NCO, the higher the polymer yield. Thus, the activation capacity of the PP-*g*-NCO seemed to be similar to that of a microactivator like Ph−NCO. (4) In view of the above facts, the products obtained from trials 3−8 had to be pure PP-*g*-PA6 graft copolymers. Its formation would follow the mechanism depicted in Figure 2.

The above facts seem to be strong enough to show that that polymerization of CL in the presence of NaCL as catalyst and PP-*g*-NCO as activator yielded a PP-*g*-PA6 graft copolymer with high purity and little homo-PA6 (if there was any). In what follows, supplementary results are provided to further confirm the above statement. They are concerned with two aspects: validation of the mechanism of formation of the PP-*g*-PA6 graft copolymer depicted in Figure 2 and evaluation of the purity of the graft copolymers obtained.

b. Validation of the Mechanism of Formation of PP-*g*-PA6 Graft Copolymers. According to the mechanism depicted in Figure 2, PP-*g*-PA6 cannot be formed only if CL does not react with PP-*g*-NCO to form the corresponding *N*-acyllactam (reaction 2), making it electrophilic (activation of CL). Did CL react with PP-*g*-NCO and how fast? To answer that question, a mixture of PP-*g*-NCO1.34 and CL in equal amounts (trial 8 without NaCL) was mixed in the mixer at 215 °C. No polymerization was detected after 10 min. However, the expected activation reaction between PP−NCO and CL (reaction 2) did take place and went very fast. That was confirmed by comparing the FTIR spectrum of PP-*g*-NCO1.34 with that after 2 min of mixing with CL (Figure 3). In the spectrum of PP-*g*-NCO1.34, there was a peak at 2255 cm^{-1}, corresponding to the NCO group. After 2 min of mixing with CL, that peak disappeared completely, indicating that the NCO group had reacted with CL. At the same time, two new peaks appeared at 3300 and 3066 cm^{-1}, corresponding to the formation of the expected acyllactam[11] (reaction 2). Those results support the mechanism of formation of the PP-*g*-PA6 graft copolymer depicted in Figure 2.

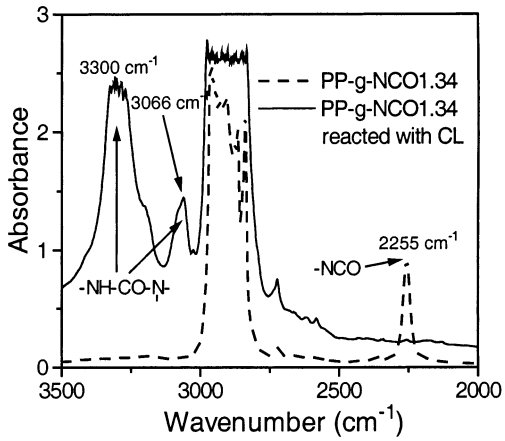

Figure 3. FTIR spectrum of PP-*g*-NCO1.34 (dotted line) and that after reaction with CL (solid line).

c. Evaluation of the Purity of PP-*g*-PA6 Graft Copolymers. Five different analytical techniques were tried to evaluate the purity of the PP-*g*-PA6 graft copolymers obtained from trials 3−8: nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), selective solvent extraction, differential scanning calorimetry (DSC), and efficiency of compatibilization. The first two techniques, i.e., NMR and SEC, were unsuccessful because of the lack of finding good solvents capable of dissolving those polymers, even in high temperatures. Solid-state NMR is being explored. The last three all provided information supportive of the formation of pure PP-*g*-PA6 graft copolymers. However, none of them was able to exclude completely the presence of homo-PA6 in those products.

The selective solvent extraction technique consisted in using xylene and formic acid as extracting solvents. The first one dissolves PP at temperatures above 80 °C and the second one PA-6 at room temperature. After successive extraction in xylene and then in formic acid, 70−90% of the initial weights of those products were not dissolved. They corresponded to pure PP-*g*-PA6 graft copolymers. The fact that some of those products were dissolved in those solvents does not necessarily mean that they were not pure graft copolymers. Those dissolved in xylene could eventually be pure PP-*g*-PA6 graft copolymers, which were very rich in PP and very poor in PA6. Similarly, those dissolved in formic could eventually correspond to pure PP-*g*-PA6 graft copolymers, which were very poor in PP and very rich in PA6.

Figure 4 compares the DSC diagrams of three products during cooling: trial 1 (homo-PA6), a product from the polymerization of CL/NaCL/Ph−NCO/PP (50/4/3/50) denoted as trial 9 and trial 8 (pure PP-*g*-PA6 expected). The product from trial 9 was expected to be a mixture of homo-PA6 and PP. In the case of trial 9, there were two crystallization peaks at 158 and 100 °C. They corresponded to the homo-PA6 and PP, respectively. In

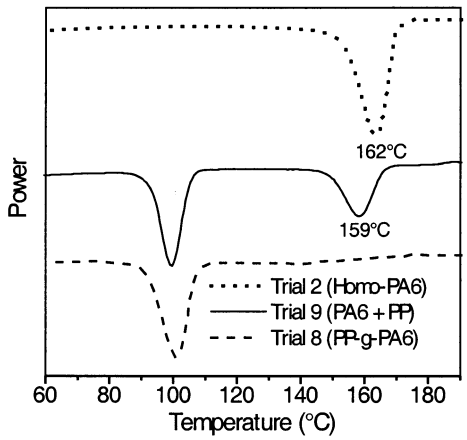

Figure 4. DSC diagrams of three different products during cooling: trial 1 (homo-PA6), trial 8 (pure PP-*g*-PA6 expected), and trial 9 (a mixture of homo-PA6 and PP expected).

the case of trial 8, the crystallization peak corresponding to PA6 disappeared completely. Those results are in favor of the formation of pure PP-*g*-PA6 graft copolymers with trials 3−8.

The last test to verify the graft copolymer formation was to compare the efficiency of compatibilization of the products obtained from trials 8 and 9. This was done by using them as compatibilizers for the melt blending of a mixture of premade PA6 and PP (20/80 by weight) in the mixer. The particle size of the PA6 phase of the PA6/PP (20/80) blend was 2.5 μm. Upon addition of 2% of the product from trial 9 to the blend, it remained unchanged, indicating that it had no compatibizing ability. By contrast, when 2% of the product of trial 8 was added, it was reduced to 0.8 μm. Therefore, it is evident that the product obtained from trial 8 contained PP-*g*-PA graft copolymer.

In summary, on the basis of the results reported above, there is no doubt that the polymerization of CL in the presence of NaCL as catalyst and PP-*g*-NCO as macroactivator leads to the formation of PP-*g*-PA6 graft copolymer. However, it has not been able to exclude completely the presence of homopolyamide 6 in the product or to confirm its presence.

4. Conclusion. This paper has reported on a two-step method for synthesizing pure graft copolymers with polyamides as grafts. The first step is to incorporate 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI) in a polymer chain by copolymerization or free radical grafting. The second is to use the corresponding NCO-bearing polymer as macroactivator. The NCO moieties are capable of initiating the polymerization of lactams such as ϵ-caprolactam, from which the corresponding polyamide grafts grow. The polymerization yields are high. Nevertheless, characterization of the polymers at the macromolecular level remains a great challenge. In any event, this method should be applied easily to other lactams. It should also be practiced easily by reactive extrusion processes.

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