

# Kinetics of the *In Situ* Polymerization and *In Situ* Compatibilization of Poly(propylene) and Polyamide 6 Blends

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**ABSTRACT:** In previous articles, we reported on a novel reactive extrusion process to obtain a compatibilized blend of polymer A and polymer B. It consisted in polymerizing the monomer of polymer A in the presence of polymer B. A fraction of the latter contained initiating sites from which the polymerization of monomer A took place. As such, both polymer A and a graft copolymer of polymer A and polymer B were formed in the process. That process was called *in situ* polymerization and *in situ* compatibilization of polymer blends. Its feasibility was illustrated for *in situ* polymerized and *in situ* compatibilized poly(propylene) and polyamide 6 (PP/PA6) blends. The latter were prepared by activated

anionic polymerization of  $\epsilon$ -caprolactam (CL) in the presence of PP in a batch mixer and a twin-screw extruder, respectively. A fraction of the PP contained isocyanate groups from which PA6 grafts were formed. Sodium caprolactam (NaCL) was used as the catalyst and a diisocyanate compound was used as the activator. In this study, we report on the effects of various parameters on the kinetics of the anionic polymerization of CL in the presence of PP. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1498–1504, 2004

**Key words:** compatibilization; poly(propylene); polyamides; reactive extrusion; blends

## INTRODUCTION

Polymer blends have found many applications. Traditionally, they are obtained by melt blending of polymers. Because most polymer pairs are thermodynamically immiscible, compatibilization is often required. It can be achieved by using premade block or graft copolymers. The latter can also be formed directly during melt blending, which is commonly called reactive blending, reactive compatibilization, or *in situ* compatibilization.<sup>1</sup> For example, blends of poly(propylene) (PP) and polyamide 6 (PA6) can be compatibilized using a maleic anhydride modified PP (PP-g-MA) as an interfacial agent precursor.<sup>2</sup> The latter can react with the terminal amine group of PA6 forming a graft copolymer of PP and PA6, designated as PP-g-PA6, at the interface between PP-g-MA and PA6.

In previous articles,<sup>3,4</sup> we reported on a novel process to obtain compatibilized blends of polymer A and polymer B. It consisted in polymerizing the monomer of polymer A in the presence of polymer B. A fraction of polymer B chains bore initiating sites either at the chain end(s) or along the chains, from which polymer A chains could grow. In that way, both the polymerization of the monomer of polymer A and the formation of a copolymer of A and B took place simultaneously, leading to *in situ* polymerized and *in situ* compatibilized A and B blends. The feasibility of the process was illustrated by polymerizing  $\epsilon$ -caprolactam (CL) in the presence of PP in a batch mixer and a twin-screw extruder, respectively. Sodium caprolactamate (NaCL) was used as a catalyst and a diisocyanate as an activator. A fraction of the PP chains bore isocyanate moieties, which acted as initiating centers from which PA6 chains grew. In that way, both PA6 and PP-g-PA6 were produced during polymerization, leading to the formation of PP/PA6 compatibilized blends of varying composition and morphology. The isocyanate-bearing PP was obtained by free-radical grafting of 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzene isocyanate (TMI) onto an inert PP, designated as PP-g-TMI.<sup>5</sup> The underlying principle of that *in situ* polymerization and *in situ* compatibilization of PP/PA6 blends can be summarized as follows:

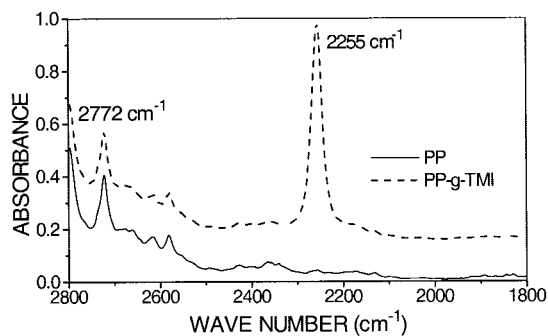
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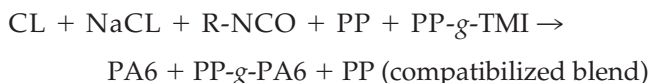
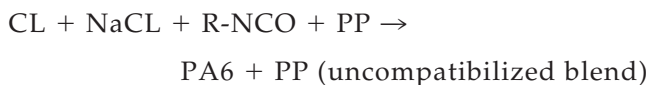
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**Figure 1** FTIR spectra of PP before (solid line) and after (dashed line) the free-radical grafting reaction with TMI.



Compared to the classical *in situ* compatibilization strategies, the above *in situ* polymerization and *in situ* compatibilization approach has additional chemical and processing parameters that can affect the resulting blend. The objective of this study was to investigate the effects of some of these parameters on the kinetics of such polymerization systems. A batch mixer was used as a mixer/reactor.

## EXPERIMENTAL

### Materials

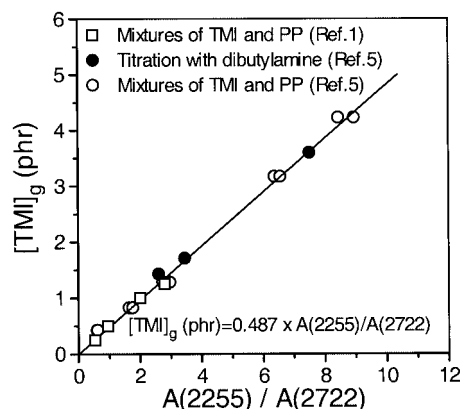
The PP used in this study was a commercial grade of Borealis (Stathelle, Norway), in the form of porous pellets [number- and mass-average molar masses: 280,000 and 62,000 g/mol, respectively; melt flow index: 3.5 g/10 min at 230°C under 2.16 kg (ASTM 1238L); melt temperature: 163°C]. The advantage of being porous allowed the PP to absorb large amounts of liquid free-radical grafting reagents. 3-Isopropenyl- $\alpha,\alpha$ -dimethylbenzene isocyanate (TMI) and styrene (St) were purchased from Aldrich (Milwaukee, WI) and used without further purification. TMI has a formula mass of 201.27 g/mol and is a liquid at room temperature. Its boiling temperature is about 270°C/760 mm Hg. 2,5-Dimethyl-2,5-di(*tert*-butylperoxy)-hexane (DHBP) was used as a free-radical initiator for the functionalization of PP with TMI. Its half-lifetime is around 6 s at 200°C.

The reagents used for the anionic polymerization of CL consisted of CL (melting point:  $\sim$  71°C/760 mm Hg; boiling point:  $\sim$  137°C/10 mm Hg), a catalyst

(NaCl), and an activator (caprolactam blocked hexamethylene diisocyanate) were kindly supplied by DSM (Geleen, The Netherlands). The catalyst was a mixture of NaCl and CL (C-10 katalysator). It was in the form of flakes and contained 1.4 mol NaCl/kg CL. The activator was a mixture of caprolactam blocked hexamethylene diisocyanate and CL (V5/C-20 Aktivator). It was powdery and contained 2.0 mol NCO/kg CL. For the sake of simplicity, in what follows, the NaCl and activator designations will refer to the catalyst and activator mixtures, respectively.

### Preparation of PP-g-TMI

The experimental procedures for the free-radical grafting of TMI and purification and characterization of TMI-modified PP were the same as those described in previous articles.<sup>1,3</sup> The reaction was carried out in a Rheocord Haake mixer (50 cm<sup>3</sup>; Haake, Bersdorff, Germany) in which two sigma rotors rotated in opposite directions at 64 rpm to ensure mixing. For a typical experimental run, PP pellets (40 g) were mixed mechanically in a cup with TMI, St, and the peroxide for about 15 min. The resulting mixture was then charged to the mixer, which was preheated to 200°C. The TMI-modified PP was collected after 10 min of reaction. It was then purified by dissolution in boiling xylene and precipitation in acetone at room temperature to remove both monomer residues and polymerized TMI species. The grafting yield of TMI was measured by FTIR using purified PP-g-TMI films ( $\sim$  100  $\mu$ m). The grafting of TMI onto PP was characterized by the appearance of a peak at 2255 cm<sup>-1</sup> corresponding to the isocyanate group of TMI (Fig. 1). That peak was thus chosen to quantify TMI's grafting yield. The peak at 2772 cm<sup>-1</sup> characteristic of PP was chosen as an internal reference. The relationship between TMI's



**Figure 2** Relationship between TMI's grafting yield in PP-g-TMI,  $[\text{TMI}]_g$ , and the IR absorbency ratio between the peaks at 2255 and 2722 cm<sup>-1</sup>,  $A(2255)/A(2722)$ . phr, parts per hundred parts of resin (PP).

TABLE I  
Compositions in PP, TMI, St, and DHBP Used for  
Preparing PP-g-TMI Samples and Corresponding  
Contents of TMI

| PP-g-TMI designation | PP/TMI/St/DHBP   | Grafted TMI (phr) |
|----------------------|------------------|-------------------|
| PP-g-TM10.5          | 100/2.5/2.5/0.63 | 0.5               |
| PP-g-TMI1.1          | 100/5.0/5.0/1.25 | 1.1               |
| PP-g-TM12.5          | 100/10/10/2.50   | 2.5               |

grafting yield and the peak absorbency ratio between the peak at  $2255\text{ cm}^{-1}$  and that at  $2772\text{ cm}^{-1}$  is shown in Figure 2. Table I shows the chemical compositions of the free-radical grafting system used for preparing the PP-g-TMI samples used in this study and the TMI grafting yields.

### Anionic polymerization kinetics

Two series of activated anionic polymerization experiments were carried out in the batch mixer: (1) polymerization of CL/NaCL/Activator/PP systems and (2) polymerization of CL/NaCL/Activator/PP + PP-g-TMI systems. The PP-g-TMI samples used were purified according to the procedure described above. The first series of experiments yielded PP/PA6 uncompatibilized blends and the second series, compatibilized PP/PA6 blends. Before polymerization, powdery mixtures of NaCL, activator, and CL were first mixed with the PP or PP + PP-g-TMI. They were then introduced to the mixing chamber preheated at a desired temperature. Samples were taken from the mixing chamber after 10 min of reaction and quenched quickly in nitrogen to stop further reaction.

The polymerization kinetics was followed up by the torque change of the polymerization systems. During polymerization, as CL was converted to PA6 and PP-g-PA6 (if PP-g-TMI was present), the viscosity and therefore the torque of the polymerization system increased. The rate of the torque increase was then a good indication of the rate of polymerization.

### Characterization of polymerized CL systems

The morphology of PP/PA6 blends resulting from the polymerization of CL was analyzed by scanning electron microscopy (SEM) on fresh cryofractured and gold-sputtered surfaces of the blends. Their melting and recrystallization behavior was examined using differential scanning calorimetry (DSC). Samples were subjected to the following thermal cycle: they were heated from 50 to  $250^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , maintained at  $250^\circ\text{C}$  for 10 min, then cooled to  $50^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  (recrystallization) and heated again to  $250^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  (melting).

## RESULTS AND DISCUSSION

### Effect of the presence of PP on the polymerization kinetics of CL

Figure 3 shows the torque versus mixing time curves of the CL/NaCL/Activator/PP systems containing different mass percentages of PP. For the system that did not contain the PP (its mass percentage was zero), the torque value was very small at time zero. It increased very rapidly after about 1.5 min of mixing, indicating that the polymerization started. It reached a maximum 1 min later and then decreased very rapidly, indicating the end of polymerization. The entire polymerization process lasted only about 2 min.

When the mass percentage of PP in the system was very high, the occurrence of the polymerization was delayed. This is illustrated by the torque versus mixing time curve of the CL/NaCL/Activator/PP (30/3/3/70) system. Again the torque was very small at time zero. As the system was being heated up, the PP pellets started to melt and consequently the torque started to increase. The latter reached a maximum after about 0.5 min of mixing. It then decreased, indicating that the PP melting process was ending. The torque started to increase again 2 or 3 min later, which corresponded to the start of the polymerization process. These results show that for this polymerization system containing a high mass percentage of PP, the polymerization process began only after 3 min of mixing.

When the mass ratio between PP and CL was smaller than 50/50, PP's melting process and CL's polymerization process took place simultaneously. In other words, both processes overlapped. Moreover, the polymerization kinetics approached that of the pure CL without PP.

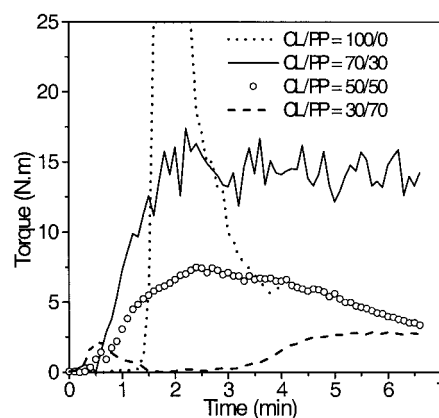
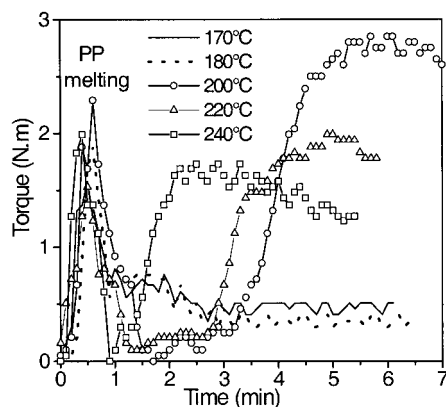


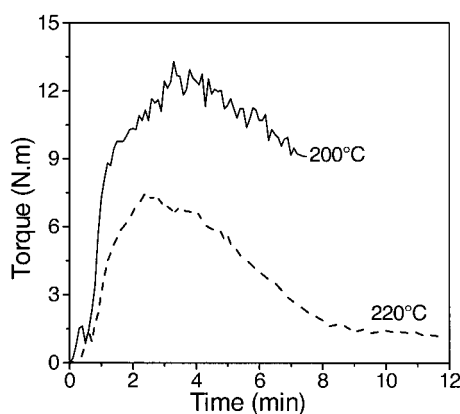
Figure 3 Effect of the CL/PP mass ratio on the polymerization kinetics (torque) of the CL/NaCL/Activator/PP (100-x/3/3/x by mass) system. Set temperature =  $220^\circ\text{C}$ .



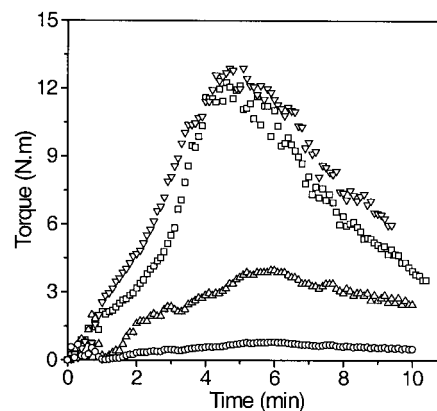
**Figure 4** Temperature effect on the polymerization kinetics (torque) of the CL/NaCL/Activator/PP (30/3/3/70 by mass) system.

#### Temperature effect on the polymerization kinetics of the CL/NaCL/Activator/PP system

Two compositions were used: CL/NaCL/Activator/PP = 30/3/3/70 or 50/3/3/50 by mass. The torque–mixing time curves of these two compositions at different temperatures are shown in Figures 4 and 5, respectively. For the first composition, the first peaks in the torque versus mixing time curves corresponded to PP's melting process. Thereafter, the torque either remained very small or increased, depending on the set temperature. When the latter was below 180°C, the torque values were small for the remaining mixing time. This suggests that the polymerization of CL did not occur or was incomplete within the reaction time scale (6 min). As a matter of fact, at 180°C the conversion of CL to PA6 was less than 50%. When the set temperature was raised to 200°C, the polymerization started to proceed after about 3 min of mixing, as indicated by the rapid torque increase. The torque reached a plateau at about 5 min of mixing, indicating



**Figure 5** Temperature effect on the polymerization kinetics (torque) of the CL/NaCL/Activator/PP (50/3/3/50 by mass) system. Solid curve: 200°C; dashed curve: 220°C.



**Figure 6** Effect of the amount of the activator on the polymerization kinetics of the CL/Cat/Activator/PP (50/3/ $x$ /50 by mass) polymerizing system. Amount of the activator = (○) 0, (△) 1, (□) 2, (▽) 3 parts.

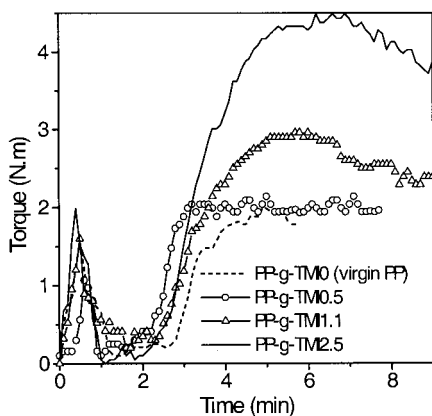
that the polymerization was completed or close to completion at that moment. The conversion of CL to PA6 was higher than 90%. The entire polymerization process lasted about 2 min under the specified conditions. A further increase in the set temperature further shortened the delay time after which the polymerization began. When the set temperature was 240°C, CL started to polymerize after less than 1.5 min of mixing. It is also noted that the torque value decreased in the following order: 200 < 220 < 240°C. This is because an increase in the set temperature led to a decrease in the viscosity of the polymerized system.

For the CL/NaCL/Activator/PP (50/3/3/50 by mass) composition, the torque versus mixing time curves obtained at 200 and 220°C show that the occurrence of PP's melting process and CL's polymerization process overlapped. The latter ended after 3 or 4 min of mixing.

#### Effect of the activator concentration

The polymerization of the CL/NaCL/Activator/PP (50/3/ $x$ /50) systems with varying mass percentage in the activator was carried out at 220°C. Their torque versus mixing time curves are shown in Figure 6. The higher the amount of the activator in the system, the greater the extent of polymerization. Little polymerization occurred without activator. The presence of 1 part of the activator somewhat increased the extent of polymerization, although it remained low. By contrast, when the amount of the activator was 2 or 3 parts, the torque increased very rapidly and the maximum torque value was very high, thus indicating that the polymerization proceeded very rapidly and the conversion of CL to PA6 was high.



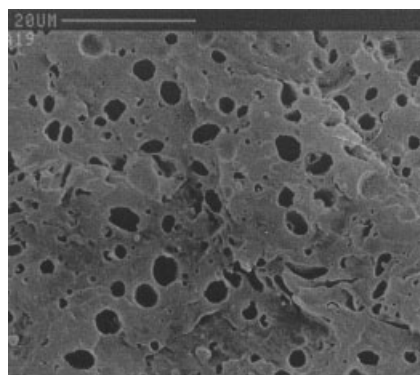


**Figure 7** Effect of TMI's content in the PP-g-TMI on the evolution of the torque as a function of time of the CL/Cat/Activator/PP + PP-g-TMI (30/3/3/30 + 40) polymerizing system. Set temperature = 220°C.

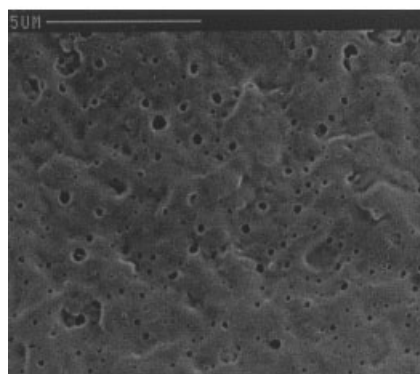
#### Effect of the presence of PP-g-TMI on the polymerization kinetics

The composition of the CL/Cat/Activator/PP + PP-g-TMI was 30/3/3/30 + 40 by mass. The PP-g-TMI was the PP-g-TMI0 (virgin PP not modified with TMI), PP-g-TMI0.5, PP-g-TMI1.1, or PP-g-TMI2.5. The corresponding torque versus mixing time curves are shown in Figure 7. The polymerization of CL began after about 2 or 3 min of mixing, irrespective of TMI's content in the PP-g-TMI. However, the maximum torque value depended substantially on TMI's content in the PP-g-TMI. The higher the content of TMI in the PP-g-TMI, the higher the maximum torque value. This is because an increase in TMI's content led to an increase in the PP-g-PA6 graft copolymer formation. This was confirmed by the SEM micrographs of the PP/PA6 blends (Fig. 8). The number-average diameter of the PA6 particles decreased with increasing content of TMI in the PP-g-TMI (Fig. 9). It was 3.5  $\mu\text{m}$  in the absence of PP-g-TMI, 1.1  $\mu\text{m}$  in the presence of the PP-g-TMI0.5, and 0.11 in the presence of the PP-g-TMI2.5.

Figure 10 shows the DSC thermograms of the four PP/PA6 blends obtained under the conditions specified in Figure 7. During heating [Fig. 10(a)], two distinct peaks at 160 and 209°C were observed. They corresponded to the melting of PP and PA6, respectively. Upon cooling [Fig. 10(b)], for the uncompatibilized blend resulting from the polymerization of the CL/Cat/Activator/PP (30/3/3/70), there were two peaks, one at 115°C and another at 165°C. They corresponded to the recrystallization of the PP and PA6, respectively. For the other three blends, there was only one peak at 115°C, which corresponded to the recrystallization of the PP phase. That of the PA6 phase was invisible, which is typical of a PP/PA6 compatibilized blend.<sup>2</sup> A plausible explanation is that upon compatibilization, the PA6 domains decreased in size. Conse-



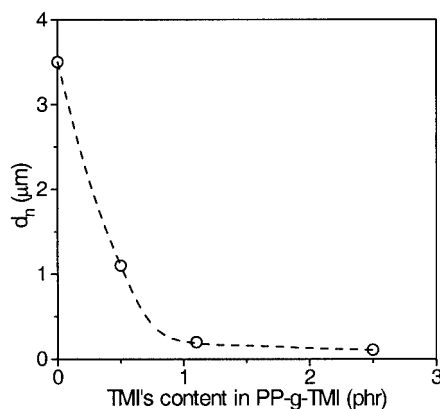
(a)



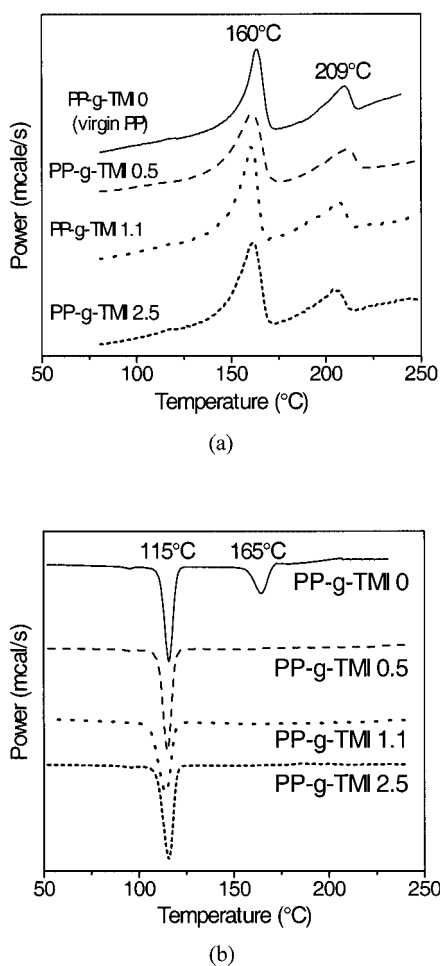
(b)

**Figure 8** Effect of the presence of PP-g-TMI on the morphology of *in situ* polymerized blends: (a) SEM micrograph of the CL/Cat/Activator/PP (30/3/3/70) *in situ* polymerized blend; (b) SEM micrograph of the CL/Cat/Activator/PP + PP-g-TMI1.1 (30/3/3/30 + 40) *in situ* polymerized blend.

quently, the number of nucleating sites per PA6 domain decreased. This would have led to a decrease in the rate of crystallization therein.



**Figure 9** Effect of TMI's content in the PP-g-TMI on the number-average diameter of the PA6 particles of the CL/Cat/Activator/PP + PP-g-TMI (30/3/3/30 + 40) system after polymerization.



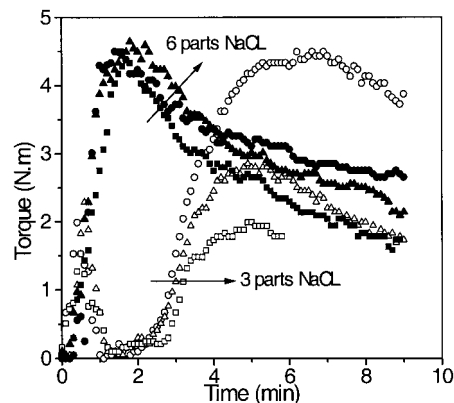
**Figure 10** DSC thermograms of the PP/PA6 blends obtained from the polymerization of the CL/Cat/Activator/PP + PP-g-TMI (30/3/3/30 + 40) system during heating (a) and cooling (b). Heating and cooling rates = 10°C/min; see Figure 7 for experimental details.

### Effect of the catalyst concentration

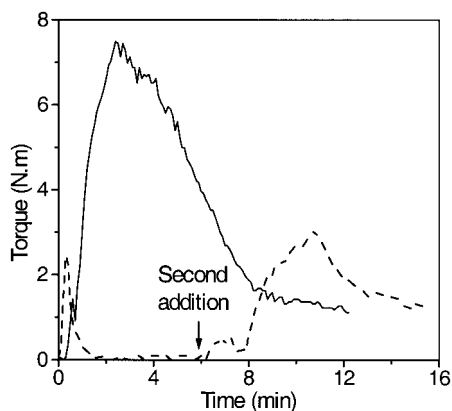
Figure 11 shows the torque versus mixing time curves of the CL/NaCL/Activator/PP + PP-g-TMI2.5 (30/ $x$ /3/70) system with 3 or 6 parts of NaCL. The polymerization kinetics of CL with 6 parts of catalyst was much faster than that with half of that amount, irrespective of the amount of the PP-g-TMI2.5. In the former case, both the PP melting and the polymerization processes occurred simultaneously, whereas in the later case, the polymerization process started to proceed after the PP was molten. The amount of the PP-g-TMI2.5 seemed to have little effect on the polymerization kinetics. On the other hand, the ultimate torque value increased with increasing PP-g-TMI2.5 content in the system. This is because an increase in the amount of the PP-g-TMI2.5 led to an increase in the amount of the PP-g-PA6 graft copolymer formed.

### Two-step feeding versus one-step feeding

The results described above correspond to the situation where all the ingredients involved in the polymerization system (CL, NaCL, Activator, PP, and/or PP-g-TMI) are charged to the batch mixer together. This is called one-step feeding. According to the polymerization mechanism, the polymerization begins with the reaction between an isocyanate group and CL to form the corresponding acyl caprolactam.<sup>6–10</sup> The latter then initiates the polymerization of CL to form PA6 chains. An alternate feeding mode (two-step feeding) consists in charging PP-g-TMI and CL to the batch mixer first to form the acyl caprolactam-bearing PP and then the catalyst and the small molecule activator. In this study, the composition of the PP-g-TMI1.1, CL, NaCL, and activator (60/40/5/3 by mass) was processed in the batch mixer using these two feeding modes. In the one-step feeding, all the ingredients were charged to the mixer at the same time. In the two-step feeding, the PP-g-TMI1.1 and half of the total amount of CL were charged to the batch mixer first and the other half of CL together with the catalyst and the small molecular activator was added 6 min later. In that way, the polymerization process was separated from PP-g-TMI's melting process. Figure 12 shows the evolution of the torque as a function of time for those two feeding modes. In the one-step feeding mode, both the PP-g-TMI melting and the polymerization processes occurred simultaneously. In the two-step feeding process, the polymerization process began 2 min after the addition of the catalyst. This implies that an induction time of 2 min was necessary for the polymerization to occur. It is interesting that there was virtually no difference in terms of the ultimate torque value between these two feeding modes.



**Figure 11** Effect of the catalyst concentration  $x$  on the polymerization kinetics of the CL/NaCL/Activator/PP + PP-g-TMI (30/ $x$ /3/70) system. Open symbols:  $x = 3$  parts; closed symbols:  $x = 6$  parts; PP-g-TMI2.5 = 2 ( $\square$ ), 10 ( $\triangle$ ), 40 ( $\circ$ ), 2 ( $\blacksquare$ ), 20 ( $\blacktriangle$ ), 30 ( $\bullet$ ).



**Figure 12** Comparison of the polymerization kinetics in terms of torque versus time between one-step feeding and two-step feeding. Composition: PP-g-TMI1.1/CL/NaCL/Activator = 60/40/5/3 by mass; set temperature = 220°C. In the one-step feeding, all the ingredients were charged to the mixer together, whereas in the two-step feeding, the PP-g-TMI1.1 and half of the total amount of CL were added first to the batch mixer and the other half of CL together with the catalyst and the activator 6 min later.

## CONCLUSIONS

Polyamide 6 (PA6) can be obtained by anionic polymerization of  $\epsilon$ -caprolactam (CL) catalyzed by sodium caprolactam (NaCL) and activated by an isocyanate compound (Activator). If polypropylene (PP) is added to the polymerization system, an uncompatibilized PP/PA6 blend is obtained. If a fraction of the PP chains bear isocyanate moieties, a compatibilized PP/PA6 blend is formed. In this study, the effects of several parameters on the kinetics of polymerization of CL/NaCL/Activator carried out in a batch mixer were investigated. The kinetics was followed up by the torque of the polymerization system. The main conclusions are as follows:

1. Adding large amounts of PP to the CL/NaCL/Activator system may increase the induction

time beyond which the polymerization starts to proceed.

2. The polymerization temperature should be above 220°C.
3. The amounts of the catalyst and the activator mixtures in the system should be above 2% by mass.
4. The PA6 particle size decreases with increasing TMI content in PP-g-TMI. For PP-g-TMI to be effective in compatibilizing PP/PA6 blends, it is better that the TMI content exceed 1% by mass.

Some of the thermal and mechanical properties of blends prepared by the above *in situ* polymerization and *in situ* compatibilization approach were already reported in previous studies.<sup>1,2</sup> This approach was also extended to the synthesis of pure graft copolymers with polyamides as grafts.<sup>10</sup> Work is under way to further study the properties of blends and graft copolymers.

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