

Follow-Up of the Course of the Anionic Ring-Opening Polymerization of Lactams onto an Isocyanate-Bearing Polymer Backbone in the Melt

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ABSTRACT: In this study, a batch mixer was used as a rheoreactor to carry out and follow up in real time the rate of the anionic polymerization of ϵ -caprolactam onto a 3-isopropenyl- α,α -dimethylbenzene isocyanate bearing polypropylene (PP-g-TMI) in the presence of sodium ϵ -caprolactam as a catalyst. The isocyanate group in the PP-g-TMI was capable of activating the anionic polymerization, leading to the formation of a graft copolymer with polypropylene as the backbone and polyamide 6 as the grafts. The polymerization rate was related to the viscosity increase of the polymerization system. The latter then resulted in a concomitant torque increase. It was shown that torque was a rapid, convenient, and approximate

measure of the polymerization rate. The use of the torque allowed for rapid and approximate evaluation of the effects of chemical and operating conditions on the polymerization rate without the need to determine the monomer conversions. Torque profiles were also a very useful piece of information for the design of a reactive extrusion process for the same type of polymerization system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4394–4403, 2006

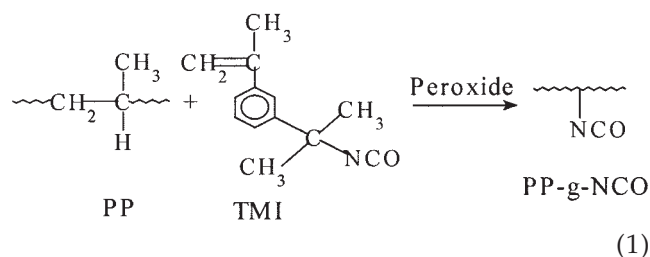
Key words: reactive extrusion; anionic polymerization; poly lactams; kinetics

INTRODUCTION

Previous studies^{1,2} reported on a two-step method to synthesize pure graft copolymers with poly lactams (polyamides) as grafts. The first step was to incorporate an isocyanate bearing vinyl monomer such as 3-isopropenyl- α,α -dimethylbenzene isocyanate (TMI) in a polymer chain by copolymerization^{3–5} or free radical grafting.^{6–9} The latter technique is most useful for polymers like polyolefins whose monomers cannot be copolymerized easily with TMI. The second step was to use the isocyanate bearing polymer as an activator. Isocyanate moieties (NCO) were expected to activate the anionic polymerization of lactams such as ϵ -caprolactam (CL) to form polyamide grafts. The feasibility of the above two-step method was confirmed by the synthesis of polypropylene (PP) and polyamide 6 (PA6) graft copolymers (PP-g-PA6) by anionic polymerization of CL onto a TMI modified PP (PP-g-TMI) in the melt. Sodium ϵ -caprolactam (NaCL) was used as a catalyst and an internal batch

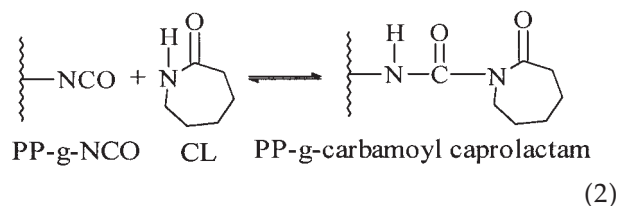
mixer was used as a reactor. High monomer conversions and high purity PP-g-PA6 graft copolymers were obtained in less than a few minutes. The chemical schemes of that two-step grafting polymerization process can be summarized as follows:

Step 1: Attachment of TMI onto PP backbone by free radical grafting



Step 2: Formation of PA6 grafts onto PP-g-TMI by activated anionic polymerization

(a) Activation



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100 g PP (mhr), respectively. For the sake of simplicity, they will be denoted as PP-g-TMI1.30, PP-g-TMI3.34, and PP-g-TMI6.48, respectively. Their melt temperatures were 161°C. The monomer, CL, was purchased from Aldrich and was recrystallized from cyclohexane before use. Its melting and boiling points were ~71°C/760 mmHg and ~137°C/10 mmHg, respectively. The catalyst was supplied by DSM (the Netherlands) in the form of flakes. It was actually a mixture composed of NaCl (16.0 wt %) and CL (84.0 wt %), which amounted to 1.4 mol NaCl per kg CL. For the sake of simplicity, the catalyst mixture will be designated as CM.

Procedures of the synthesis of PP-g-PA6 graft copolymers

A batch mixer of type Haake Rheocord (60 cm³), a simulator of a twin screw extruder, was used to carry out the polymerization reactions. Unless specified otherwise, the experimental procedure was as follows. Desired amounts of CL, PP-g-TMI, and CM were first mixed up in a cup and were then charged to the mixing chamber, which was preheated to a prescribed set temperature (between 200 and 220°C). The two roller blades inside the chamber rotated at 64 revolutions per minute (rpm) to ensure mixing. The variations of the torque and temperature of the polymerization system were recorded as a function of time using a data acquisition system. The real temperature of the system, denoted as the polymerization temperature, was measured by a thermocouple inserted inside the chamber and thus, was in contact with the polymerization system. It could be very different from the temperature of the chamber walls (set temperature). Samples were taken out of the mixing chamber as rapidly as possible (about 10 s) and quenched immediately in liquid nitrogen to stop the reaction and to reduce the loss of CL for subsequent polymer yield and monomer conversion measurements. A sampling time of 10 s was systematically added to the reaction time.

Polymer yield and monomer conversion

The polymer yield was defined as the ratio of the mass of the polymerization system (PP-g-TMI, CM, and CL) after polymerization and removal of small molecule residues over its initial mass. To measure the polymer yield, a known amount of the reacting system after polymerization was first pressed into a thin film of about 100 μm. The monomer and catalyst residues in the film were then extracted by Soxhlet extraction for 36 h using water as solvent. The film thus purified was dried in a vacuum oven at 100°C overnight and then weighed. The polymer yield (y) was then calculated according to the following expression:

$$y(\%) = \frac{W}{W_0} \times 100 \quad (7)$$

where W_0 and W were the masses of the film before and after extraction, respectively. The monomer conversion was defined as:

$$p(\%) = \frac{\text{Mass of polymerized CL}}{\text{Initial mass of CL}} = \frac{W_{m,p}}{W_{m,0} + W_{cm,0}} \times 84.0\% \quad (8)$$

where $W_{m,0}$ and $W_{cm,0}$ were the masses of the monomer and the catalyst mixture charged to the mixer, respectively; $W_{m,p}$ was the mass of the monomer converted to polymer; and the coefficient 84.0% corresponded to the percentage of CL in the catalyst mixture. However, it should be noted that theoretically all CL and NaCl could polymerize, and Na⁺ in the polymer could be replaced by H⁺ not only by CL (eq. (6)) but also by proton releasing impurities and water used for extraction. Consequently, the coefficient 84% in eq. (8) should be replaced by 97.4% (The mass percentage of Na replaced with H in the catalyst is 2.6%). Nevertheless, in this work, since $W_{cm,0}$ was relatively small compared to $W_{m,0}$, differences in p values obtained using both coefficients were very small.

Based on eqs. (7) and (8) and the above arguments, one obtains the following equation:

$$y(\%) = \frac{W}{W_0} \times 100 = \frac{(W_{m,0} + W_{cm,0} \times 97.4\%) \times p + W_{a,0}}{W_{m,0} + W_{a,0} + W_{cm,0}} \times 100 \quad (9)$$

where $W_{a,0}$ was the initial mass of the activator, PP-g-TMI. Re-arrangement of eq. (9) leads to the following equation:

$$p(\%) = \frac{(W_{m,0} + W_{a,0} + W_{cm,0})y - W_{a,0}}{W_{m,0} + W_{cm,0} \times 97.4\%} \times 100 \quad (10)$$

It should be noted that the use of eq. (10) underestimates the values of p . In fact, the use of hot water underestimates the values of y , because hot water extracts not only the unpolymersed CL, but also other small molecular substances like NaCl, the cyclic dimer and linear oligomers of CL.

RESULTS AND DISCUSSION

The polymerization system studied in this work was composed of the following three components: PP-g-

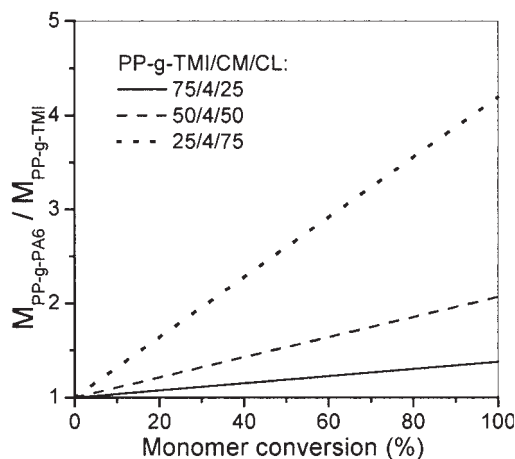


Figure 1 Theoretical relationship between $M_{PP-g-PA6}/M_{PP-g-TMI}$ and the monomer conversion of the PP-g-TMI/CM/CL polymerization system for three different mass compositions.

TMI (activator), CM (catalyst mixture), and CL. It was heterogeneous because neither CL nor CM was miscible with PP-g-TMI in the molten state. Moreover, in the course of the polymerization, the real temperature of the polymerization system, called the polymerization temperature, did not and could not remain constant. This is because the polymerization components were charged to the mixer at room temperature. A certain period of time was necessary for the polymerization temperature to reach the set temperature. Heat released during the polymerization might contribute to the polymerization temperature increase. Viscous dissipation associated with the rotation of the blades in the mixer might also increase the polymerization temperature. Thus, the polymerization temperature was a result of complex interactions among the set temperature, the polymerization rate, and the rotation speed of the blades. For all those reasons, this could be significantly different from the set temperature.

During the polymerization, the molar mass of the PP-g-PA6 graft copolymer, $M_{PP-g-PA6}$, increased with increasing monomer conversion. According to the simplified reaction mechanism described above, it could be related to the molar mass of PP-g-TMI, $M_{PP-g-TMI}$, by the following equation:

$$\frac{M_{PP-g-PA6}}{M_{PP-g-TMI}} = 1 + \frac{W_{n,0} + W_{cm,0} \times 97.4\%}{W_{a,0}} \times p \quad (11)$$

Figure 1 is a schematic representation of eq. (11) of the PP-g-TMI/CM/CL polymerization system for three different mass compositions. For a given PP-g-TMI/CM/CL mass composition, the molar mass of the PP-g-PA6 graft copolymer is expected to increase linearly with increasing monomer conversion, regardless of TMI's content in the PP-g-TMI. On the other

hand, for a given monomer conversion, it increases linearly with increasing CL/PP-g-TMI mass composition. For example, the molar mass of the PP-g-PA6 graft copolymer is expected to be about four times that of the PP-g-TMI, when 90% of the monomer of the PP-g-TMI/CM/CL (25/4/75) system is converted to PA6 grafts. As the monomer is converted to polymer and the molar mass of the PP-g-PA6 graft copolymer increases concomitantly, the viscosity of the PP-g-TMI/CM/CL polymerization system increases and so does the torque. Therefore, the variations of the polymerization temperature and torque were both the direct consequences and at the same time the direct signatures of the polymerization rate and/or molar mass of the PP-g-PA6 graft copolymer formed. For example, a higher polymerization rate necessarily leads to a more rapid increase in the viscosity of the polymerization system and consequently higher increases in the polymerization temperature and torque, and *vice versa*. For the sake of clarity, Table I gives a glance of the selected information about 14 experimental trials carried out in this work, in terms of the mass composition, three overall NCO/CL, NaCL/CL, and NCO/NaCL molar ratios, set temperature (T_{set}), rotating speed, and feeding mode.

Figure 2 shows the effects of the CM concentration on the variations of the polymerization temperature, torque, and the monomer conversion as a function of time for the PP-g-TMI6.48/CM/CL polymerization system (experiments E1, E2, and E3), respectively. Figure 2(a) shows that the polymerization proceeded relatively rapidly as the monomer conversion reached a plateau in about 4 min, regardless of the CM concentration. Moreover, an increase in the CM concentration led to an increase both in the polymerization rate and in the ultimate monomer conversion. These results were supported by the variations of the torque shown in Figure 2(b). In fact, the torque *vs.* time curves showed more clearly the effects of the CM concentration on the polymerization rate and the final monomer conversion. Note that the initial torque values were all low. This is because CL's melting point was only 71°C/760 mmHg. It melted very rapidly, and the PP-g-TMI powder was then suspended in the low viscosity CL liquid. As the system was further heated up and mixed, the polymerization began to take place and the torque started increasing. The time at which the torque value started rapidly increasing corresponded to the moment where the polymerization had already proceeded to a certain extent. The higher the CM concentration, the shorter the time necessary for the torque to start increasing and the higher the final torque value. A shorter time necessary for the torque to start rapidly increasing implies that the polymerization took place more rapidly. Since the NCO/CL molar ratios were almost constant for the experiments E1, E2, and E3, a higher torque value resulted, both

TABLE I
Selected Information About 16 Experimental Trials Carried Out in this Work

Exp. No.	Type of PP-g-TMI	Mass composition (PP-g-TMI/CM/CL)	Molar ratio			T_{set} (°C)
			NCO/CL	NaCL/CL	NCO/NaCL	
E1 ^a	PP-g-TMI6.48	50/2/50	3.31/100	0.53/100	6.25	200
E2 ^a	PP-g-TMI6.48	50/3/50	3.26/100	0.75/100	4.35	200
E3 ^a	PP-g-TMI6.48	50/4/50	3.15/100	0.98/100	3.23	200
E4 ^a	PP-g-TMI3.34	50/4/50	1.79/100	1.06/100	1.69	200
E5 ^a	PP-g-TMI1.30	50/4/50	0.68/100	1.01/100	0.67	215
E6 ^a	PP-g-TMI1.30	50/3/50	0.69/100	0.76/100	0.90	215
E7 ^a	PP-g-TMI3.34	50/3/50	1.73/100	0.76/100	2.27	215
E8 ^a	PP-g-TMI3.34	50/4/50	1.79/100	1.06/100	1.69	215
E10 ^a	PP-g-TMI3.34	50/4/50	1.79/100	1.06/100	1.69	220
E11 ^a	PP-g-TMI6.48	25/4/75	1.09/100	0.69/100	1.59	200
E12 ^a	PP-g-TMI3.34	25/4/75	0.60/100	0.71/100	0.85	215
E13 ^b	PP-g-TMI3.34	25/4/75	0.60/100	0.71/100	0.85	215
E14 ^a	PP-g-TMI1.30	25/4/75	0.24/100	0.71/100	0.34	215
E15 ^c	PP-g-TMI1.30	25/4/75	0.24/100	0.71/100	0.34	215
E16 ^d	PP-g-TMI1.30	25/4/75	0.24/100	0.71/100	0.34	215

^a One-pot feeding (all reaction ingredients were charged to the mixer at the same time); rotation speed was 64 rpm.

^b One-pot feeding; rotation speed at 100 rpm.

^c Two-step feeding: the total amount of PP-g-TMI1.30 and two thirds of the total amount of CL were first charged to the mixer and the remaining CL and the total amount of CM were added 4 min later. The rotation speed was 64 rpm.

^d Same as c, except that the remaining CL and the total amount of CM were charged to the mixer 7 min later.

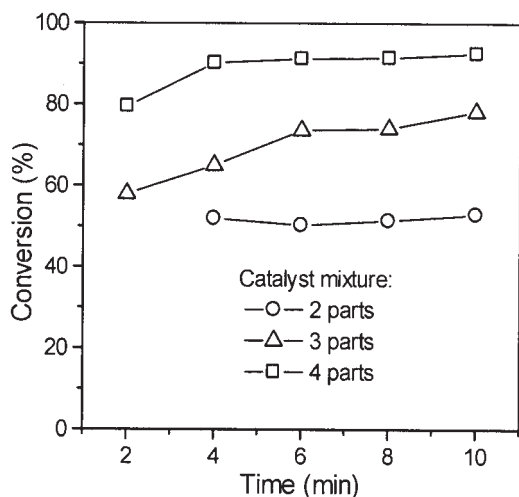
from a higher final monomer conversion and from a higher molar mass of the PP-g-PA6 graft copolymer. The results in Figure 2(c) were more or less in line with that expectation, even though the difference in the polymerization temperature profile was small between the experiments E2 and E3. All those results showed that the variations of the torque and polymerization temperature were the direct consequences and signatures of the course of polymerization of the PP-g-TMI/CM/CL system. Therefore, they could be used as rapid and convenient measures for evaluating and controlling the effects of chemical and operating conditions on the polymerization rate of the above or similar systems, without the need to determine the monomer conversions. The latter is known to be tedious and time consuming.

Effects of TMI's content in PP-g-TMI

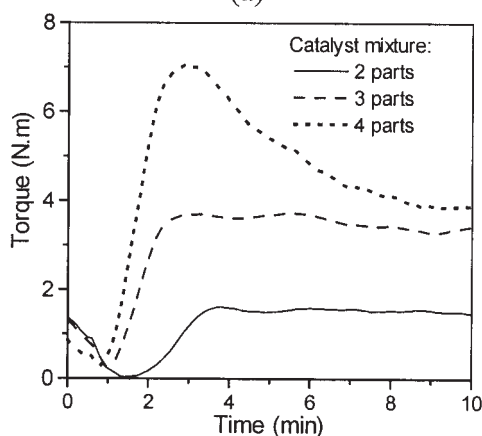
Table II shows the effect of TMI's content in PP-g-TMI on the monomer conversion for three PP-g-TMI/CM/CL mass compositions: 50/3/50, 50/4/50, and 25/4/75. The monomer conversion values were those obtained after 10 min of polymerization. They were all between 70 and 93%, which were of the same order of magnitude as that of the anionic polymerization of CL under similar polymerization conditions, using small-molecule isocyanate compounds as activators.¹⁰ For all the three PP-g-TMIs, the monomer conversion increased with increasing TMI's content in PP-g-TMI, except for the experiment E2. The reason for that exception was that the NCO/NaCL molar ratio of that mass composition was 4.35, the highest among all

mass compositions in Table II. A previous work² showed that when it exceeded 4, the monomer conversion would be low. This is because under such conditions most anionic species would be consumed by a so-called C-acylation reaction. The polymerization rate would slow down before the monomer equilibrium was reached.¹⁷ This may explain why the monomer conversion of the PP-g-TMI6.48/CM/CL system after 10 min of polymerization was able to increase from 78.2 to 92.6% when the NCO/NaCL molar ratio was decreased from 4.35 (experiment E2) down to 3.23 (experiment E3). It was also noted that the values of the polymerization temperature after 10 min of polymerization were always higher than those of the set temperature. This indicates that a significant amount of heat was generated by viscous dissipation, implying that the viscosity of the polymerization system inside the mixing chamber was significantly increased as a result of the conversion of the monomer to the polymer and a concomitant increase in the molar mass of the PP-g-PA6 graft copolymer. In summary, an increase in TMI's content in PP-g-TMI increased the polymerization rate, and the final monomer conversion provided that the NCO/NaCL ratio was below 4.

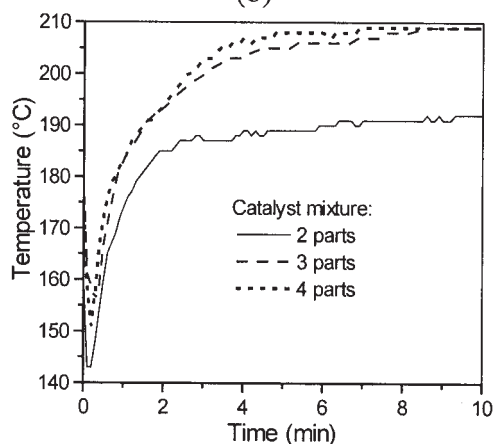
Figure 3(a,b) show the effects of TMI's content in PP-g-TMI on the polymerization rate in terms of the variations in the polymerization temperature and torque as a function of time for the PP-g-TMI/CM/CL mass compositions of 50/3/50 and 50/4/50, respectively. For both mass compositions, the polymerization temperature varied considerably during the course of the polymerization and was significantly



(a)



(b)



(c)

Figure 2 Variations of the monomer conversion (a), torque (b), and polymerization temperature (c) of the PP-g-TMI6.48/CM/CL polymerization system as a function of time. Note that the value of the monomer conversion at 2 min for the experiment E1 was unavailable because it was too low to be measured by the method developed in this work.

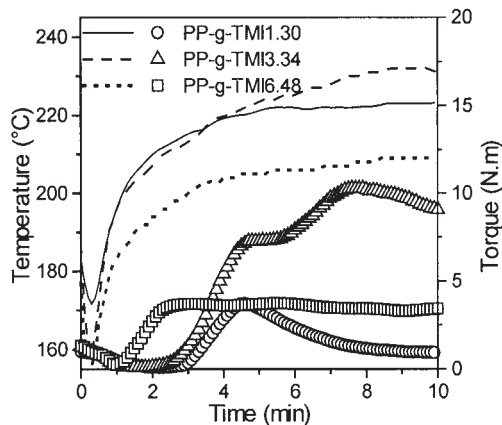
TABLE II
Effects of TMI's Content in PP-g-TMI on the Monomer Conversion and Polymerization Temperature of the PP-g-TMI/CM/CL Polymerization System

Exp. No.	Type of PP-g-TMI	PP-g-TMI/CM/CL mass composition	Monomer conversion (%)	Polymerization temperature (°C)
E6	PP-g-TMI1.30	50/3/50	71.3	223
E7	PP-g-TMI3.34	50/3/50	84.8	232
E2	PP-g-TMI6.48	50/3/50	78.2	209
E5	PP-g-TMI1.30	50/4/50	86.0	224
E8	PP-g-TMI3.34	50/4/50	89.5	235
E3	PP-g-TMI6.48	50/4/50	92.6	209
E14	PP-g-TMI1.30	25/4/75	84.1	224
E12	PP-g-TMI3.34	25/4/75	86.9	239
E11	PP-g-TMI6.48	25/4/75	91.4	223

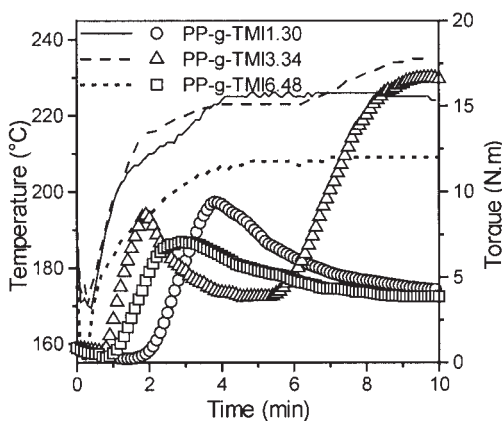
Set temperature, 215°C for PP-g-TMI1.30 and PP-g-TMI3.34 and 200°C for PP-g-TMI6.48; polymerization time, 10 min.

different from the set temperature, regardless of TMI's content in the PP-g-TMI. It took about 3 min for the polymerization temperature to reach the set temperature. Thereafter, the polymerization temperature continued to increase and its ultimate values were 8–20°C above those of the set temperature. The differences between the ultimate polymerization temperatures and the set temperatures were slightly greater for the 50/4/50 mass composition than for the 50/3/50, because the ultimate monomer conversions were higher with the former mass composition. Concerning the torque, for the 50/3/50 mass composition, it started rapidly increasing after approximately 3, 2, and 1 min of mixing, when TMI's content in PP-g-TMI was 1.30, 3.34, and 6.48 phr, respectively. This indicates that the polymerization rate of that mass composition followed the order PP-g-TMI1.30 < PP-g-TMI3.34 < PP-g-TMI6.48, despite the fact that the set temperature was 200°C for PP-g-TMI6.48, which was lower than that for PP-g-TMI1.30 and PP-g-TMI3.34 (215°C). Basically, the 50/4/50 mass composition behaved in a manner similar to the 50/3/50 mass composition, except that the torque started increasing earlier: 2, 0.7, and 1 min for PP-g-TMI1.30, PP-g-TMI3.34, and PP-g-TMI6.48, respectively. The fact that the time necessary for the torque to start rapidly increasing was slightly longer for PP-g-TMI6.48 than for PP-g-TMI3.34 was related to the fact that the set temperature was 200°C for the former and 215°C for the latter.

It was expected that the effect of TMI's content on the polymerization rate would be better revealed by the variations of the polymerization temperature and torque through a PP-g-TMI/CM/CL mass composition of 25/4/75 than through a mass composition of 50/4/50. The reason was that based on eq. (11), for given TMI's content in PP-g-TMI and the monomer



(a)



(b)

Figure 3 Effects of TMI's content in PP-g-TMI on the polymerization rate in terms of the variations of the polymerization temperature and torque of the PP-g-TMI/CM/CL system as a function of time for two mass compositions differing in the CM concentration: 50/3/50 (a) and 50/4/50 (b). Set temperature, 215°C for PP-g-TMI1.30 and PP-g-TMI3.34, and 200°C for PP-g-TMI6.48; lines, polymerization temperature; symbols, torque.

conversion, the magnitudes of increase in the molar mass of the PP-g-PA6 graft copolymer and in the viscosity were much more pronounced in the former than in the latter. That was indeed the case, as shown in Figure 4. The time at which the torque started rapidly increasing was 8, 7, and 3 min for PP-g-TMI1.30, PP-g-TMI3.34, and PP-g-TMI6.48, respectively. This indicates that for the 25/4/75 mass composition, an increase in TMI's content in PP-g-TMI always led to an increase in the polymerization rate (note that the NCO/NaCl molar ratios were always below the critical threshold of 4). As for the polymerization temperature, it reached the set temperature in about 3 min, regardless of TMI's content. The difference between the ultimate polymerization tempera-

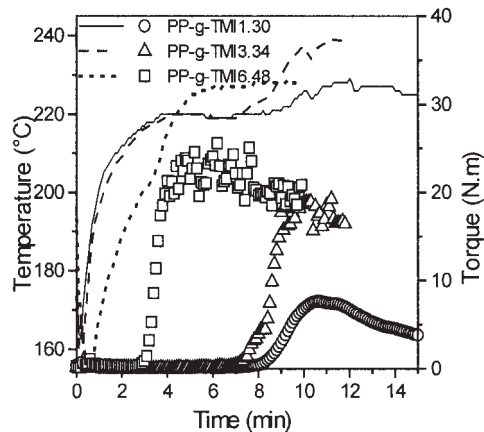


Figure 4 Effects of TMI's content in PP-g-TMI on the variations of the polymerization temperature and torque of the PP-g-TMI/CM/CL (25/4/75) system as a function of time. Set temperature, 215°C for PP-g-TMI1.30 and PP-g-TMI3.34 and 200°C for PP-g-TMI6.48; lines, polymerization temperature; symbols, torque.

ture and the set temperature was 9°C for PP-g-TMI1.30 and more than 20°C for PP-g-TMI3.34 and PP-g-TMI6.48.

Effects of mixing intensity

Mixing intensity in the mixer could be varied by changing the rotation speed of its blades. All the results reported above were obtained at a rotation speed of 64 rpm. Figure 5 compares the variations of the polymerization temperature and torque of the PP-g-TMI3.34/CM/CL polymerization system between 64 and 100 rpm (E10 vs. E11). The mass composition was 25/4/75. At 64 rpm, the torque started rapidly increas-

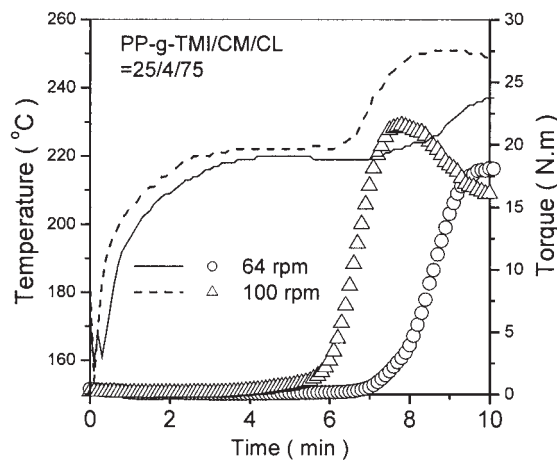


Figure 5 Effects of mixing intensity on the polymerization rate measured by the variations of the polymerization temperature and torque as a function of time for the PP-g-TMI3.34/CM/CL system. Mass composition, 25/4/75; set temperature, 215°C; rotation speed, 64 or 100 rpm.

ing at 7 min. That time was reduced to 5 min when the rotation speed was increased to 100 rpm. This indicates that the polymerization rate was higher at the higher rotation speed, as expected. This is also consistent with the fact that the polymerization temperature at 100 rpm was always higher than that at 64 rpm. The positive effect of mixing on the polymerization rate can be explained as follows. The higher the rotation speed, the shorter the time needed for heating up and mixing the heterogeneous polymerization system. As a result, the polymerization started taking place earlier. An earlier start of the polymerization process resulted in an earlier increase in the viscosity and consequently more rapid heating of the polymerization system through more severe viscous dissipation. More rapid heating then further accelerated the polymerization rate, which in turn resulted in a further earlier increase in torque. The monomer conversion obtained after 10 min of polymerization was 86.0% at 64 rpm and 89.2% at 100 rpm. The corresponding polymerization temperatures were 239 and 249°C, respectively, which were 24 and 34°C above the set temperature (215°C), respectively. These results show that the polymerization rate can be increased by using a more intensive-mixing mixer such as a twin-screw extruder.

Effects of feeding mode

Thus far, all the polymerization ingredients involved in the polymerization system (PP-g-TMI, CM, and CL) were charged to the mixer at the same time. This feeding mode may be called one-pot feeding. An alternative feeding mode may be that PP-g-TMI and CL are charged to the mixer first and CM some time later. This feeding mode will be denoted as two-step feeding. A comparison was made between these two feeding modes in terms of the variations of the polymerization temperature and torque of the PP-g-TMI1.30/CM/CL system as a function of time. The mass composition was 25/4/75. Two experiments were carried out following two different two-step feeding modes. In the first one (E13), the total amount of PP-g-TMI1.30 and two thirds of the total amount of CL were first charged to the mixing chamber. The remaining one-third of the total amount of CL and the total amount of CM were added in 4 min later. The second experiment (E14) differed from the first one in that the remaining one third of CL and the total amount of CM were charged 7 min later.

Figure 6 compares the variations of the polymerization temperature and torque as a function of time for the one-pot feeding experiment and the two two-step feeding experiments. In the latter cases, the time at which the second feed was added was demarcated by an abrupt decrease in the polymerization temperature. The torque started increasing rapidly at approxi-

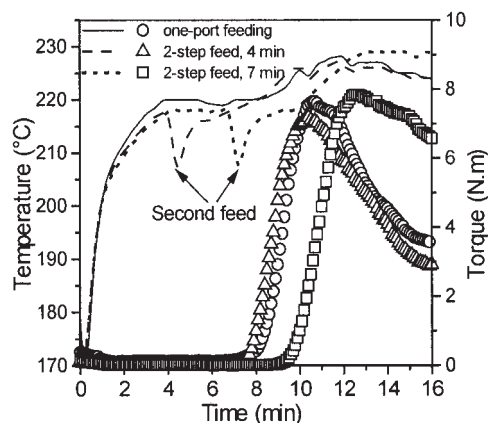


Figure 6 Effect of the feeding mode on the polymerization rate in terms of the variations of the polymerization temperature and torque as a function of time for the PP-g-TMI1.30/CM/CL system. Mass composition, 25/4/75; set temperature, 215°C; rotation speed, 64 rpm.

mately 8, 8, and 9 min for the one-pot feeding, the first two-step feeding, and the second two-step feeding experiments, respectively. Considering the fact that under the specified conditions, CL did not polymerize onto PP-g-TMI1.30 without CM within the experimental time scale, the moment where CM was charged to the mixer should be taken as the starting point of the polymerization process. Therefore, the effective time at which the torque started rapidly increasing should be 8, 3, and 2 min for the one-pot feeding, the first two-step feeding, and the second two-step feeding experiments, respectively.

Recall that the overall polymerization process of the PP-g-TMI/CM/CL immiscible system was mainly composed of the following conceptually distinct and consecutive elements: heating (from the room temperature to a prescribed set temperature), mixing (homogenization of the reaction ingredients), activation (eq. (2)), initiation (eqs. (3) and (4)), and propagation (eqs. (5) and (6)). In those two two-step feeding experiments, the first feeding step was to accomplish, to a very large extent, the heating, mixing, and activation while the second feeding step allowed for the initiation and propagation to proceed.

Since for the PP-g-TMI1.30/CM/CL (25/4/75) immiscible system the effective times at which the torque started rapidly increasing were only 3 and 2 min for the first and second two-step feeding experiments, respectively, instead of 8 min for the one-pot feeding one, it could be concluded that about 5 min was needed to accomplish the heating, mixing, and activation and about 2 min was necessary for the subsequent initiation and propagation. If a more efficient mixer in terms of heating and mixing is used, the time necessary for accomplishing the heating, mixing, and activation is expected to be shorter. On the other hand, if

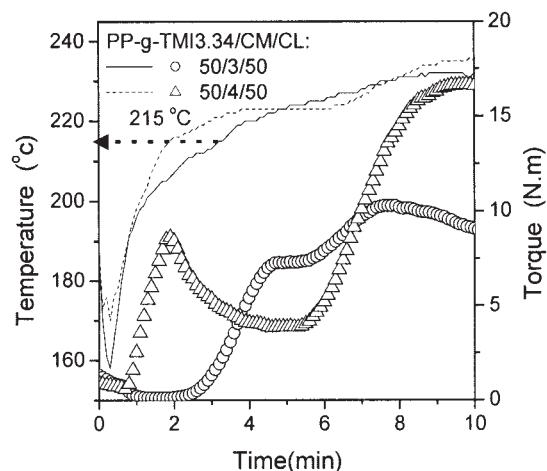


Figure 7 Variations of the polymerization temperature and torque of the PP-g-TMI3.34/CM/CL polymerization system. Mass composition, 50/3/50 or 50/4/50; set temperature, 215°C; lines, polymerization temperature; symbols, torque.

TMI's content in the PP-g-TMI is higher, then the time needed for the initiation and propagation is also expected to be shorter. Note also that the monomer conversions obtained at the end of the polymerization were 84.1, 86.2, and 87.6% for the one-pot feeding, the first two-step feeding and the second two-step feeding experiments, respectively. A practical implication of these results would be the following: instead of using PP-g-TMI as it is, one may first convert it to PP-g-carbonyl caprolactam (eq. (2)). The latter is the true activator and is expected to have a longer storage time than PP-g-TMI.

Open issues

It is worthwhile to comment further on the torque *vs.* time curves of the PP-g-TMI3.34/CM/CL polymerization system in Figure 3 for the mass compositions of 50/4/50 and 50/3/50. For the sake of clarity, they are plotted in Figure 7. Note that the torque evolved very differently from other polymerization systems studied in this work. In the case of the 50/3/50 mass composition, it started increasing rapidly at about 2 min, reached a plateau 2.5 min later, and started increasing again after 5.5 min of polymerization. The torque *vs.* time curve of the 50/4/50 mass composition followed more or less the same trend as the 50/3/50 mass composition, except that the features mentioned earlier became more distinct. It started increasing rapidly at 0.7 min, reached a maximum about 1 min later, and then started decreasing till 5.5 min. Thereafter, it started increasing rapidly again.

The aforementioned peculiar torque *vs.* time curves remain to be understood. Keep in mind that the polymerization system was an immiscible mixture of a

polymer (PP-g-TMI3.34) and small molecules (CL and CM). The viscosity mismatch between them being very important, the low viscosity components (CL and CM) always had tendency to migrate to the walls of the mixer and the rotating blades to lower the torque of the system. As the polymerization proceeded, the amount of CL decreased and the molar mass of the PP-g-PA6 graft copolymer increased accordingly. This led to the first increase in torque. At the same time, the unpolymerized CL trapped inside the polymerization mixture tended to migrate to the walls of the mixer and the surfaces of the blades, bringing about a decrease in torque. The first peak on the torque *vs.* time curve might result from the competition between the polymerization and migration of CL. As the polymerization proceeded further, the torque started increasing again.

The above phenomenon might be more pronounced if the polymerization of CL and the crystallization of the polymer occurred simultaneously. Simultaneous occurrence of these two processes might be possible if the polymerization temperature was well below the melting temperature of the PA6 grafts. The set temperature for the polymerization of the above compositions was 215°C, at which crystallization was expected to be extremely slow or impossible. It was reported that the temperature for maximum crystallization rate in PA6 was about 140–145°C.¹⁸ However, the polymerization temperature was below the set temperature during the first 3 and 2 min of polymerization for the 50/3/50 and 50/4/50 mass compositions, respectively. During that period of time, both the polymerization of CL and the crystallization of PA6 grafts might have taken place at the same time, leading to a rapid increase in torque. As the crystallization proceeded, the growing centers of the PA6 grafts might have become frozen and the polymerization process might have then slowed down. Meanwhile the unpolymerized CL was expelled to the walls of the mixer and the surfaces of the blades, causing a decrease in torque. The torque started increasing again after the expelled CL had polymerized to a certain degree. This scenario seems to be in line with the fact that a slight increase in the set temperature from 215 to 220°C shortened the time at which the torque started to undergo a second increase (see Fig. 8). The latter was reduced from 5.5 min at 215°C to less than 4 min at 220°C.

A better understanding of the aforementioned peculiar torque *vs.* time curves would be worthy of efforts as it would allow better controlling and optimizing interactions among thermal, physical and chemical processes involved in the polymerization process. This is out of the scope of this article.

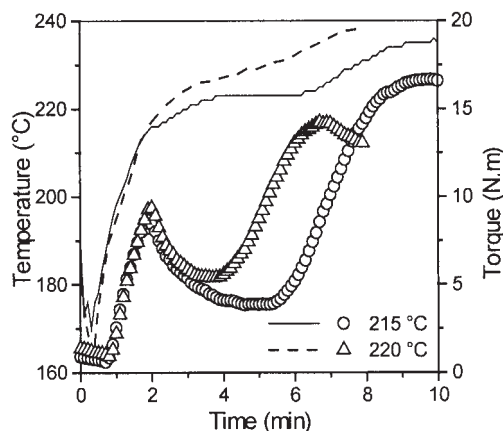


Figure 8 Effects of the set temperature on the variations of the polymerization temperature and torque of the PP-g-TMI_{3.34}/CM/CL (50/4/50) polymerization system. Set temperature, 215 or 220°C.

CONCLUDING REMARKS

The work reported in this article aimed at using a batch mixer as a rheoreactor to carry out and follow up in real time the rate of the anionic polymerization of CL onto PP-g-TMI in the presence of NaCl as a catalyst. The polymer formed was a graft copolymer with PP as the backbone and PA6 as the grafts. The main conclusions drawn were the following:

- Torque was a rapid, convenient, and approximate measure of the polymerization rate. It allowed for rapid evaluation of the effects of chemical and operating conditions on the polymerization rate, avoiding the determination of the monomer conversions which would be tedious and time-consuming. It also provided qualitative/semiquantitative information useful for the design of a reactive extrusion process for carrying out the same type of polymerization. The variation of the temperature of the polymerization system was a complementary piece of information.
- An increase in TMI's content in PP-g-TMI led to an increase in the polymerization rate and the ultimate monomer conversion, as long as the molar ratio between the isocyanate group and NaCl was kept below 4.

- Mixing had an important effect on the overall polymerization rate. The higher the mixing intensity, the more rapid was the overall polymerization rate. The reason was that an increase in mixing intensity shortened the time necessary for heating and mixing up the polymerization system, which for the mixer used in this work was very significant compared with the time of polymerization *per se*.
- The above conclusion was further corroborated by comparing one-pot feeding and two-step feeding experiments. Those results also suggested that, in practice, it would be preferable to first convert PP-g-TMI with CL to PP-g-carbamoyl caprolactam, the true activator of the anionic polymerization. The latter was even easier to store than PP-g-TMI.

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