



Rate of the activated anionic polymerisation of ϵ -caprolactam onto an isocyanate bearing polypropylene in the melt

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Abstract

This paper concerns the rate of the activated anionic polymerisation of ϵ -caprolactam (CL) onto 3-isopropenyl- α,α -dimethylbenzyl isocyanate bearing PP (PP-*g*-TMI) in the melt to form a graft copolymer with PP as backbone and PA6 as grafts. The polymerisation was catalysed by sodium ϵ -caprolactam (NaCL). The PP-*g*-TMI/NaCL/CL polymerisation system being heterogeneous, the polymerisation was carried out in a batch mixer. Emphasis was placed on the effects of temperature and the concentrations of NaCL and the isocyanate group in the form of PP-*g*-TMI on the polymerisation rate. Results suggested that if the polymerisation is to be carried out by a reactive extrusion process whose mean residence time is less than a few minutes, it is recommended that the polymerisation temperature be higher than 220 °C. Moreover, the molar ratio between NaCL and CL should be higher than 0.5 and at the same time that between the isocyanate group in the form of PP-*g*-TMI and NaCL, should be smaller than 4.

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1. Introduction

Block and graft copolymers possess unique properties compared to their homopolymers. One of the applications of such copolymers lies in the compatibilisation of immiscible polymer blends. Their presence at the interfaces between polymer components of the blend decreases the interfacial tension, helps the dispersion of one polymer component in the other, enhances the interfacial adhesion and stabilises morphology. Moreover, it enhances the interfacial heat transfer between polymer phases by increasing the interfacial thermal conductivity [1]. Block or graft copolymers needed for the compatibilisation of immiscible polymer blends can be either synthesised separately or produced in situ during melt blending-reactive polymer blending [2].

The first approach has given way to the second for several reasons. Not all block or graft copolymers can be synthesised by existing chemical routes. In cases, where chemical routes are available, they are not necessarily suitable for particular block or graft copolymers for technical and/or economical reasons. This is particularly so at industrial scales. For example, polypropylene and polyamide 6 (PP/PA6) immiscible blends are almost exclusively compatibilised by adding a maleic anhydride functionalised PP. The latter is capable of reacting with the terminal amine group of PA6, forming a PP-*g*-PA6 graft copolymer at the PP and PA6 interfaces. This approach is technically very attractive and economically appealing for preparing PP/PA6 blends. However, it does not allow to obtain pure PP-*g*-PA6 graft copolymers because of limited interfacial volume compared to the bulk phases, unless the molar mass of at least one of the reactive polymer components is smaller than its critical entanglement molar mass.

In a previous study [3], a novel method was developed to synthesise pure PP-*g*-PA6 graft copolymers by activated anionic polymerisation of ϵ -caprolactam (CL) using sodium

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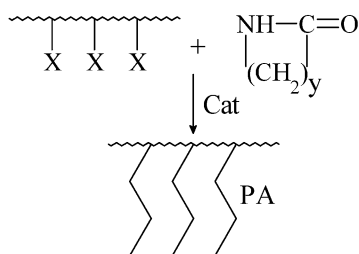


Fig. 1. Expected structure of the graft copolymer formed by the anionic polymerisation of lactam activated by an activator (X) bearing polymer (macro-activator). CL corresponds to ϵ -caprolactam with $y=6$.

ϵ -caprolactam (NaCL) as catalyst and a 3-isopropenyl- α,α -dimethylbenzene isocyanate bearing PP as activator (PP-g-TMI). The aim of the present work was to study the rate of polymerisation of that heterogeneous system in a batch mixer with emphasis on the effects of temperature and the concentrations of the catalyst and the activator. The ultimate goal was to define conditions under which the polymerisation could be carried out by a reactive extrusion process with a residence time of less than a few minutes.

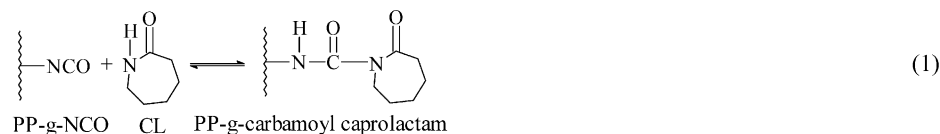
2. Mechanism of the graft copolymer formation

CL can be polymerised anionically above 100 °C in the presence of catalysts like NaCL [5,6] to form PA6. However, the polymerisation rate is often very slow due

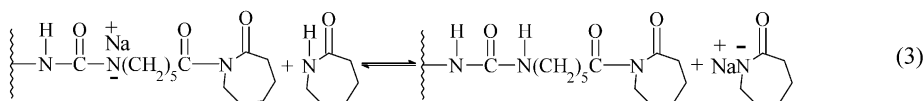
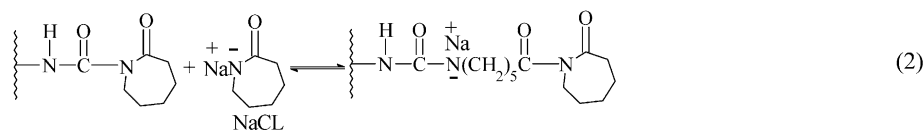
to the very slow initiation step and is thus incompatible with reactive extrusion processes. An activator is thus required to accelerate the initiation rate and consequently the overall polymerisation rate. It can be an isocyanate or an ester compound. The polymerisation of lactams such as CL in the presence of a catalyst and an activator is called activated anionic polymerisation [7–10]. The activating group is incorporated in the starting end of the PA6 chain. If it is attached onto a polymer backbone (macro-activator), then a graft copolymer will be formed (Fig. 1) [3,4]. If all the activating moieties participate in the initiation, the number of PA grafts of the resulting graft copolymer is then equal to the number of the activating moieties attached onto the polymer backbone. In other words, the number of PA grafts formed in the graft copolymer is controlled by the number of the activating moieties per macro-activator chain. As for their length, it is controlled by the molar ratio between the polymerised lactam and the activating group.

Fig. 2 depicts the mechanism of the PP-g-PA6 graft copolymer formation using PP-g-TMI as macro-activator. There are three main steps involved: activation, initiation and propagation. Note that the anionic polymerisation of lactams differs from the anionic polymerisation of most unsaturated and heterocyclic monomers. The growing centre at the chain end is not an anionically activated group but a neutral *N*-acylated lactam and the anionically activated species is the incoming monomer. The validity of this mechanism was discussed in a previous paper [3]. It

(a) Activation:



(b) Initiation:



(c) Propagation:

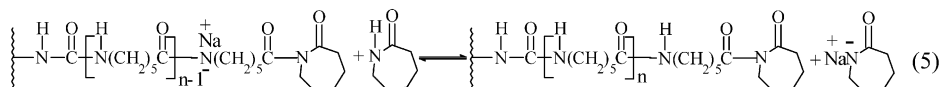
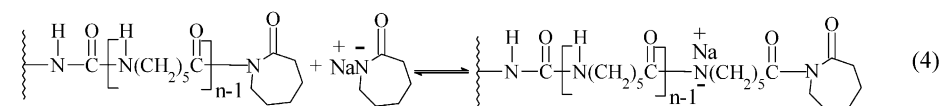


Fig. 2. Mechanism of the PP-g-PA6 graft copolymer formation by the anionic polymerisation of CL catalysed by NaCL and activated by PP-g-TMI.

Table 1
Selected characteristics of the activator, PP-g-TMI, used in this work

Melting point ^a	\bar{M}_n kg/mol ^b	\bar{M}_m kg/mol ^b	TMI content in PP-g-TMI ^c	NCO molar number per kg PP-g-TMI	NCO number per PP-g-TMI chain
161 °C	213	510	6.1 wt%	0.30	63.9

^a Measured by DSC at 10 °C/min.

^b Measured by high temperature size exclusion chromatography in 1,2,4-trichlorobenzene using polystyrene standards for the calibration. The use of the Mark–Houwink equations for polystyrene and polypropylene in that solvent allowed obtaining the number average and mass average molar masses of the PP-g-TMI.

^c Measured by FTIR according to Ref. [14] using a calibration curve established therein.

should be pointed that the above mechanism is presented only for the sake of simplicity. In fact, many side reactions may also participate in the polymerisation process, especially at elevated temperatures [11,12].

3. Experimental

3.1. Materials

The monomer, CL, was purchased from Aldrich and recrystallised from cyclohexane before use. Its melting and boiling points were ~ 71 °C/760 mmHg and ~ 137 °C/10 mmHg, respectively. The catalyst was kindly supplied by DSM, the Netherlands, as a mixture of CL and NaCL in the form of flake and will be denoted as CM. The mass percentages of CL and NaCL were 84.0 and 16.0%, respectively, which corresponded to 1.4 mol NaCL per kg CL. The activator, PP-g-TMI, was prepared in the authors' laboratory by free radical grafting in the melt and the residual TMI left therein after free radical grafting removed according to the procedures described elsewhere [13,14]. Table 1 shows some of its characteristics.

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

A batch mixer of type Haake Rheocord with a volume capacity of 60 cm³, a simulator of a twin screw extruder, was used to carry out the synthesis without inert gas protection. For a typical experimental run, desired amounts of CL, PP-g-TMI, and CM were first mixed in a cup and then charged to the mixing chamber which was preheated to a prescribed temperature. The latter was called the set temperature. Unless specified otherwise, it was always at 200 °C and the two roller blades inside the chamber rotated at 64 revolutions per minute (rpm) to ensure mixing. The torque and temperature of the polymerisation system were recorded as a function of time using a data acquisition system. The temperature of the polymerisation system, denoted as the polymerisation temperature, was measured by a thermocouple inserted inside the chamber in contact with the polymerisation system. Its accuracy was within ± 1 °C. Samples were taken out from the mixing chamber at chosen time intervals 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.

3.3. Polymer yield and monomer conversion

The polymer yield was defined as the ratio of the mass of the polymerisation system (CL, PP-g-TMI, and CM) after polymerisation and removal of small molecule residues over its initial mass. To measure the polymer yield, a known amount of the reacting system after polymerisation was first pressed into a thin film of about 100 μ m. 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:

$$y(\%) = \frac{W}{W_0} \times 100 \quad (6)$$

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

$$p(\%) = \frac{\text{Mass of polymerised CL}}{\text{Initial mass of CL}} = \frac{W_{m,p}}{W_{m,0} + W_{cm,0} \times 84.0\%} \times 100 \quad (7)$$

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; 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. (5) but also by proton releasing impurities and water used for extraction. Consequently, the coefficient 84% in Eq. (7) 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.

According to Eqs. (6) and (7) together with the above

arguments, one obtains the following equation:

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

$$= \frac{(W_{m,0} + W_{cm,0} \times 97.4\%)p + W_{a,0}}{W_{m,0} + W_{a,0} + W_{cm,0}} \times 100 \quad (8)$$

where $W_{a,0}$ was the initial mass of the activator, PP-g-TMI. Re-arrangement of Eq. (8) leads to the following equation:

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

It should be noted that the use of Eq. (9) underestimates the values of p . In fact, the use of hot water underestimates the values of y , because hot water extracts not only the unpolymerised CL, but also other small molecule substances like NaCl, the cyclic dimmer and linear oligomers of CL.

4. Results and discussion

In this work, the effects of the set temperature, molar concentrations of NaCl and the isocyanate group and their ratio on the rate of polymerisation of the PP-g-TMI/NaCl/CL were studied. In what follows, they will be reported in terms of the monomer conversion, polymerisation temperature and torque as a function of time. The polymerisation temperature and the torque were both the consequences and at the same time the signatures of the polymerisation process. For example, a high polymerisation rate will necessarily lead to a fast increase in the viscosity of the polymerisation system and consequently a rapid increase in the polymerisation temperature and torque, and vice versa. For the sake of clarity, Table 2 gives a glance at selected information about 12 experimental trials carried out in this work in terms of the mass composition components, three nominal molar ratios: NCO/CL, NaCl/CL and NCO/NaCl, set temperature (T_{set}) and polymerisation temperatures at 5 and 10 min of reaction, $T_{5 \text{ min}}$ and $T_{10 \text{ min}}$, respectively.

4.1. Effects of the set temperature

A mass composition of 50/4/50 was chosen for the PP-g-TMI/CM/CL system to study the effects of the set temperature. The latter was set at 180, 200 and 230 °C, respectively, corresponding to E1, E2 and E3, respectively. Fig. 3 shows the monomer conversion as a function of time at the set temperatures of 200 and 230 °C, respectively. The data of the monomer conversion at 180 °C are not available because they were too low to be measured by the method developed in this work. There were two possible reasons for the very low monomer conversion values at 180 °C. First, the temperature was low and consequently the polymerisation rate was low. Second, growing centres of the PA6

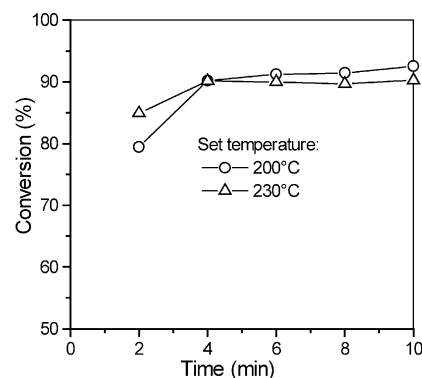


Fig. 3. Effect of the set temperature on the evolution of the CL conversion as a function of time. Mass composition: PP-g-TMI/CM/CL = 50/4/50. Set temperature = 200 °C (E2) or 230 °C (E3).

grafts might crystallise at that temperature considering the fact that their melting temperature was around 220 °C. Once crystallised, their mobility would be largely reduced and consequently the polymerisation would be slowed down or stopped completely [9]. Nevertheless, the second reason likely did not stand because at 180 °C PA6 grafts would crystallise very slowly if they crystallised at all. In any event, if they did crystallise, their degree of crystallinity would be low. This is confirmed by the data in Table 3 which shows the degrees of crystallinity, the melting temperatures and the recrystallisation of the graft copolymer corresponding to experiment E3, a representative experiment of this work.

The situation was very different when the set temperature was increased to 200 or 230 °C. In fact, the polymerisation process went to completion in less than 4 min. The time of the polymerisation process per se was surely much shorter. This is because in order for the polymerisation to occur, all the components of the polymerisation system (PP-g-TMI, CM and CL) had to be molten and mixed up correctly. This always required a certain period of time, depending on the mixing and thermal conditions. The ultimate monomer conversion, taken at 10 min of polymerisation, was 92.6% at 200 °C and 90.3% at 230 °C. As shown in Table 2, the corresponding polymerisation temperature was 209 and 237 °C, respectively. Puffr and Šebenda [15] established an equation relating the fraction of water extractable species at equilibrium, E , to the equilibrium CL conversion, p_e , and the polymerization temperature for non-crystallized PA6:

$$P_e = 100 - E = 104.67 - 0.05852T(\%, ^\circ\text{C}) \quad (10)$$

According to this equation, the values of p_e at 209 and 237 are 92.4 and 90.8%, respectively. The agreement is surprising good between the calculated values and the experimental ones.

Fig. 4(a) shows the evolution of the polymerisation temperature as a function of time for E1, E2 and E3. Approximately 3 min were needed for the polymerisation temperature initially at room temperature to reach the set

Table 2
Selected information about 12 experimental trials carried out in this work

Exp. Nb.	Mass composition PP-g-TMI/CM/CL	Molar ratio NCO/CL	Molar ratio NaCl/CL	Molar ratio NCO/NaCl	$T_{\text{set}} \text{ } ^\circ\text{C}$	$T_{5 \text{ min}} \text{ } ^\circ\text{C}$	$T_{10 \text{ min}} \text{ } ^\circ\text{C}$
E1	50.00/4.00/50.00	3.15/100	0.98/100	3.23	180	174	174
E2	50.00/4.00/50.00	3.15/100	0.98/100	3.23	200	208	209
E3	50.00/4.00/50.00	3.15/100	0.98/100	3.23	230	235	237
E4	50.00/3.00/50.00	3.26/100	0.75/100	4.35	200	205	209
E5	50.00/2.00/50.00	3.31/100	0.53/100	6.25	200	189	192
E6	25.00/4.00/75.00	1.09/100	0.69/100	1.59	200	224	228
E7	25.00/3.00/75.00	1.10/100	0.52/100	2.13	200	207	223
E8	25.00/2.00/75.00	1.12/100	0.35/100	3.23	200	205	205
E9	12.50/4.00/87.50	0.47/100	0.58/100	0.81	200	233	233
E10	25.00/4.00/75.00	1.09/100	0.68/100	1.61	200	209	223
E11	75.00/4.00/25.00	9.05/100	1.87/100	4.84	200	–	–
E12	87.50/4.00/12.50	18.87/100	3.34/100	5.65	200	207	208

temperature. Thereafter, the polymerisation temperature remained unchanged when the set temperature was 180 °C and exceeded the set temperature when the latter was 200 or 230 °C.

At the lowest set temperature of 180 °C, the polymerisation temperature was very close to the set temperature. This is expected because the CL conversions were very low. Very low CL conversions imply that the amount of the heat released by the polymerisation was very small and could easily be removed by the cooling system of the mixer. Moreover, the amount of the heat generated by the rotation of the blades of the mixer was also low because of the very low viscosity of the system. By contrast, at the set temperature of 200 or 230 °C, more than 90% of the monomer was polymerised onto PP-g-TMI chains in less than 4 min. As a result, both the rate of the monomer conversion and that of the corresponding heat release were high. The concomitant increase in the molar mass of the corresponding PP-g-PA6 graft copolymer, $M_{\text{PP-g-PA6}}$, with respect to that of PP-g-TMI, $M_{\text{PP-g-TMI}}$, was important. The ratio between them can be calculated by the following equation:

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

When the PP-g-TMI/CM/CL mass composition was 50/4/50, the molar mass of the PP-g-PA6 graft copolymer was twice that of PP-g-TMI when the monomer conversion was 90%. As the polymerisation proceeded, the fraction of

the monomer in the system decreased. The fraction and molar mass of the PP-g-PA6 graft copolymer increased concomitantly. As a result, the viscosity of the system increased and the rate of the heat generated by the rotation of the blades of the mixer (viscous dissipation) became important. The fact that the polymerisation temperature exceeded the set temperature was directly related to the combined effects of the heat release of the polymerisation reaction and the viscous dissipation. It should be noted that the difference between the polymerisation temperature corresponding to 10 min reaction, $T_{10 \text{ min}}$, and the set temperature was only related to the viscous dissipation and had nothing to do with the heat of polymerisation. This is because the polymerisation process ended much earlier. The above results suggest that polymerisation conditions should be above 220 °C so that the polymerization rate is high enough.

Fig. 4(b) shows the evolution of the torque during the polymerisation. The ultimate torque value at the set temperature of 180 °C was much smaller than that at 200 °C and was close to that at 230 °C. This is in line with the very low CL conversions at 180 °C. The peak on the torque-time curve corresponded mainly to the melting process of PP-g-TMI. As for the peaks on the torque-time curves at 200 and 230 °C, they corresponded to the melting of PP-g-TMI and the polymerisation of CL. In other words, at those two temperatures, both the melting of the PP-g-TMI and the polymerisation of CL took place almost simultaneously.

Table 3
Selected characteristics of the graft copolymer obtained by experiment E3

	Mass composition (%)	Molar mass averages		Melting temperature ^a (°C)	Recrystallisation temperature ^a	Degree of crystallinity ^a (%)
		\bar{M}_n	\bar{M}_m			
PP backbone	50	213 kg/mol	510 kg/mol	145	100 °C	30
PA6 grafts	50	3.3 kg/mol per PA6 graft ^b		215	Not detected	20

^a Measured by DSC at a heating or cooling rate of 10 °C/min.

^b Calculated assuming that all NCO groups have participated in polymerisation.

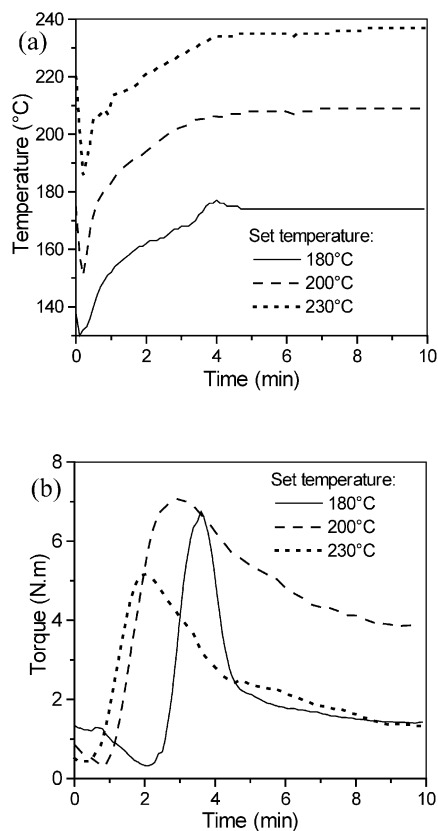


Fig. 4. Effect of the set temperature on the evolution of the polymerisation temperature (a) and that of torque (b). Mass composition: PP-g-TMI/CM/CL=50/4/50; set temperature=180 (E1), 200 (E2) or 230 °C (E3).

4.2. Effects of the NaCL/CL molar ratio

Fig. 5(a) and (b) show, respectively, the evolution of the polymerisation temperature and that of the torque as a function of time. The mass composition PP-g-TMI/CM/CL was 50/50/ x with x being 4 (E2), 3 (E4) or 2 parts (E5). The set temperature was 200 °C. The polymerisation temperature exceeded the set temperature when the CM was 3 or 4 parts and was very close to the set temperature when CM was 2 parts. This infers that the monomer conversion was low with 2 parts of CM and was much higher with 3 or 4 parts of CM. As for the torque, the higher the CM concentration, the shorter the time after which the torque started to increase and the higher the ultimate torque value. This implies that an increase in the catalyst concentration led to an early start of the polymerisation and an increase in the ultimate monomer conversion.

The above results are in accordance with the evolution of the monomer conversion as a function of time (Fig. 6). The value of the ultimate monomer conversion was 52.8, 78.2 and 92.6% when the CM was 2, 3 and 4 parts, respectively. At the first glance, the catalyst concentration dependency of the ultimate monomer conversion was surprising. However, it may be explained as follows. When the PP-g-TMI/CL mass ratio in the PP-g-TMI/CM/CL system was fixed,

the lower CM concentration, the higher NCO/NaCL molar ratio and consequently the higher the molar ratio between the corresponding *N*-acyl- ϵ -caprolactam and NaCL. It was reported that when the *N*-acyl- ϵ -caprolactam and NaCL molar ratio exceeded 2.5, the lactam anions started to disappear so rapidly that the polymerisation kinetics slowed down considerably before the monomer–polymer equilibrium could be reached [16]. Reduction in the rate of polymerisation and monomer conversion at high activator concentrations was attributed to the so-called C-acylation reaction [5]. This is what might have happened to E5 whose NCO/NaCL molar ratio was 6.25. Indeed, the polymerisation stopped after 4 min of mixing, despite the fact that the monomer conversion was only 52.8%, which was far from the corresponding equilibrium monomer conversion value. In the case, where the concentration in CM was 3 parts, the monomer conversion increased very rapidly in the first 2 min and then slowed down considerably. The value of the monomer conversion obtained after 10 min of mixing was only 78.2%, which was also much lower than the corresponding equilibrium monomer conversion. Thus, the CM in the PP-g-TMI/CM/CL polymerisation system should be higher than 3 parts so that sufficient monomer conversions can be obtained. This amounts to saying that

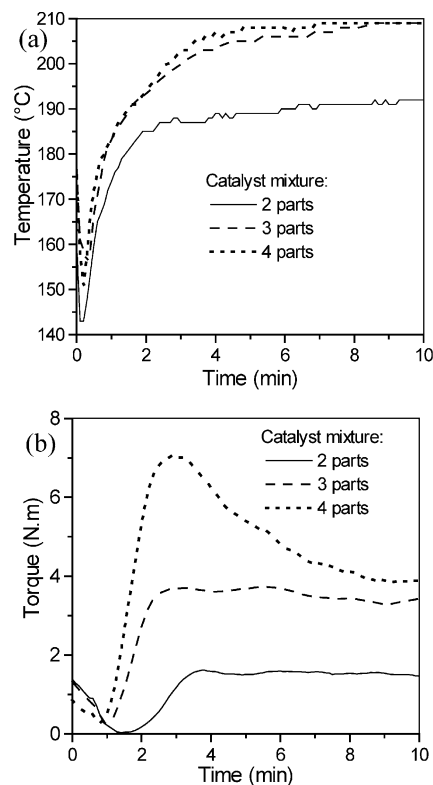


Fig. 5. Effects of the CM concentration on the evolution of the polymerisation temperature (a) and that of the torque (b) as a function of time. Mass composition PP-g-TMI/CM/CL=50/ x /50 with x being 4, 3 or 2 corresponding to E5, E4 and E2, respectively. The set temperature was 200 °C.

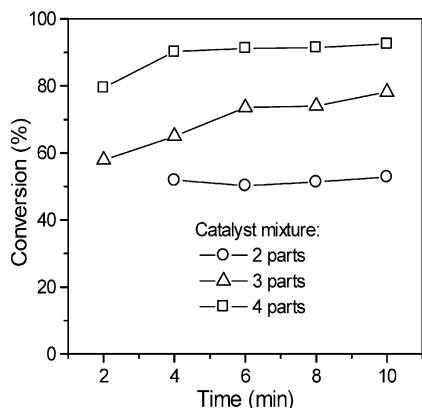


Fig. 6. Effect of the catalyst mixture concentration on the evolution of the monomer conversion as a function of time. See Fig. 5 for experimental details.

the NCO/NaCL molar ratio should be smaller than 4.3. This will be further discussed later.

The positive effect of the CM concentration on the CL conversion for the mass composition PP-g-TMI/CM/CL of 50/x/50 reported above was better observed for the mass composition of 25/x/75 (E6–E8). As shown in Fig. 7, when the CM was 2 parts, the polymerisation temperature was very close to the set temperature and the torque remained low, indicating that the CL conversion was low. When it was increased to 3 or 4 parts, the ultimate polymerisation temperature was significantly higher than the set temperature and the ultimate torque value was high. This implies that a significant amount of polymerisation had taken place. The values of the ultimate polymerisation temperature and ultimate torque were higher with 4 parts of CM than those with 3 parts of CM. The time after which the torque started to increase was 6 and 3 min for 3 and 4 parts of CM, respectively. This indicates that the polymerisation rate increased with increasing CM concentration. The ultimate monomer conversion was 88.3 and 91.4% when the CM was 3 and 4 parts, respectively. According to Eq. (11), the molar mass of the corresponding PP-g-PA6 graft copolymer was expected to be approximately four times that of PP-g-TMI. This is why the ultimate polymerisation temperatures exceeded the set temperature by almost 30 °C.

The above results showed that for both 50/x/50 and 25/x/75 mass compositions, only when x exceeded 3 were the monomer conversions high enough. According to Table 2, when x was 3, the corresponding NaCL/CL molar ratio was 0.75 and 0.52 for the first and second mass compositions, respectively. Thus, in order to obtain sufficiently high CL conversions it is recommended that the NaCL/CL molar ratio be above 0.5.

4.3. Effects of the NCO/CL molar ratio

Fig. 8 shows the evolution of the monomer conversion as a function of time for five different NCO/CL molar ratios corresponding to five different PP-g-TMI/CL mass ratios

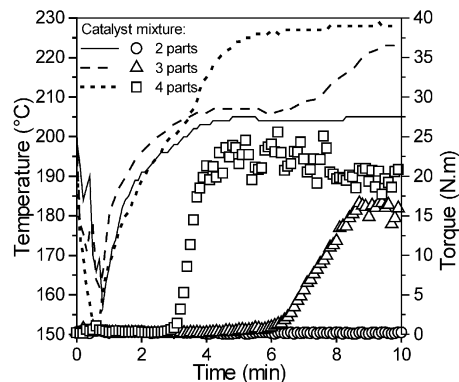


Fig. 7. Effects of the catalyst mixture concentration on the evolutions of the polymerisation temperature and torque. Mass composition PP-g-TMI/CM/CL=25/x/75 with x being 2, 3 or 4 corresponding to E8, E7 and E6, respectively. The set temperature was 200 °C. Lines: polymerisation temperature; open symbols: torque.

(E9–E12). The set temperature was 200 °C. In the case of E9 in which the NCO/CL was the lowest, only the CL conversion at the end of polymerisation (10 min) was available because of sampling difficulties. In fact, the polymerised product quickly became solid-like. This is because the initial NCO/CL was so low that the molar mass of the corresponding PP-g-PA6 was very high. According to Eq. (11), it became 7.5 times that of the PP-g-TMI when the monomer conversion was 89.6%, corresponding to 10 min of polymerisation. From Fig. 8, for the three lower NCO/CL molar ratios, both the polymerisation rate and the ultimate monomer conversion were high. The polymerisation process went to completion in less than 4 min and the ultimate monomer conversion was about 90%. This was not the case for the two higher NCO/CL molar ratios. The value of the monomer conversion after 10 min of reaction was only 54.2 and 38.6% for the NCO/CL molar ratios of 4.84 and 5.65, respectively. For those two high NCO/CL molar ratios, the above mentioned acylation reaction could have been important.

Fig. 9(a) and (b) show, respectively, the evolution of the

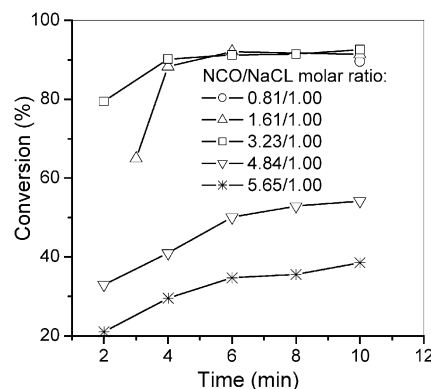


Fig. 8. Effect of the NCO/NaCL molar ratio on the evolution of the monomer conversion as a function of time. NCO/NaCL molar ratio: 0.81 (○), 1.61 (△), 3.23 (□), 4.84 (▽), 5.65 (*); set temperature: 200 °C.

polymerisation temperature and that of the torque. The values of the ultimate polymerisation temperature were much higher for the two lower NCO/CL molar ratios than for the two higher ones. The values of the ultimate torque were also much higher for the two lower NCO/CL molar ratios than for the two higher ones because both the monomer conversions and the molar masses of the corresponding PP-g-PA6 graft copolymers were higher.

Fig. 10 shows the evolutions of the ultimate monomer conversion and the ultimate polymerisation temperature are plotted as a function of the NCO/CL molar ratio. On the one hand, the trend that the ultimate conversion decreased with increasing temperature is in agreement with the CL/PA6 equilibrium. On the other hand, the ultimate monomer conversion first increased slightly with increasing NCO/CL molar ratio till the latter was 3.23. It then dropped markedly when that ratio was increased to 4.84 because of the C-acylation reaction mentioned above. The ultimate polymerisation temperature always decreased with increasing NCO/CL molar ratio because both the monomer conversion molar mass of the PP-g-PA6 graft copolymer decreased. These results indicate that the NCO/CL molar ratio should be lower than a certain value which would be located somewhere between 3.23 and 4.84, say, 4.00/1.00, so as for the polymerisation rate and the monomer

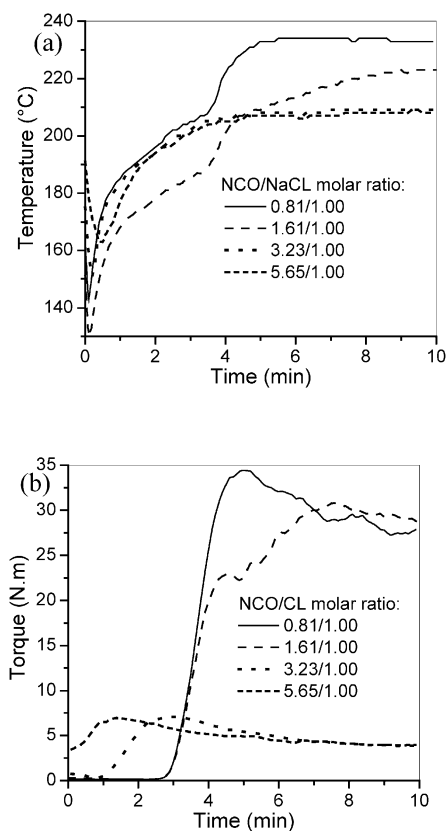


Fig. 9. Effect of the NCO/NaCL molar ratio on the evolution of the polymerisation temperature (a) and that of the torque (b) as a function of time. See Fig. 8 for experimental details.

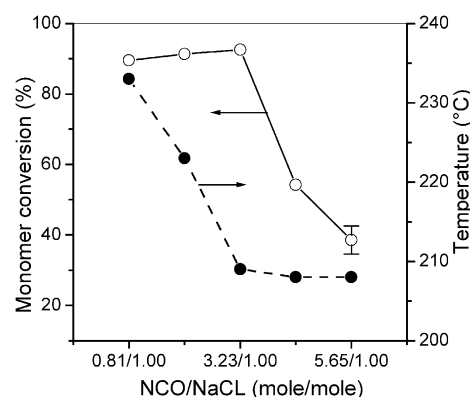


Fig. 10. Effect of the NCO/NaCL molar ratio on the ultimate monomer conversion and ultimate polymerisation temperature. See Fig. 8 for experimental details.

conversion to be high enough. In the preceding section, it has been suggested that this ratio be lower than 4.3. Thus, it is recommended that the NCO/NaCL be smaller than 4.

5. Concluding remarks

This paper deals with the synthesis of polypropylene (PP) and polyamide 6 (PA6) graft copolymers with the former as the backbone and the latter as grafts (PP-g-PA6) by activated anionic polymerisation of ϵ -caprolactam (CL) in the melt. Sodium ϵ -caprolactam (NaCL) was used as a catalyst and a 3-isopropenyl- α,α -dimethylbenzene isocyanate (TMI) bearing PP as an activator. The effects of temperature and the concentrations of the catalyst and the activator on the kinetics of the above heterogeneous polymerisation system were investigated.

An increase in temperature or in the catalyst concentration led to an increase in the polymerisation kinetics and the monomer conversion. Increasing the concentration of the activator also favoured the polymerisation rate and the monomer conversion provided that it was not very high. Otherwise, lactam anions would be destroyed, at least in part, by the C-acylation reactions. The polymerisation rate would then slow down.

It is suggested that if the synthesis is to be carried out by a reactive extrusion process whose mean residence time is less than a few minutes and whose mixing and heat transfer capacities are known to be well above those of the batch mixer used in this work, it is recommended that the temperature be above 220 °C. Moreover, the molar ratio between NaCL and CL be higher than 0.5 and at the same time that between the isocyanate group and CL be lower than 4.

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