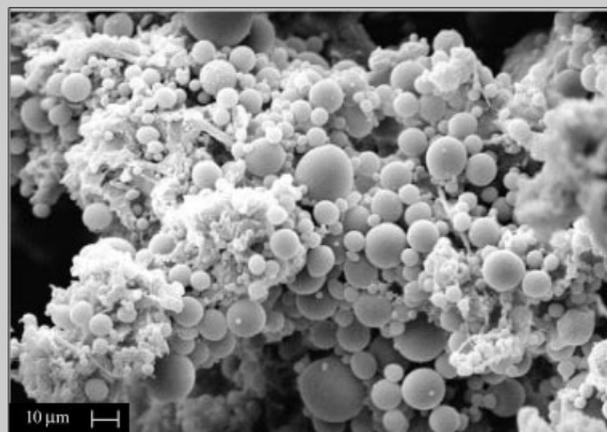


Full Paper: The fast-activated anionic polymerization of ϵ -caprolactam has been performed in suspension in order not only to efficiently dissipate the heat of polymerization, but also to directly synthesize powdered polyamide 6. The continuous phase of the system is composed of polyisobutene oils: five fractions, different in their molecular weights and viscosities, have been used and thoroughly studied in terms of their influence on polymerization yield, as well as on polyamide 6 chemical and physical properties, and on shape and size of the polymer particles. The above characterizations have been performed on samples synthesized varying the weight ratio between the suspending medium and the droplets made of monomer, initiator (sodium caprolactamate) and ultra-fast activator (cyclohexyl carbamoyl caprolactam).

Sample LR14 (PIB 200, CL wt.-% = 6.7).



Fast-Activated Anionic Polymerization of ϵ -Caprolactam in Suspension, 1

Role of the Continuous Phase on Characteristics and Properties of Powdered PA6

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Introduction

Almost all methods accomplished so far for the production of powdered polyamide 6 (PA6) are based on some processing operations on the polymer, previously synthesized by hydrolytic polymerization in bulk. The most common processing method is the cryogenic grinding of hydrolytic PA6 pellets: the resultant powders are made with sizes (50–300 μm) adequate to subsequent applications, but irregularly shaped with several edges and sinterized zones, and characterized by low porosity. Another, less employed method is based on polyamide precipitation in powder form from its solution by addition of a suitable non-solvent: by this way, the powders have similar sizes, but higher porosity and

greater specific area, as compared to those previously mentioned, and are characterized by an almost spherical shape.

At present, only very few methods to directly synthesize powdered PA6 on a laboratory^[1–3] or industrial scale^[4] are known: namely, some exploratory studies, dealing with ϵ -caprolactam (CL) precipitation polymerization by the anionic route in solution, have been performed.^[1–3] As far as we know, this approach did not undergo significant scaling-up, because the high polymer yields were too low and a relevant agglomeration phenomenon among the reacting droplets was likely to occur. Other approaches,^[4] presumably based on low-conversion anionic polymerization of CL in bulk, have found limited applications in the cosmetics area.

On the basis of the above considerations on the present state-of-the-art and taking also in account the interesting applications linked to the many ways the powdered PA6 can be processed (pressing and sintering, powder coating, rotational molding, etc.), the approach described in the following is worth of some attention for its innovative aspects, namely the fine tunability of polymer properties besides the very high conversion yields in rather short reaction times, which cannot be achieved by other approaches.

The polymerization of CL has been performed in suspension taking advantage of the 'activated anionic mechanism', both factors which allowed us to work quasi-isothermally at relatively low polymerization temperatures (T_{pol} of ca. 150 °C) and short reaction times (few minutes), thanks to the action of an ultra-fast activator. The latter has been chosen on the basis of our previous studies^[5] carried out in isothermal conditions in bulk. The above reaction conditions very favorably compare to the much higher operational temperatures (T_{pol} of ca. 270 °C) and the much longer reaction times (≥ 16 h) needed for a typical run of the hydrolytic process.

The search of suitable suspending media for the anionic polymerization of CL has been a rather difficult task, not only because specific properties of the fluid (such as chemical inertia, high resistance at T_{pol} in presence of strongly basic agents, low environmental impact, low cost, etc.) are requested, but also for the high solubility of molten CL in most tested fluids. Some low molar mass polyisobutene (PIB) oils resulted the most efficient fluids to be used as suspending media for CL. Accordingly, they have been comparatively evaluated in terms of their effects not only on the polymerization process, but also on the characteristics of the obtained powders. No specific suspension stabilizer has been introduced in the reacting medium at this stage. It will be taken in consideration in further work,^[6] after a full understanding of the role played by the other process parameters on the neat system. Analogously, no nucleating agent has been added to the reacting mixture. Some preliminary experiments using polymeric stabilizers have shown, however, an increased CL solubility in the PIB continuous phase, strongly decreasing yields and worsening properties of the PA6 powders.

Experimental Part

Materials

CL was kindly supplied by DSM Research, Geleen, the Netherlands, and utilized after drying over P_2O_5 . Sodium hydride was used as a 60% dispersion in mineral oil (Aldrich), in order to promote the in situ formation of sodium caprolactamate (NaCL), which was the actual polymerization initiator. Cyclohexyl carbamoyl caprolactam (CCCL) was a laboratory preparation, obtained by blocking cyclohexyl isocyanate (Fluka) with CL in boiling toluene and removing the solvent by vacuum distillation. Five samples of poly-

isobutene, characterized in terms of different viscosities, were kindly supplied by BP Company: PIB 30, PIB 120, PIB 200, PIB 600, and PIB 2000.

After performing the anionic polymerization run in suspension, PIB was removed using petroleum ether (Fluka) as received. To purify PA6 from the low-molar mass species, methanol (Prolabo) was used as received. For the UV analyses, anhydrous formic acid was prepared by distillation of 98% formic acid (Fluka) under reduced pressure after reaction with boric anhydride. H_2SO_4 for viscometric measurements was 95–97% (Fluka) and used as received.

Polymerization Runs

The polymerization reactions were carried out in a cylindrical glass reactor (capacity 250 ml), provided with mechanical stirrer, dry nitrogen inlet and outlet, temperature measurement device and injecting system for the introduction of the reactant mixture (CL + NaCL + CCCL). The reactor, filled with 160 g of PIB, was immersed in an oil bath thermostated at the polymerization temperature (155 °C). The reactant mixture was prepared in another glass vessel kept at 95 °C (temperature sufficient to reach homogeneity of the molten system, but too low to start the polymerization reaction in the time scale used) and injected into the reactor with the aid of a dry nitrogen stream under moderate pressure. Typical recipes are given in Table 1. After 600 s, which is a time largely adequate to reach reaction completion under all chosen conditions, as verified by preliminary tests, the mixture of PIB and PA6 (plus catalytic residues, unreacted CL and low-molar mass species) was carefully added with petroleum ether in order to ensure a quick cooling, as well as to dilute the highly viscous suspending medium.

PA6 Purification

The diluted system was kept at room temperature under stirring for ca. 10 h, and then filtered to collect the PA6 powders, which subsequently underwent extensive Soxhlet extraction by petroleum ether in order to completely remove PIB and unreacted CL. To further purify PA6 from higher oligomers and other low-molar mass products, if any, a Soxhlet extraction with methanol for 8 h was finally carried out. Fully purified powders were dried under vacuum at 70 °C for 20 h.

Product Characterization

The high polymer yield was evaluated as percent ratio of the weight of dried PA6 sample to the weight of CL injected in the suspending medium.

A Perkin-Elmer Lambda 9 UV spectrophotometer was used to monitor the possible presence of structural irregularities in PA6 chains, as most of them are able to strongly absorb in the UV region^[5] with O.D. maxima at 270–280 nm. It is customary to assume that UV absorption is directly proportional to the total amount of irregular structures.^[7] The UV spectra were performed on 1% (w/w) PA6 solutions in anhydrous formic acid and recorded between 250 and 400 nm (1 cm path length) in search of absorption bands.

Table 1. Influence of the suspending medium and the monomer content in the reacting mixture on high polymer yield. $T_{\text{pol}} = 155\text{ }^{\circ}\text{C}$, $[\text{NaCL}] = [\text{CCCL}] = 0.6\%$ (mol/100 mol of CL).

Sample code	PIB code	PIB viscosity at 100 °C		PIB \overline{M}_n (GPC)	CL		High polymer yield	
		cSt			wt.-%	%		
LR1	30	635		1 300	20.0		85	
LR2	30	635		1 300	14.3		64	
LR3	30	635		1 300	9.1		48	
LR4	30	635		1 300	6.7		0	
LR5	120	2 500		2 250	20.0		90	
LR6	120	2 500		2 250	14.3		82	
LR7	120	2 500		2 250	9.1		67	
LR8	120	2 500		2 250	6.7		67	
LR9	200	4 250		2 600	20.0		91	
LR10	200	4 250		2 600	14.3		84	
LR11	200	4 250		2 600	10.5		75	
LR12	200	4 250		2 600	9.1		67	
LR13	200	4 250		2 600	7.7		56	
LR14	200	4 250		2 600	6.7		37	
LR15	600	12 200		4 200	20.0		91	
LR16	600	12 200		4 200	14.3		87	
LR17	600	12 200		4 200	9.1		75	
LR18	600	12 200		4 200	6.7		67	
LR19	2 000	40 500		5 900	20.0		86	
LR20	2 000	40 500		5 900	14.3		54	
LR21	2 000	40 500		5 900	9.1		33	
LR22	2 000	40 500		5 900	6.7		53	

An Ubbelohde viscometer was used to determine PA6 solution viscosities and evaluate weight average molar masses. The measurements were performed at 20 °C on polymer solutions in H_2SO_4 ($c = 0.5\text{--}1\text{ g/dL}$).

Glass transition temperature (T_g), melting temperature (T_m), and degree of crystallinity (x_c) of our PA6 samples were measured by a Mettler Differential Scanning Calorimeter (DSC) Mod. TC 10A. All samples underwent a cycle of three temperature scans, as follows: a first heating from 0 to 270 °C (at 20 K/min); followed by cooling from 270 to 0 °C (at 10 K/min) and a second heating from 0 to 270 °C (at 20 K/min).

Micrographs of the particles were obtained with a LEO scanning electron microscope (SEM) Mod. stereoscan 440, while particle size distribution and average dimensions were evaluated by a Malvern Particle Sizer Mod. 2600C.

Results and Discussion

The present work is based on the working hypothesis that a careful control of the polymerization temperature can minimize all drawbacks of CL anionic polymerization. If we assume that the very poor dissipation of the polymerization heat in CL bulk polymerization, typically run in quasi-adiabatic conditions, is responsible for Claisen-type condensation reactions, color center formation, extensive chain branching and, ultimately, crosslinking, it may be sufficient to have, together with extremely fast polymerization rates, very efficient means of heat transfer in order to achieve product quality comparable to that of hydrolytic PA6. The above hypothesis has been fully proven quite recently, when we performed the quasi-isothermal anionic

polymerization of CL in bulk.^[5] Very thin discs of PA6 have been produced in the 0.8 mm cavity of a thick stainless steel mold, thus allowing to accurately maintain a constant temperature throughout polymerization. By choosing suitable experimental conditions (polymerization temperature between 150 and 165 °C and ultra-fast activators, like CCCL) the above drawbacks have been completely eliminated.

The subsequent steps are herein described. As is well known, the best methods for the dissipation of polymerization heat are based on monomer compartmentalization in small droplets acting as polymerization micro-reactors, surrounded by an immiscible fluid characterized by efficient heat transfer properties. We will present here our results on the fast-activated anionic polymerization of ϵ -caprolactam in PIB suspension, using experimental conditions based on the optimization of our previous results in bulk.^[5] As a consequence of our set-up, fine PA6 powders, characterized by very high structural regularity, have been produced, as mentioned in the Introduction. Preliminary accounts on the above process have already been given elsewhere.^[8,9]

Polymerization Yields

Polymerization data are given in Table 1, where the high polymer yields are listed as functions of CL content for each of the five PIB oils. Viscosity (at 100 °C) and number average molar mass of the oils are also given. For all syntheses, the polymerization temperature of 155 °C has been chosen, and NaCL and activator (CCCL) concentrations have been fixed at 0.6% (mol/100 mol of CL). As already mentioned,

the experimental data given in a previous paper^[5] and referred to quasi-isothermal bulk conditions, have shown that the above values of temperature and catalytic species concentration are the optimum ones in terms of high polymer yield, reduction of polymerization time and minimization of side reactions.

As shown in Table 1, the high polymer yield seems to be strongly influenced by monomer content in the reacting mixture, i.e. is sharply decreasing when CL content decreases. The expected behavior for an ideal suspension polymerization process is, on the contrary, a constant conversion value at fixed experimental conditions.

Indeed, in spite of the fact that polyisobutene was discovered as the most suitable suspending medium among all tested fluids, we have found that it cannot be considered completely immiscible with CL at the chosen polymerization temperature. Under vigorous stirring, PIB is able to slowly dissolve even large amounts of CL. However, in actual polymerization runs, this slow homogenization process is contrasted or largely prevented by the very fast polymerization reaction. The overall effect, therefore, is a complex function of various parameters, often opposing each other: rate of polymerization, stirring rate, droplet dimensions, total amount of CL, viscosity of the continuous phase, CL diffusion through the polymer particles, etc. A qualitative explanation of the apparently anomalous behavior, shown in Table 1, is linked to differences in rates and extent of CL solubilization for the various PIB oils during polymerization. In general, we may expect that the rate and the extent of CL homogeneous mixing with PIB be higher the lower the molar mass of PIB is. Indeed, with PIB 30 and 6.7 wt.-% of CL, polymerization does not occur due to complete miscibility of the components.

For each PIB, increasing the CL content in the suspension medium causes an increase of polymer yield, due to the increased amount of the immiscible CL fraction as compared to the total CL content.

The influence of the five PIB oils on polymer yields at constant values of CL content can also be evaluated from the data of Table 1. In the whole range of CL content values, PIB 600 gives the highest high polymer yields. Differences with the other oils are emphasized at lower CL contents, whereas for 20 wt.-% of CL (the maximum allowable CL content) they are reduced to only a few percent. It should be noticed that the data referred to PIB 2000, given in the last column, are affected by poor reproducibility because of the slow and difficult monomer dispersion in the oil, which is very viscous at T_{pol} , even at the highest stirring rate. If we do not take in consideration the data pertaining to PIB 2000, there is a general trend to higher yields for higher molar mass PIBs, i.e. when we are in presence of a decreased CL solubility. As mentioned above, PIB 30, characterized by the lowest molar mass, is able to completely solubilize 6.7 wt.-% of CL in our experimental conditions, thus preventing its polymerization.

Although the above considerations are qualitatively valid, a word of caution is, however, necessary: presumably, the whole amount of high polymer could not be easily separated from PIB and recovered, due to some experimental difficulties linked mainly to the high viscosity of the system at room temperature. This fact can explain not only the relatively low polymer yields pertaining to PIB 2000, which has a much higher viscosity as compared to the other PIB oils, but also the relatively lower conversions found in the suspension process, as compared to the corresponding runs in bulk (98.9 wt.-%).^[5]

Temperature Control, UV Absorption and Chain Regularity

As mentioned above, the non-isothermal anionic polymerization of CL is usually affected by many side reactions^[10] leading both to low-molar mass side products and to irregular structures present in the polyamide chain, which can act not only as branching and/or crosslinking points, but also as extensive structural defects and as color centers.

On the basis of our previous studies,^[5,11] key conditions to minimize the above side reactions are: i) the use of some ultra-fast activators, able to further increase the polymerization rate, and ii) the maintenance of lower and almost constant temperatures (quasi-isothermal conditions) throughout the polymerization reaction. Careful control of the latter parameter is a major factor for preventing the negative effects linked both to the relatively high heat of polymerization and to the strong basicity of the medium, while the use of ultra-fast activation agents allows for an additional increase of the already very high polymerization rate. As a consequence, the quick achievement of high conversions strongly reduces polymer chain mobility, thus preventing the occurrence of side reactions to any significant extent.

If we now consider the suspension process we are dealing with, both conditions are verified: the activator CCCL is able to decrease the polymerization time to only a couple of minutes, while the polymerization temperature can be kept almost constant at ca. 155 °C, due to the very fast dissipation of the polymerization heat ($-\Delta H_{\text{pol}}$), linked to the effective heat transfer from the polymer microparticles to the suspending fluid. Temperature control has been verified monitoring the temperature of the suspending medium during the polymerization process: as an example, the temperature profile in the case of PIB 200 is shown in Figure 1 for two different monomer contents: a) 6.7, and b) 20 wt.-%. At $t = 0$ the feed, made of monomer, activator and initiator and kept at ca. 95 °C, is injected in the continuous phase maintained at 155 °C. The sudden decrease of temperature to 148 (a) or 141 °C (b) is very rapidly counterbalanced by the heat of polymerization and the heater action, jointly. The difference between the full point curve (polymerization run) and the curve representing the

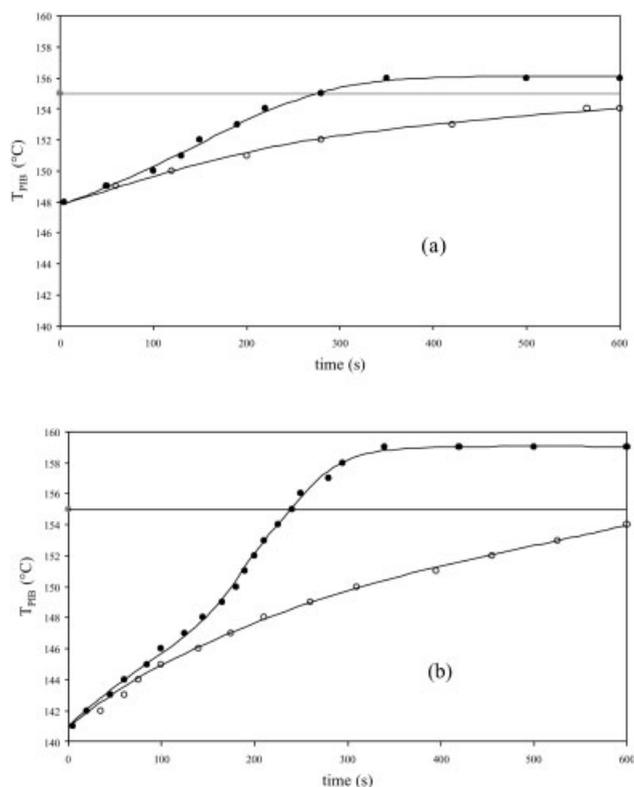


Figure 1. Temperature profile as a function of time a) CL, wt.-% = 6.7; b) CL, wt.-% = 20. ● polymerization run (monomer+activator+initiator injected at 95 °C); ○ reference run (only monomer injected at 95 °C); — heater temperature.

temperature increase due only to the heater action (open points) measures the effect of ΔH_{pol} only. From the data of Figure 1 it is evident not only that temperature control is sufficiently good (+ 4 °C at the utmost), but also that ca. 200 s are sufficient to re-establish initial conditions.

All PA6 samples have been analyzed by UV spectroscopy to evaluate the extension of side reactions in the above experimental conditions and, as expected, in every case no UV absorption whatsoever has been found. Therefore, a very high level of chain regularity, analogous to that found for samples synthesized in bulk with the same activator (CCCL) under quasi-isothermal conditions,^[5] can be safely claimed.

Viscometry and Molecular Weight

Measurements of solution viscosity have been performed in the conditions described in the Experimental in order to evaluate the average molar masses (\overline{M}_w) of our powdered samples as functions of both CL content and PIB type. \overline{M}_w has been calculated by the following equation:^[12]

$$[\eta] = 0.51 \cdot 10^{-3} \overline{M}_w^{0.74} \quad (1)$$

The results, in terms of $[\eta]$ and \overline{M}_w , are listed in Table 2, where data pertaining to samples synthesized employing

Table 2. Influence of the suspending medium and the monomer content in the reacting mixture on PA6 $[\eta]$ and \overline{M}_w .

Sample code	PIB code	CL	$[\eta]$	\overline{M}_w
		wt.-%	dL/g	
LR1	30	20.0	1.48	48 000
LR3	30	9.1	1.20	36 000
LR5	120	20.0	1.42	45 000
LR8	120	6.7	1.28	39 000
LR9	200	20.0	1.49	48 000
LR14	200	6.7	1.32	41 000
LR15	600	20.0	1.53	50 000
LR18	600	6.7	1.20	36 000
LR19	2 000	20.0	1.54	50 000
LR22	2 000	6.7	1.30	40 000
LR23	200 (+6 wt.-% CL)	20.0	1.74	60 000
PCL1	—	bulk	1.55	51 000

the maximum (20.0 wt.-%) and the minimum (usually 6.7 wt.-%) CL content are listed for each type of PIB used. For comparison, a sample (PCL1) of PA6 synthesized in bulk in the same isothermal conditions^[5] (T_{pol} , t_{pol} , [CCCL], [NaCl]) adopted for the samples obtained in suspension is also given in Table 2.

It is evident that the PIB used has almost no influence on PA6 molar mass, while CL content in the suspension medium plays a more significant role. In particular, when the content of CL increases, \overline{M}_w also increases, although not very much. Indeed, \overline{M}_w variations between the maximum and the minimum CL content are limited to 13–25% only. Moreover, all samples synthesized in suspension have molar masses lower than the molar mass of PCL1. It is worth noting that \overline{M}_w of the latter is 51 000, as calculated from solution viscosity data. If we assume that the most probable distribution of molar masses holds also for anionically synthesized PA6 samples, the corresponding \overline{M}_n value is 25 500. The calculated value for 0.6 mol-% of CCCL, in the absence of any other interfering factors, is close to 18 900. Therefore, we may conclude that some limited amount of branching points are present in PCL1, as well as in all samples synthesized in bulk, and they contribute to increase PA6 molar mass. As mentioned above, however, these irregularities of the chain do not cause any further development of defects, such as UV-absorbing structures, color centers, etc., thus keeping the structure of the PA6 chain almost perfectly regular. Going from bulk to suspension, the lower values of \overline{M}_w suggest a decrease of side reactions leading to branching points. Again, the absence of any UV absorption supports the very regular structure of our PA6 samples. The dependence of \overline{M}_w on CL content is not quite obvious, but we can try to explain the results taking in consideration two relevant phenomena: i) as shown also by the high polymer yields given in Table 1, a fraction of the reacting mixture can dissolve in the PIB oils; ii) suitable tests have evidenced that dissolved CCCL is not

effective anymore as activator because of some chemical reactions with impurities present in industrial PIB. As a consequence of the occurrence of these phenomena, solubilized CL, which cannot polymerize in solution (see sample LR4), remains partly adsorbed on the surface of the growing particles. Therefore, further chain growth can occur on the external surface of the droplets by the adsorbed monomer and its addition to those growing centers located close to the external surface. The contribution of CL in solution to the overall chain growth is greater when the amount of dispersed droplets is higher because of the higher content of growing centers at or near the surface.

To confirm this hypothesis, a sample of PA6 (LR23) has been synthesized in the same conditions of the sample LR9 but using a 6 wt.-% solution of CL in PIB 200 as the suspending medium. After purification and drying, the result in terms of high polymer yield was 109% (evaluated, as usual, as percent ratio between the weight of the polymer and the weight of CL injected in the suspending medium). In other words, for 100 g of the mixture and 20 g of injected CL additional 3.6 g of PA6 were produced at the expenses of 4.8 g of CL added to PIB. In terms of \bar{M}_w , (see last row of Table 2), a value of 60 000 was found ($[\eta] = 1.74$). From the above data, the contribution of the pre-dissolved CL to PA6 chain growth in the suspension process is evident.

Thermal Behavior

As mentioned in the Experimental, for the various PA6 samples prepared under different experimental conditions

(namely, CL content and PIB type), a thorough investigation on both the thermal transitions and the degree of crystallinity has been made by DSC analysis. Table 3 shows PA6 melting temperature (T_m) and crystallinity degree (x_c), measured during both the first and the second heating, and the glass transition temperature (T_g) clearly evident only during the second heating. The crystallinity degree in the first run exhibits a value ranging between 0.39 and 0.45, with an average value of 0.43, without any clear dependence on the experimental conditions chosen for PA6 synthesis. The same considerations are also valid observing the values of T_m (first heating): they range between 216 and 222 °C with an average melting temperature of 219 °C. On second heating, as expected, a significant decrease of the crystalline content has been found with an average value of $x_c = 0.30$. T_m (second heating, average value) is 217 °C. Also T_g does not show any appreciable dependence on the experimental conditions chosen for PA6 synthesis, with an average value of 55 °C.

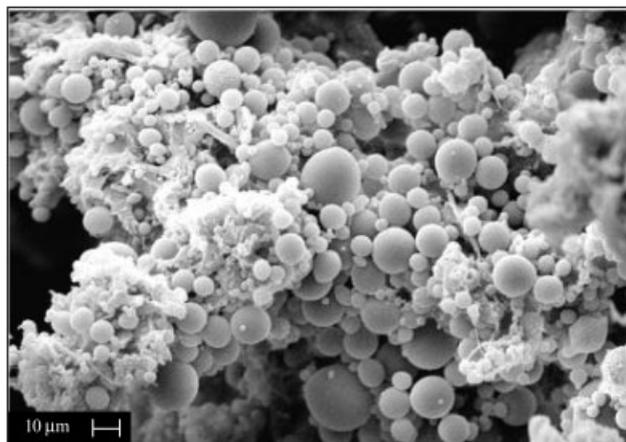
SEM Characterization

The observation of our PA6 samples under optical microscope already underlines the relevance of particle coalescence phenomenon: the powders, characterized by sizes (always less than 1 mm) and size distributions linked to the conditions of synthesis, do not show only regular, spherical shapes, but are constituted of a mixture of individual, almost spherical particles and irregularly shaped multi-particle microaggregates or granules.

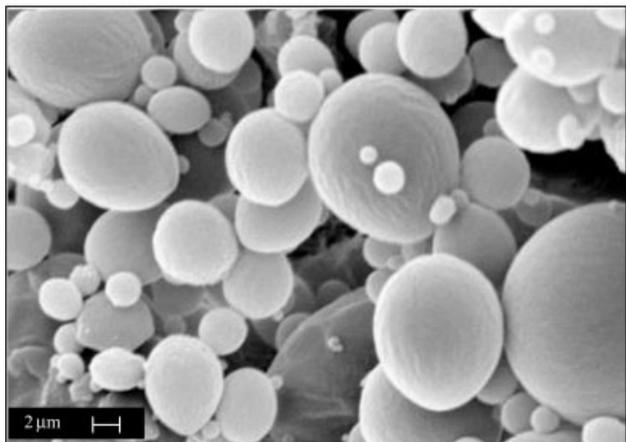
Table 3. Influence of the suspending medium and the monomer content in the reacting mixture on PA6 thermal properties and degree of crystallinity.

Sample code	PIB code	CL	T_m (1 st run)	x_c (1 st run)	T_g (2 nd run)	T_m (2 nd run)	x_c (2 nd run)
		wt.-%	°C		°C	°C	
LR1	30	20.0	221	0.44	54	217	0.28
LR2	30	14.3	220	0.45	56	218	0.31
LR3	30	9.1	219	0.41	57	217	0.31
LR5	120	20.0	219	0.43	54	218	0.30
LR6	120	14.3	218	0.41	56	217	0.28
LR7	120	9.1	219	0.42	56	217	0.31
LR8	120	6.7	216	0.40	57	217	0.29
LR9	200	20.0	219	0.45	49	217	0.31
LR10	200	14.3	219	0.45	52	217	0.30
LR11	200	10.5	218	0.45	59	218	0.29
LR12	200	9.1	219	0.40	56	216	0.28
LR13	200	7.7	218	0.42	57	217	0.29
LR14	200	6.7	218	0.38	58	218	0.30
LR15	600	20.0	220	0.43	55	217	0.30
LR16	600	14.3	219	0.43	55	216	0.32
LR17	600	9.1	218	0.47	57	217	0.33
LR18	600	6.7	218	0.48	56	218	0.34
LR19	2 000	20.0	221	0.45	56	218	0.28
LR20	2 000	14.3	222	0.45	56	219	0.27
LR21	2 000	9.1	221	0.42	55	219	0.30
LR22	2 000	6.7	218	0.39	56	218	0.29

A deeper evaluation of powder size and shape has been performed using scanning electron microscopy. For many systems the majority of spherical units are deprived of their individuality because of the coalescence phenomenon occurring during the polymerization. However, when the less viscous suspending agent (PIB 30) and the lowest CL content (9.1 wt.-%) were used, several individual spherical particles of rather small particle size could be observed, thus suggesting that the coalescence phenomenon can be properly reduced by lowering the content of monomer droplets. Even better results were obtained with a more viscous suspending medium (PIB 200). In this case, the agglomeration was less likely to occur, as evidenced by the much higher fraction of individual spherical particles, even when high CL content was used. By lowering the monomer content in the system to 6.7 wt.-%, the particle size further decreased with a limited coalescence, so that most particles maintained their original, almost spherical shape (Figure 2 (a) and (b)). PIB 600 and PIB 2000 had



(a)



(b)

Figure 2. Sample LR14 (PIB 200, CL wt.-% = 6.7). (a) General view, (b) detail.

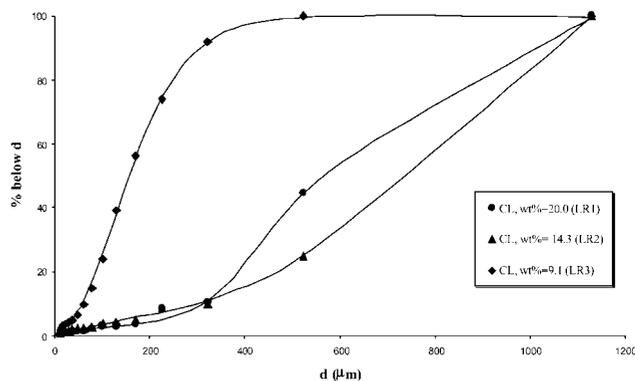


Figure 3. Particle size distribution as a function of CL content using PIB 30.

a similar influence on particle shape, as already shown by PIB 200.

Particle Size

As mentioned in the Experimental Part, the particle size distribution and the average particle size have been determined for all PA6 samples using a Malvern Particle Sizer.

Particle size distributions are shown in Figure 3–7, where the PA6 samples have been divided in five different groups depending on the PIB used. In each inset, CL contents are given. The average dimensions of the particles (expressed as d_{32}) are listed in Table 4 as functions of both variables of the process, CL content and PIB type. The values of d_{32} have been evaluated by the classical equation:

$$d_{32} = \frac{\int_{-\infty}^{+\infty} x^3 \cdot f(x) \cdot dx}{\int_{-\infty}^{+\infty} x^2 \cdot f(x) \cdot dx} \quad (2)$$

where the numerical particle distribution $f(x)$ gives the number of particles having the dimension x .

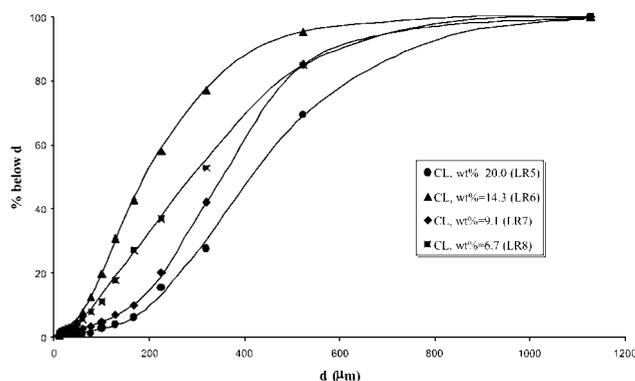


Figure 4. Particle size distribution as a function of CL content using PIB 120.

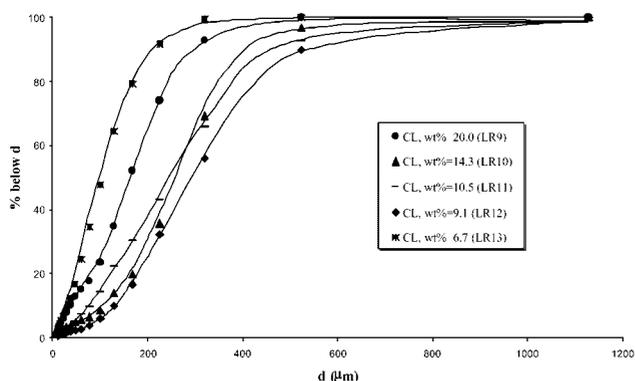


Figure 5. Particle size distribution as a function of CL content using PIB 200.

The plots of Figure 3–7 show the relative content of particles having dimensions lower than the dimension given in abscissa. Let us comment first on particle size distribution when PIB 30 has been used (Figure 3). It can be seen that the lowest monomer content in the suspending medium leads to the narrowest particle size distribution. More than 70% of the particles have dimensions $\leq 200 \mu\text{m}$. Much larger particle size distributions are present when higher CL content is used. The average dimensions of the particles are greatly decreased only for the lowest CL content (9.1 wt.-%), thus supporting SEM observation of reduced coalescence phenomenon for that sample.

A different situation is shown in Figure 4, where the suspending medium is the more viscous PIB 120. In this case, the sigmoidal curves exhibit a narrower particle size distribution, as compared to the above system of Figure 3, although it still remains quite wide. Here again, the average particle dimensions are strongly reduced only for the lowest CL content (6.7 wt.-%). However, the influence of CL content is not so clearly evident as in the previous case.

The PA6 samples obtained using PIB 200 (Figure 5) consist of even smaller particles, characterized by average

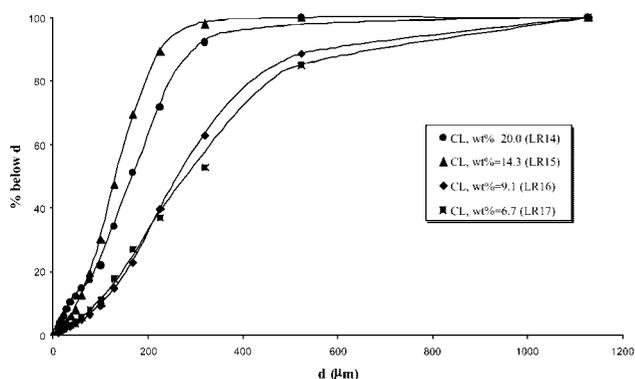


Figure 6. Particle size distribution as a function of CL content using PIB 600.

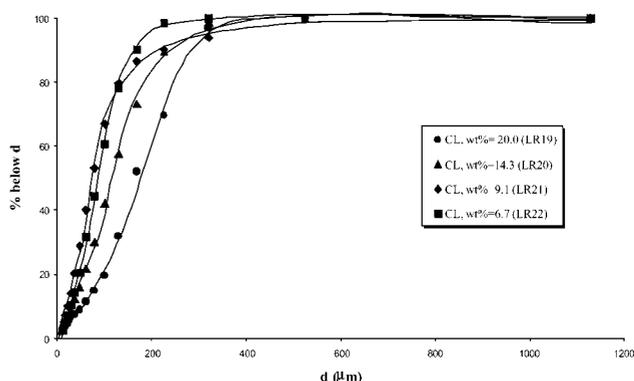


Figure 7. Particle size distribution as a function of CL content using PIB 2000.

dimensions ranging from 70 to $240 \mu\text{m}$, as functions of CL content. In particular, the smallest sizes and narrowest size distributions of PA6 particles have been obtained using the outmost values of CL content: 20.0 and 6.7 wt.-%. SEM observations, given above, are in full agreement with the present findings.

Similar results have been found when PIB 600 has been used (Figure 6). In this case, the best experimental conditions in order to limit the coalescence are linked to 20.0 and 14.3 wt.-% of CL content.

Figure 7 shows size distributions pertaining to the most viscous suspending medium: PIB 2000. The curves are much narrower than in all previous cases and differences due to CL content are less evident.

Table 4. Influence of the suspending medium and the monomer content in the reacting mixture on PA6 average dimensions.

Sample code	PIB code	CL	d_{32} μm
		wt.-%	
LR1	30	20.0	467
LR2	30	14.3	479
LR3	30	9.1	115
LR5	120	20.0	279
LR6	120	14.3	302
LR7	120	9.1	356
LR8	120	6.7	146
LR9	200	20.0	94
LR10	200	14.3	187
LR11	200	10.5	170
LR12	200	9.1	240
LR13	200	7.7	132
LR14	200	6.7	70
LR15	600	20.0	95
LR16	600	14.3	101
LR17	600	9.1	197
LR18	600	6.7	196
LR19	2000	20.0	108
LR20	2000	14.3	72
LR21	2000	9.1	53
LR22	2000	6.7	61

Conclusions

The fast activated anionic polymerization of CL has been successfully performed in suspension, providing powdered PA6 characterized by high yields, very high structural regularity (comparable to that of PA6 samples obtained from the hydrolytic process), a wide range of molar masses. The inter-particle coalescence phenomenon can be minimized using suitable PIB oil and CL content. As a consequence, particle size distribution can become rather narrow.

Average dimensions of the particles can be controlled by the polymerization parameters, namely CL content and PIB type. A detailed SEC analysis of our PA6 samples, as a function of the different experimental conditions of their synthesis, is under way.^[13]

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