

On the Relation Between Synthesis Parameters and Morphology of Anionic Polycaproamide Obtained in Organic Media. II. Influence of the $\text{Na}[\text{O}(\text{CH}_2)_2\text{OCH}_3]_2\text{AlH}_2$ /Aliphatic Diisocyanates Catalytic Systems

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ABSTRACT: The morphology and structure of polycaproamide granules obtained by anionic polymerization of caprolactam in ethylbenzene in the presence of different activators (isocyanates) were investigated. The granules, which consist of a large number of initially separated small particles, were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and wide-angle X-ray scattering. On keeping all the synthesis parameters identical, correlations between the type of activator used, on the one side, and the high polymer content, chemical structure, agglomerates size, and fine morphology, on the other side, were found. The chemical structure of the components of the catalytic system seems to be the determining factor for the obtaining of some kinetically controlled morphologies. The results suggest that an adequate selection of the catalytic species is able to orient the process toward the obtention of materials with desired morphologies, in agreement with certain specific applications. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2575–2583, 1997

Key words: caprolactam; ethylbenzene; anionic polymerization; agglomerates; compact dense or spherulitic structures

INTRODUCTION

Anionic polymerization of caprolactam in nonpolar solvents (aromatic hydrocarbons) occurs with high polymerization rates at low temperatures, with granular or powdered polycaproadides which exhibit high molecular homogeneity and relatively high average molecular weights being thus obtained.^{1–4} An important group of activators of alkaline polymerization of caprolactam is represented by isocyanates or their addition products with caprolactam, viz., the *N*-carbamoylcaprolactams.^{5,6} Compounds of either type are very

efficient activators, even at low temperatures. They are particularly useful when a fast polymerization process and a high monomer conversion are required.⁷

As described earlier,⁸ the most important steps in granular or powdered polycaproamide formation are the following ones: initiation, growth of macromolecules in the homogeneous medium, precipitation and aggregation of the growing chains, solidification of the separated polymer, and, finally, its crystallization. All the above mentioned steps occur rapidly and partly overlap. A model describing the formation of polycaproamide granules, using a sodium bis-(2-methoxyethoxy)-aluminum hydride/isophorone diisocyanate catalytic system has also been proposed.⁸

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Because the longest period of time corresponds to the reactions occurring in a homogeneous medium (initiation and the initial growth of macromolecules), we expected the initiation step, i.e., addition of diisocyanates to caprolactam and, subsequently, the addition of lactam anions to the *N*-acyllactam groups of the activator, to be the rate-determining step of the process. The type of activator that influences the induction period could affect, beside the thermodynamic and rheological factors, not only the polymerization rate but also the length of chains, their structure (linear, branched or crosslinked, respectively), and, in the last instance, even the morphology.

In this context, the present article investigated the influence of some aliphatic diisocyanates on the morphology of polycapramide particles. Thus, keeping constant all experimental conditions (temperature, solvent, initial concentration of caprolactam, amount of catalyst, activator/catalyst ratio, and hydrodynamic conditions), the relation between the type of activator and the morphology of polycapramide granules has been established.

EXPERIMENTAL

Materials

A 3.5*M* RedAl solution of sodium bis-(2-methoxyethoxy)aluminum hydride in toluene (Fluka), isophorone diisocyanate (IDI) (Aldrich), hexamethylene diisocyanate (HDI) (Fluka), 2,2,4-trimethylhexamethylene diisocyanate (THDI), phenylisocyanate (PhI) (Fluka), tolylene-2,4-diisocyanate (TDI) (Riedel deHaen), and 4,4'-methylenediphenyl diisocyanate (MDI) were used as received. The purification of caprolactam (CL) and of ethylbenzene (EB) was described elsewhere.⁸

Polymerization

The polymerization procedure and the workup of polymers were detailed in Part I. Briefly, in the reaction vessel, the monomer, solvent, initiator (RedAl), and activator were sequentially added under nitrogen with stirring. The first three components were added at 80°C and the last one at the reaction temperature. Except for MDI, all activators were added volumetrically.

Characterization

All characterizations, i.e., high polymer yield, average molecular weight, SEM photos, and DSC and WAXS curves, were performed by following the already-described methods⁸ and using the same apparatus. In addition, Soxhlet extraction by formic acid (85% aq sol) was applied for the gravimetric determination of the polycapramide cross-linked fraction when aromatic diisocyanates were used as activators.

RESULTS AND DISCUSSION

Polymerization

Although this work was aimed mainly at investigating the relation between the chemical structure of aliphatic diisocyanates (their efficiency) and the morphology of the formed polymer, some aromatic mono- and diisocyanates were also used to activate the polymerization reactions. Using isocyanates as activators and the "reduced caprolactam salt" as the initiator (the choice of this initiator was previously explained⁸), the anionic polymerization of CL in EB as the solvent begins in a homogeneous medium. After a certain period of time, strongly correlated with the polymerization conditions (especially temperature and chemical structure of isocyanate), the reaction medium becomes translucent and, after a very short period of time (few seconds), becomes clear and, as a rule, white or slightly yellow dispersed granules are obtained. In all syntheses performed at temperatures near the boiling point of EB, the overall process was completed within 2 min. However, at the above-mentioned temperatures, no polycapramide powders or granules were formed in either experiment when aromatic diisocyanates were used as activators.

Some characteristics of the anionic polycapramides obtained in EB, when using three aliphatic diisocyanates (IDI, THDI, and HDI), an aromatic monoisocyanate (PhI), and two aromatic diisocyanates (TDI and MDI) as activators are given in Table I. The reactions were carried out on keeping constant all the experimental conditions, except the type of activator.

It is evident from Table I that the isocyanate chemical structure affects not only the chemical structure of the macromolecular chains and the degree of polymerization but also the particle size.

The differences observed can be related to the effect of substituents on the NH acidity of *N,N'*-

Table I Influence of Activator Type on the Separation Time of Polymer, t_s , High Polymer Yield, Crosslinked Fraction, and Particles Size^a

Sample	Activator	t_s (s)	Yield ^b (%)	P_η ^c	Particle Size (μm)	85% aq HCOOH Insoluble Fraction (%)
Aliphatic diisocyanates						
a	IDI	72	73.5	225	250–500	—
b	THDI	61	64.7	205	600–1000	—
c	HDI	53	54.6	211	900–1500	—
Aromatic isocyanates						
d	PhI	44	26.8	98	5–50	—
e	TDI	35	54.0	—	Blocks	43.9
f	MDI	62	31.0	—	Platelets	79.2

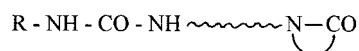
^a Reaction conditions: solvent, ethylbenzene (EB); temperature, 130°C; initial concentration of CL, 3 mol/L; initiator (the “reduced lactam salt”) concentration, 3.3% mol/mol CL; activator/initiator, 1 eq NCO/mol of “reduced lactam salt”; polymerization time, 20 min.

^b Calculated from conversion of CL into polymer.

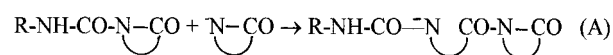
^c Viscometric average of the polymerization degree.

^d Including the time of activator’s dissolution.

disubstituted urea structures incorporated in the polymer chains:



The N,N' -disubstituted urea structures are formed by deacylation of N -carbamoylcaprolactams in the first propagation step (reaction A):



It is obvious that the acidity of N -carbamoyllactams affects the concentration of lactam anions only at the onset of polymerization, while the acidity of N,N' -disubstituted structures affects the whole polymerization process. The values of the equilibrium acidities (pK) of CL and of the disubstituted ureas in DMSO, found by Sebenda and co-workers,⁹ are the following: 27.2,¹⁰ 26.0, 20.6, and 22.4 for CL, N,N' -diethyl-, N,N' -diphenyl-, and N -butyl- N' -phenylurea, respectively. Due to the differences between the acidity values of these compounds and of CL, the concentration of lactam anions may decrease, the whole polymerization process being thus affected.

As shown in Table I, high conversions and high degrees of polymerization were obtained when aliphatic diisocyanates were used as activators. In

this case, the interaction of the end groups of the polymer chains with the caprolactam anion is negligible, because the arising end group corresponds to the dialkylsubstituted urea whose acidity is much weaker and comparable to that of CL.

Unlike the polymerization degree, which does not seem to be essentially affected, conversion and especially the size of particles are strongly related to the chemical structure of the aliphatic diisocyanate. A kinetic comparison between the three activators, in terms of separation times of the polymer, t_s (the period of time between the addition of the activator and the moment when the reaction medium becomes translucent), is shown in the two columns of Table I. The data show that among the investigated aliphatic diisocyanates the highest activation effect is manifested by HDI followed by THDI, while IDI presents the lowest effect.

With decreasing of the separation time, t_s , the polymer yield decreases, while the particles size sharply increases. In our opinion, the observed differences in polymer yield should be linked to its fast precipitation when the access of caprolactam anions to the growing macromolecules is hindered. Furthermore, if the polymer precipitates from the reaction mixture, the corresponding part of N anions is bound to the polymer in solid state, where their further participation in polymerization equilibria and reactions is limited. As expected, using the above-mentioned activators, ap-

proximately twofold average molecular weights were obtained against the case when a monoisocyanate (PhI) was used.

Using the latest activating agent, the polymerization was stopped at low conversions, the polymer being obtained as a fine powder. This behavior can be explained by a shorter time required for polymer separation, as well as by the presence of the *N*-aryluureido end groups in the macromolecular chains. The *N*-aryluureido end groups affect the polymerization process due to the presence of an aromatic substituent containing a hydrogen atom of such an acidity that it may interact with the lactam anion, thus decreasing the concentration of lactam anions and affecting the initiator/activator ratio. The morphology of these powders is still under investigation and will be published in the near future.

Apart from the above-mentioned activators, when aromatic diisocyanates were used to activate the anionic polymerization of CL in nonpolar solvents, a considerable fraction of crosslinked polycapraamide and much lower conversions were obtained. From the data given in the last column of Table I, the amount of crosslinked polycapraamide results as being strongly dependent on the type of activator. The branching and crosslinking interchain reactions are indeed originated by the acylation of the active sites (amidic anions, carbanions, and ureic anions) present in the polymer

chains. Also, the high amount of the catalytic components used to promote polymerization could affect the interchain exchange, giving rise to the network. As shown in Table I, the highest gel fraction was obtained when polymerization was activated with MDI. As already pointed out, no powders or granules were formed when using these activators. Thus, large blocks with a small fraction of granules, formed in the latter stages of polymerization, and slightly elliptical platelets (3–5 mm across and 200–400 μm in thickness) were obtained using TDI and MDI, respectively.

Morphology

Throughout this work, the conditions of synthesis were kept identical; this allows a correlation between the morphology of a series of polycapraamide granules and the efficiency of the activating additives. Therefore, the structure of the three types of polycapraamide granules was examined using scanning electron microscopy. Several analogies but also some differences were found between the investigated samples. In all experiments, irregularly shaped granules with a considerable variation of the size and length/diameter ratio were obtained, as illustrated in Figure 1. Their dimensions are strongly related to the type of activator. Thus, particle sizes ranging from 250 to 500, 600 to 1100, and 1000 to 1500 μm were

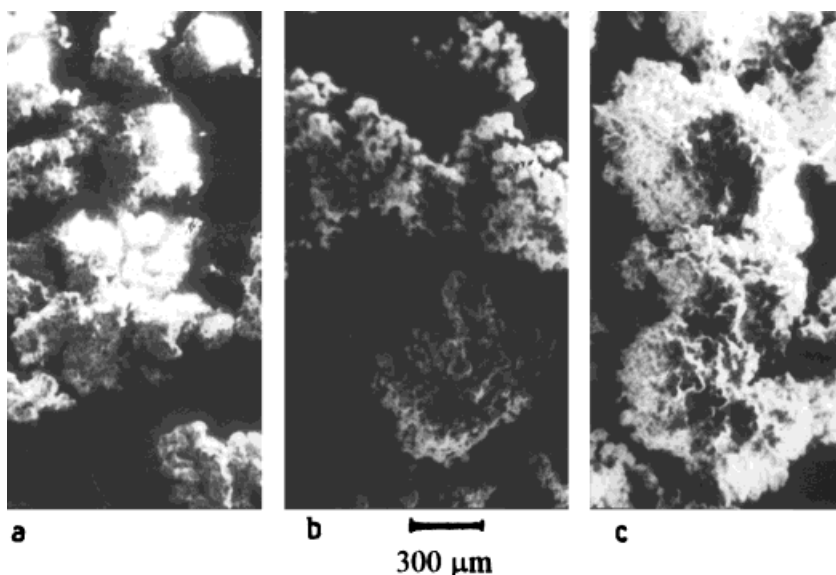


Figure 1 Scanning electron micrographs showing the irregularly shaped polycapraamide granules prepared as described in Table I. Micrographs (a), (b), and (c) correspond to the following aliphatic diisocyanates used as activators: IDI, THDI, and HDI, respectively.

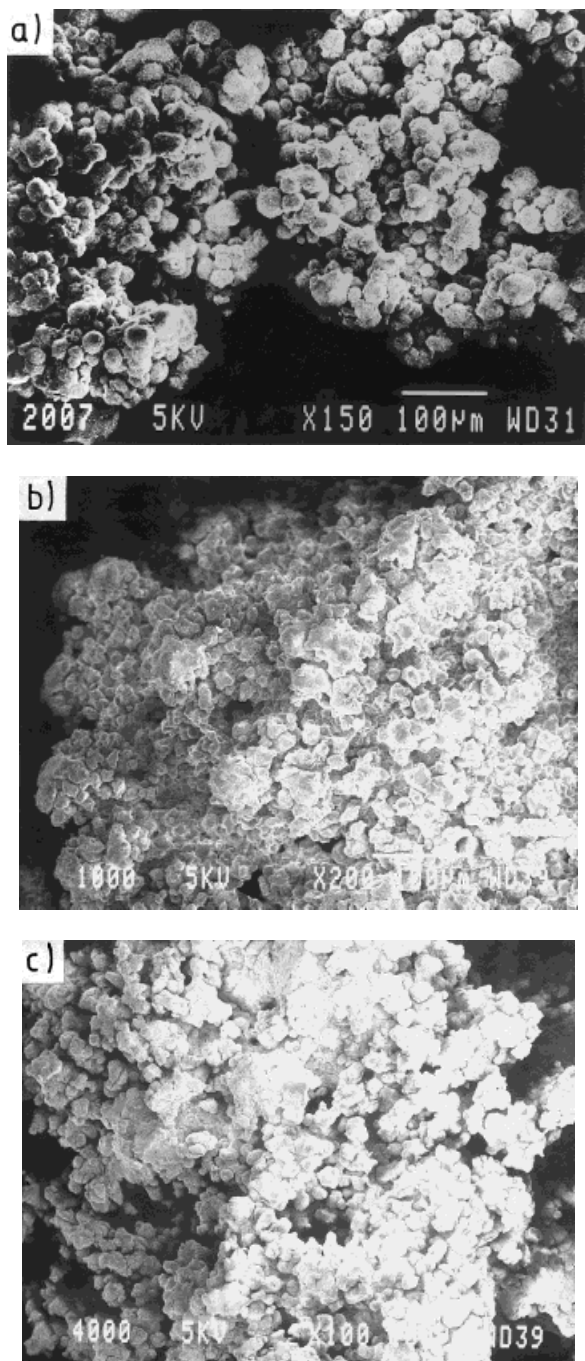


Figure 2 Scanning electron micrographs showing the similar structure of the three types of polycapraamide granules, i.e., the aggregates of a great number of initially separated particles.

obtained using IDI, THDI, and HDI, respectively. As shown in Figure 2(a)–(c), in spite of the considerable differences between the particles size, they have similar structures, being, in fact, agglomerates of a large number of small particles.

The agglomeration process occurs from the coalescence of an important number of initially separated viscous particles, just before solidification. It was previously suggested⁸ that the already precipitated macromolecules may undergo aggregation to form small droplets. Subsequently, progressive polymerization inside the above-mentioned droplets leads to an increase in viscosity so that, on further collision, the droplets adhere to one another in the form of fused agglomerates.

Comparing Figure 3(a)–(c), one can see that, concomitantly with increasing of the agglomerates size, the shape of the primary particles composing the agglomerates is altered, passing from an approximate spherical to more and more irregular shapes. In addition, the size distribution of this primary particles is influenced by the efficiency of the activators. As one may notice, the narrowest and the broadest particle size distributions were attained by the use of IDI and HDI, respectively, as activators. On the other hand, when THDI or HDI were used to promote the reaction, particles with diameters above 40 μm with a very rough external structure can be observed within each agglomerate. All the above-mentioned differences can be related to the separation time of polymer, t_s . Thus, with more efficient activators, the initial number of growing chains is higher, the propagation proceeds faster, and the concentration of CL in the reaction mixture decreases. Consequently, the reaction medium becomes a weaker solvent for the polymer, which favors its separation after a shorter period of time. Furthermore, with the concentration of the separated viscous particles being higher, the agglomeration process is also favored just before their solidification occurs. In this stage, coalescence of some particles can also occur, giving rise to the above-mentioned bigger particles, with a “cactuslike” external structure, as shown in Figures 3(b) and (c) and 4(b).

The inner structure of the particles forming the agglomerates is also related to the efficiency of activators. Figure 4(a)–(c) show that the individual particles pass from a compact structure with few pores on the surface [Fig. 4(a)] to a spherulitic structure [Fig. 4(c)] when IDI and HDI, respectively, are used as activators.

Between the two limits, a less developed spherulitic structure was achieved using THDI as the activator [Fig. 4(b)]. These differences are more clearly shown at high magnification in Figure 5(a)–(c). By use of the most efficient activators, the greater amount of polymer resulted from the

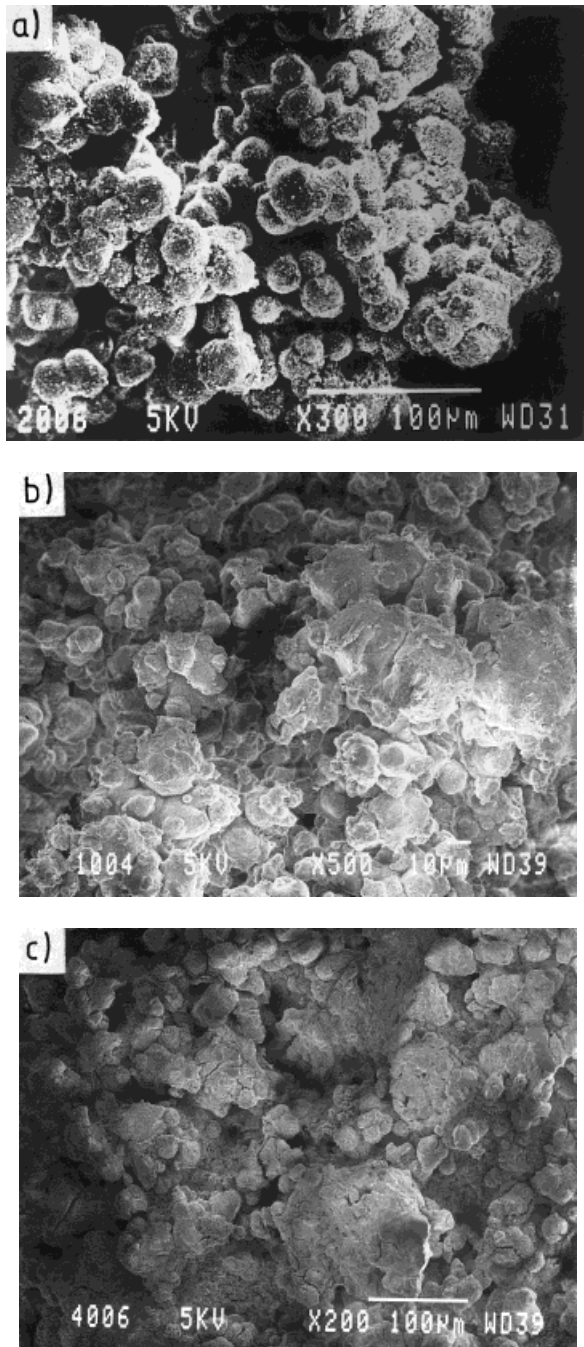


Figure 3 Medium magnification of polycapramide granules showing the change of shape and size of the primary particles, from an approximate spherical to an irregular shape with broad distribution concomitantly with increasing the activator efficiency.

reaction seems to favor the development of spherulitic structures. These have a densely packed core and their morphology becomes more open toward the periphery. Figure 4(c) shows a three-dimensionally developed spherulite that has a

layered structure which, in conjunction with the radial texture, would indicate a sheaflike type of growth, as described by Peltzbauer¹¹ on studying a powder of polycapramide prepared by alkaline

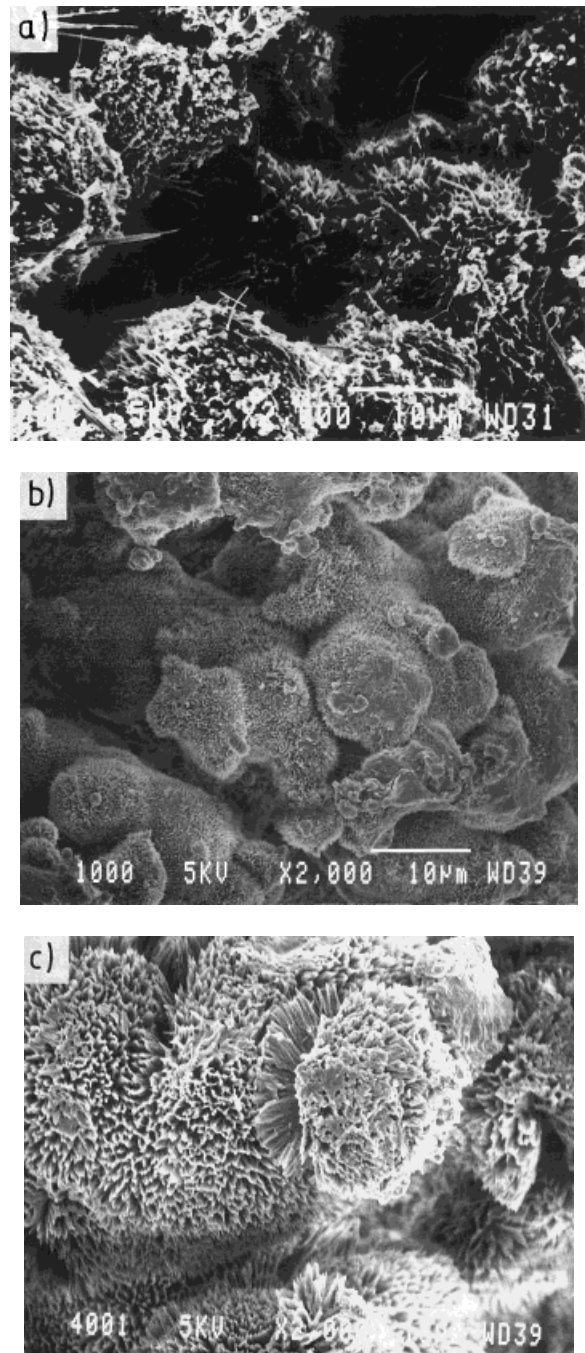


Figure 4 High magnification of the individual particles composing the granules showing alteration of their structure, from a compact and dense one, with few pores, to a better and better developed spherulitic structure, concomitantly with increasing the activator efficiency.

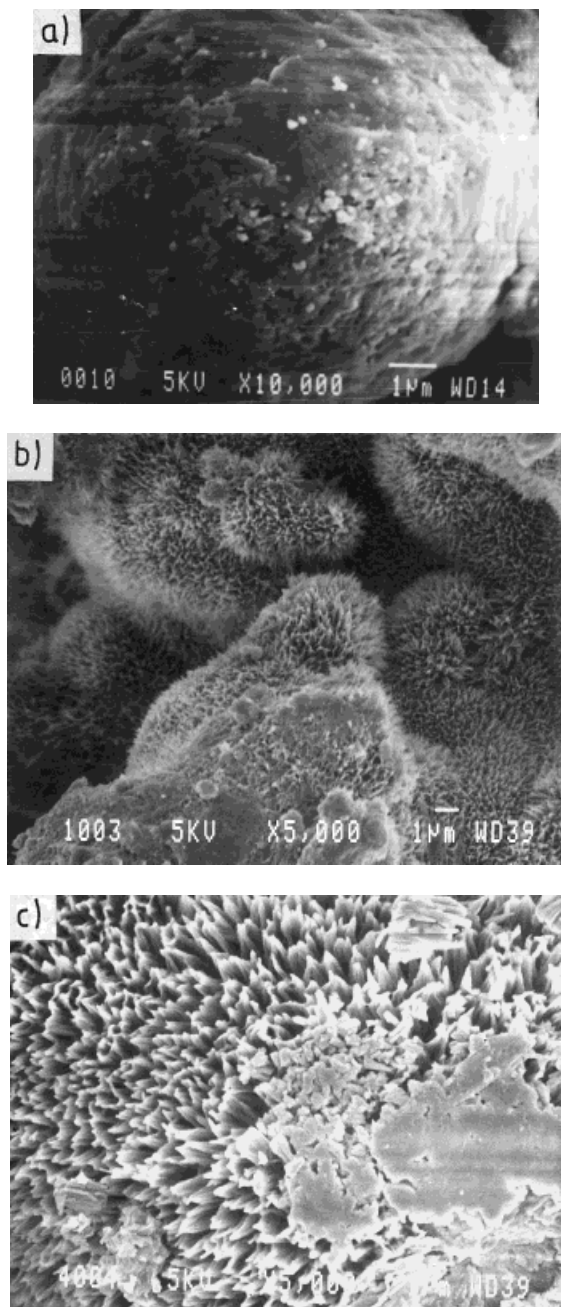


Figure 5 High magnification of the individual particles showing details of the external surface. The zone where two particles were stuck to one another is also illustrated in (c).

polymerization of CL followed by crystallization of the polymer from a monomer solution at 85°C. The zone where two particles were stuck to one another is also illustrated in Figure 5(c).

Taking into account the DSC and WAXS data concerning the agglomerates obtained when using IDI as an activator,⁸ a similar spherulitic super-

structure for the individual particles may be assumed, with amorphous material filling the voids between the crystalline formations, as described by Cohen et al.,¹² in their “domains model” on the morphology of nylon 6 spherulites in bulk.

Differential Scanning Calorimetry

The thermal behavior of the three types of granules, measured by DSC, is shown in Table II. One may observe that the heat of fusion, ΔH_f , and the corresponding degree of crystallinity, ΔX_c , of the investigated samples slightly increases with increasing of the agglomerates' diameter or with decreasing of the separation time of the polymer, t_s (for the calculation of crystallinity, a heat of fusion of 189 J/g^{13,14} for 100% crystalline polyamide was used). This behavior could be related both to the higher amount of polymer resulting from the reaction (which favors high rates of crystallization) and to the increasing of the temperature inside the bigger granules (when the lower undercooling favours the development of the crystalline structures).

Wide-angle X-ray Diffraction

The wide-angle X-ray diffraction intensity distributions, for the three samples, are depicted in Figure 6. Specific to the alkaline polyamide, all the investigated samples contain predominantly the α crystalline phase, a small fraction of γ crystalline phase being also present. As Figure 6 shows, the intensity of the peaks corresponding to the crystallographic plane α_2 (002, 202) is always stronger as compared to those corresponding to the crystallographic plane α_1 (200). However, it should be noted that the intensity of the peaks in the α_1 (200) plane gradually decreases [which is not the case in the α_2 (002, 202) one] with increasing of the activator efficiency (when the separation time of polymer, t_s , becomes smaller). Thus, in the presence of solvent, it could be concluded that, at high polymerization rates, the growth of crystal in the α_1 (200) plane could be retarded. As indicated by Heuvel et al.,¹⁵ there exists a physical relationship between the two peaks because both originate from the α -phase crystals. In the specific systems investigated, complex kinetic, thermodynamic, and rheological factors could induce small rotations of the unit cell around the normal to the plane 002, N_{002} . In the inset, the manner in which the ratio between the areas of the two peaks could decrease with increasing the

Table II Thermal Properties of the Granular Polyamides Obtained Using Aliphatic Diisocyanates as Activators

Sample	Activator	Melting Temperature		ΔH_i^a	Crystallinity ^b ΔX_c
		Onset (°C)	Peak (°C)		
a	IDI	195.04	205.33	70.07	37.07
b	THDI	191.06	208.24	73.35	38.80
c	HDI	197.90	210.79	77.61	41.06

^a ΔH_i , heat of fusion of the investigated samples.

^b ΔH_f of crystalline polycaproatamide = 189 J/g.^{13,14}

angle of rotation around N_{002} is presented. Therefore, the type of activator might finally influence the orientation of crystalline entities.

CONCLUSIONS

The chemical structure of the isocyanates used as activators in the anionic polymerization of CL in organic nonpolar media influences not only the overall polymerization rate, conversion, and degree of polymerization, but also the fine morphology of the polymer. A number of distinct, sequential events occur during polymerization. These

succeed rapidly and are partly overlapped. Their degree of overlapping—strongly related to the induction period, i.e., to the efficiency of the catalytic species—influences decisively the morphology. When aliphatic diisocyanates are used as activators, polycaproatamide granules, resulting from the agglomeration of a large number of initially separated particles, have been obtained. The particle size is strongly related to the chemical structure of the aliphatic diisocyanates and increases with increasing the efficiency of activators. The morphology of the individual particles composing the granules is also related to the efficiency of activators. It passes from dense and nonporous

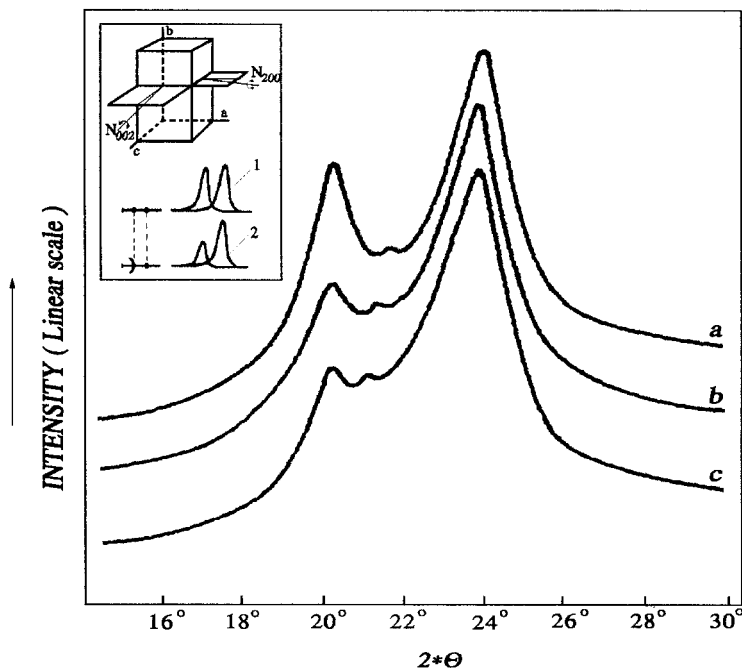


Figure 6 WAXS powder patterns; sample code refers to Table I. In the inset, the effect of orientation on the ratio between the areas of two peaks is illustrated. (1) Perfect orientation and (2) rotation about N_{002} .

microspheres to spherulitic structures as the efficiency of activators increases. The crystalline structure could also be related to activator efficiency. In all cases, an α -structure is mainly obtained, the peaks from the crystallographic plane α_2 (002, 202) being more intense than those from the crystallographic one α_1 (200), while the intensity of the peaks in the last crystallographic plane gradually decreases with increasing activator efficiency. The differences found could have potential consequences on the fine control of particle's morphology, in correlation with specific applications.

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