Anionic Poly(ϵ-caprolactam): Relationships among Conditions of Synthesis, Chain Regularity, Reticular Order, and Polymorphism

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ABSTRACT: Anionic poly(ϵ-caprolactam), isothermally synthesized at temperatures between 155 and 195 °C by very fast carbamoyl-type activators, has been characterized by UV, DSC, and wide-angle X-ray scattering (WAXS) techniques in terms of high polymer yield, irregular structures along the chain, extent of cross-linking, T_g and T_m values, degree of crystallinity, and polymorphism. The specific role of four different activators on the above properties has been compared. From the whole set of characterization data it is evident that cyclohexylcarbamoylcaprolactam behaves as the most suitable activator and provides poly(ϵ-caprolactam) with properties that favorably match those of the corresponding hydrolytic polyamide.

Introduction

In a previous paper[1] we have described the anionic polymerization of ϵ-caprolactam (CL) in bulk, under *quasi-adiabatic* conditions, by means of two fast activation agents: hexamethylene-1,6-dicarbamoylcaprolactam (HDCL) and its 2,2,4-trimethyl derivative. For most of the experimental conditions chosen, the reaction has been characterized by rather low polymerization times, high polymer yields, excellent monomer conversions, and variable amounts of a cross-linked fraction somehow related to the γ crystalline form of the obtained poly(ϵ-caprolactam) (PCL).

In the present study, we have thoroughly investigated *isothermal* conditions applied to the fast anionic polymerization of CL, activated by HDCL and three other agents: cyclohexylcarbamoylcaprolactam (CCCL), isophorone dicarbamoylcaprolactam (IDCL), and 4,4′-methylenebis(cyclohexylcarbamoylcaprolactam) (MCCL). Some preliminary results, related to the role of HDCL and CCCL in these conditions, have already been published:[2] in particular, a careful choice of reaction parameters enabled us to find optimum experimental conditions, able to minimize side reactions (such as Claisen-type condensations), which are responsible for the presence of structural irregularities in PCL chains. The above side reactions, typical of CL anionic polymerization, are not only linked to the strong basicity of the reaction medium but also highly favored by its high temperature increase (up to 52 °C), due to the polymerization heat and the very poor heat exchange with the surroundings.[3]

The present study aims to fully investigate the specific role of the aforementioned “fast activation” agents on some relevant properties of PCL prepared in isothermal conditions at different polymerization temperatures (T_{pol}). In particular, besides their influence on high polymer yield and structural regularity, the extent of cross-linking, as well as the degree of crystallinity and the presence of polymorphism in as-polymerized and annealed PCL samples, has also been considered.

Experimental Section

Materials. CL and HDCL were kindly supplied by DSM Research, Geleen, The Netherlands, and utilized after vacuum-drying over P_2O_5. Sodium hydride was used as a 60% dispersion in mineral oil (Aldrich), to promote in situ formation of sodium caprolactamate (NaCL), polymerization initiator. CCCL was a laboratory preparation, obtained by blocking cyclohexyl isocyanate (Fluka) with CL in boiling toluene and removing the solvent by vacuum distillation. With the same procedure IDCL was prepared from isophorone diisocyanate (Fluka) and MCCL from 4,4′-methylenebis(cyclohexyl isocyanate) (Aldrich).

To purify PCL from the low-molar species, methanol (Prolabo) was used as received. For the UV analyses, anhydrous formic acid was obtained from a 98% formic acid (Fluka) by distillation under reduced pressure after reaction with boric anhydride.

Polymerization Runs. Polymerization reactions have been carried out in a stainless steel mold, with a disk-shaped die (inner diameter 83 mm; thickness 0.8 mm) The mold, immersed in an oil bath kept at the polymerization temperature, was previously connected with a vacuum pump by using a three-way valve and then filled with the molten reaction mixture under a pressure of dry nitrogen. After 600 s, which is adequate time to reach reaction completion under all chosen conditions (as verified using glass vessel reactors), the mold was quickly cooled by immersion in a cold water bath.

Product Characterization. The evaluation of high polymer yield was performed by weighing the samples, cut in small pieces, before and after Soxhlet extraction by methanol for 48 h in order to remove unreacted CL, higher oligomers, and low molecular weight side products.

A Perkin-Elmer Lambda 9 UV spectrophotometer was used to monitor the presence of structural irregularities in PCL chains, as they are able to strongly absorb in the UV region: it is customary to assume that the UV absorption is directly proportional to the total amount of side products.[4] The UV spectra were performed on 1% (w/w) PCL solutions in anhydrous formic acid between 250 and 400 nm (path length = 1 cm), and the optical density maximum (OD_{max}) at 270−280 nm was considered.

Crystalline melting temperatures (T_m), glass transition temperatures (T_g), and degree of crystallinity (x_c) of PCL samples were determined by a Mettler differential scanning calorimeter (DSC), model TC 10A. All samples were subjected

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Table 1. Dependence of High Polymer Yield (%) on the Chosen Activator and Polymerization Temperature[a]

sample	activator	T_{pol} (°C)	high polymer yield
PCL 1	CCCL	155	98.9
PCL 2	CCCL	162	98.9
PCL 3	CCCL	170	98.4
PCL 4	CCCL	175	98.0
PCL 5	CCCL	180	97.8
PCL 6	CCCL	185	97.6
PCL 7	CCCL	190	98.2
PCL 8	CCCL	195	98.6
PCL 9	HDCL	155	98.6
PCL 10	HDCL	162	98.7
PCL 11	HDCL	170	98.5
PCL 12	HDCL	175	97.1
PCL 13	HDCL	180	97.4
PCL 14	HDCL	185	96.3
PCL 15	HDCL	190	97.4
PCL 16	HDCL	195	95.5
PCL 17	IDCL	155	98.7
PCL 18	IDCL	162	99.2
PCL 19	IDCL	170	99.3
PCL 20	IDCL	175	98.5
PCL 21	IDCL	180	98.1
PCL 22	IDCL	185	97.2
PCL 23	IDCL	190	94.4
PCL 24	IDCL	195	92.9
PCL 25	MCCL	155	96.6
PCL 26	MCCL	162	98.4
PCL 27	MCCL	170	98.1
PCL 28	MCCL	175	97.5
PCL 29	MCCL	180	96.8
PCL 30	MCCL	185	97.9
PCL 31	MCCL	190	94.0
PCL 32	MCCL	195	94.1

[a] [NaCL] = 0.6% (mol/mol of CL). [CCCL] = 0.6% (mol/mol of CL). [HDCL] = [IDCL] = [MCCL] = 0.3% (mol/mol of CL).

to the following cycle of three scannings: first heating from 0 to 270 °C (at 20 °C/min); cooling from 270 to 0 °C (at 10 °C/min); second heating from 0 to 270 °C (at 20 °C/min).

x_c was evaluated also by X-ray diffraction; the same technique was used to identify the presence of polymorph crystalline forms and to evaluate their extent. WAXS intensity profiles were collected by a PW1050/71 Philips powder diffractometer (Ni-filtered Cu Kα radiation) in the reflection mode. The scan and the chart speed were 0.25° of 2θ min^{-1} and 0.5 cm min^{-1}, respectively. Step-by-step measurements on some of the investigated samples were carried out also by a PW3020/00 Philips automatic powder diffractometer (APD).

Results and Discussion

Polymerization Yields. Polymerization data are listed in Table 1, where the high polymer yields are given as functions of both the chosen activator and the polymerization temperature. The samples are assembled in four groups depending on the activator used: the polymerization temperature for each series has been varied between 155 and 195 °C. The sodium caprolactamate concentration has been 0.6% (mol/mol of CL) for all syntheses, whereas activator concentration has been 0.6 in the case of CCCL and 0.3% (mol/mol of CL) for the difunctional activators. The experimental data reported in a previous paper of ours[1] have shown that these concentrations of catalytic species are the most favorable ones in terms of both high polymer yield and shortening of polymerization time. As shown in Table 1, nature and functionality of the activation agent have little influence on high polymer yields at relatively low T_{pol}'s. Differences become increasingly relevant, however, when $T_{pol} > 185$ °C. In particular, the best results have been obtained with the monofunctional activator (CCCL), which keeps the above yields very high and almost constant, whereas all difunctional activators show an appreciable yield decrease. In absolute terms, however, all conditions lead to higher yields of PCL, as compared to the traditional methods of CL polymerization (anionic quasi-adiabatic,[1] hydrolytic polymerization[5]).

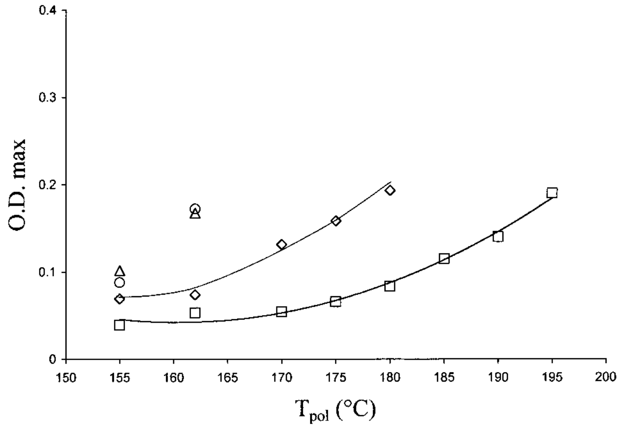

Figure 1. Optical density, OD$_{max}$, at the band maximum (270−280 nm) for PCL samples in anhydrous formic acid (1% w/w). Activator: ◇, HDCL; □, CCCL; △, IDCL; ○, MCCL.

UV Absorption and Chain Regularity. An evaluation of the relevance and extent of side reactions, as a function of the polymerization conditions, is shown in Figure 1 in terms of PCL OD$_{max}$ vs T_{pol}. The best results throughout the T_{pol} range (in terms of minimum extension of side reactions leading to insertion of UV-absorbing groups in PCL chain) have been obtained by CCCL. On the other hand, PCL samples prepared with IDCL and MDCL showed the strongest UV absorption, whereas HDCL played an intermediate role. Moreover, the alicyclic, monofunctional activator gave no cross-linking of PCL at all T_{pol}'s, whereas the other three activators provided extensive cross-linking from a specific T_{pol} on. For this reason, the UV analysis has been possible only for CCCL-derived samples in the entire T_{pol} range; the results show almost no influence of T_{pol} on the formation of structural irregularities up to 170 °C. At higher T_{pol}, there is a regular increase of OD$_{max}$, revealing an increasing relevance of side reactions. Below 170 °C the OD$_{max}$ values found are very close to those pertaining to hydrolytic PCL. Two relevant conclusions can be drawn from the above findings: a careful control of T_{pol}, together with a suitable choice of the activator, can minimize the side reactions. Moreover, potential applications, so far restricted to hydrolytic PCL because of the poor quality of the anionic polymer, in terms of chain regularity, can open new and relevant perspectives to the latter, when "fast polymerized" isothermally at $T_{pol} < 175$ °C. For the sake of comparison, the OD$_{max}$ of a typical hydrolytic PCL is 0.044.[2] As mentioned above, the use of difunctional activators from a specific T_{pol} leads to cross-linked samples, so that the OD$_{max}$ curves for these systems cannot cover the entire T_{pol} range. In particular, the use of HDCL provided fully soluble PCL samples only for $T_{pol} < 185$ °C, and their OD$_{max}$ values are systematically higher than those corresponding to the CCCL series, with a sharper temperature dependence. IDCL and MCCL provided soluble polyamides only for the lowest T_{pol} values (up to 165 °C). For these systems, structural irregularities of the corresponding PCL samples are even larger, as compared to the previous series. Although soluble, all PCL samples prepared from HDCL, IDCL, and MCCL

Table 2. T_m and T_g Observed by DSC (First and Second Heating)

	first heating		second heating	
sample	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
PCL 1	46	219	57	219
PCL 2	48	225	59	220
PCL 3	47	221	58	221
PCL 4	46	223	55	220
PCL 5	47	222	58	222
PCL 6	49	221	59	219
PCL 7	49	222	60	221
PCL 8	47	223	60	220
PCL 9	53	221	60	217
PCL 10	47	216	53	218
PCL 11	46	219	53	220
PCL 12	49	221	54	221
PCL 13	57	222	62	219
PCL 14	48	224	53	220
PCL 15	46	218	57	219
PCL 16	47	219	60	220
PCL 17	48	223	57	219
PCL 18	50	216	59	214
PCL 19	50	217	53	215
PCL 20	48	217	51	215
PCL 21	46	219	54	215
PCL 22	44	218	52	212
PCL 23	45	212	56	216
PCL 24	45	217	52	219
PCL 25	47	227	55	219
PCL 26	48	222	54	219
PCL 27	49	218	56	216
PCL 28	46	219	56	219
PCL 29	48	217	57	217
PCL 30	48	221	57	219
PCL 31	48	216	54	218
PCL 32	45	214	53	216

activators at low T_{pol} show OD_{max} values too high to be successfully employed in the vast majority of PCL applications. Only CCCL seems to fulfill all requirements in this respect.

In our opinion, the relevant reduction of side reactions for the latter system is linked to five main requisites: (1) sufficiently low T_{pol}; (2) reaction under strictly isothermal conditions, able to efficiently prevent any local temperature raise of the reacting mixture; (3) very fast polymerization reactions allowing medium viscosity to grow very rapidly; correspondingly, both chain mobility and susceptibility to side reactions decrease; (4) T_{pol} lower than PCL melting temperature, with further reduction of side reactions due to crystallization immediately after polymerization; (5) fast cooling which entirely stops side reactions.

Point 3 is specifically relevant for CCCL.

Thermal Behavior. As mentioned in the Experimental Section, for the various PCL samples, prepared by using the above activators, an accurate investigation into both the thermal transitions and the degree of crystallinity has been made by DSC analysis. Table 2 shows PCL melting and glass transition temperatures observed during the first and the second heating. On first heating, T_m shows differences of only a few degrees from one sample to another, without highlighting any particular relationship with the conditions used for the synthesis. More precisely, polymerization temperature and nature of the activator do not seem to exert any relevant influence on PCL melting point, although the mean T_m value of samples originated by CCCL is slightly higher than the others. We can draw the same conclusions on T_m data pertaining to the second heating, generally characterized by slightly lower values. An average T_m value for the four groups and the two runs can be fixed at ca. 221 °C.

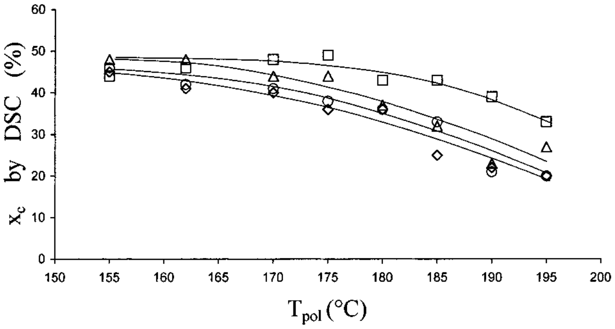

Figure 2. Crystallinity degree, x_c, of PCL samples by DSC (first heating). Activator: ◇, HDCL; □, CCCL; △, IDCL; ○, MCCL.

As far as T_g values are concerned, similar considerations can be drawn: the only appreciable difference is between the first and the second heating: the latter shows an average increase of ca. 8 °C (from ca. 48 to ca. 56 °C).

The lack of a clear dependence of the above results upon the conditions of synthesis (T_{pol} and activator type) not only supports the finding that differences among the various PCL structures are too subtle to be revealed by thermal analysis but also shows that cross-linking, when present, is very loose and does not effect chain mobility and packing. In other words, chain segments between cross-links maintain enough freedom to behave very similarly to un-cross-linked PCL. The peculiar chemistry of PCL cross-linking by difunctional activators fully justifies our findings.[1]

An evaluation of the degree of crystallinity on as-polymerized PCL has been made on DSC first heating traces: the experimental data are shown in Figure 2. Generally, PCL chains synthesized from the alicyclic, monofunctional activator (CCCL) are almost always characterized by higher values of x_c: the corresponding curve also underlines a rather weak dependence of x_c upon T_{pol}, except for the highest temperatures (190 and 195 °C). On the contrary, samples originating from the difunctional activators show a lower degree of crystallinity, which continuously decreases by increasing T_{pol} in the whole temperature range. Differences with samples derived from CCCL are particularly strong in the high-T_{pol} region. HDCL and MCCL behave very similarly and cause the largest x_c decrease. IDCL acts in an intermediate manner. The close similarity of HDCL and MCCL behaviors in terms of x_c is in contrast with their sharp differences as far as cross-linking is concerned (see Figure 1). Indeed, cross-linking is strongly present in PCL samples originating by MCCL at T_{pol} higher than 160 °C, whereas HDCL provides completely soluble PCL samples up to T_{pol} of 180 °C. On these grounds, we may infer that cross-linking centers, when present, are widely spaced so that segmental mobility between cross-links is scarcely influenced. T_m and T_g data, as shown above, fully confirm this finding. The extent of crystallinity is therefore determined by two main contributions: (i) the thermal history during (and after) polymerization; (ii) the molecular and structural characteristics of PCL, namely its molecular weight (MW) and molecular weight distribution (MWD), as well as the presence of constitutional irregularities.

Detailed data on MW and MWD as functions of the experimental conditions chosen for PCL synthesis will

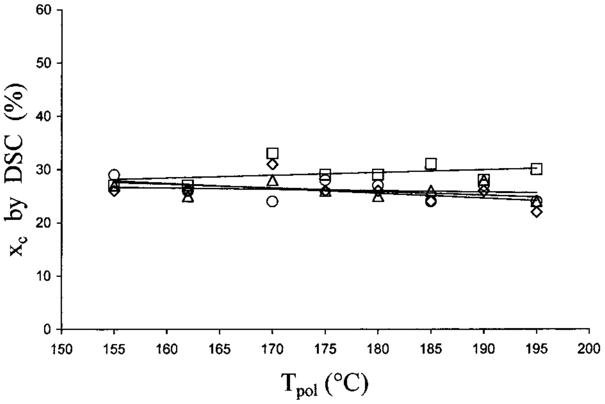

Figure 3. Crystallinity degree, x_c, of PCL samples by DSC (second heating). Activator: ◇, HDCL; □, CCCL; △, IDCL; ○, MCCL.

be reported elsewhere.[6]

To evaluate the relevance of the different contributions, all PCL samples have been analyzed after the same thermal history; i.e., x_c has been recalculated on the second heating trace. The results are shown in Figure 3. It can be seen that the decrease in crystalline content from the first to the second heating is rather significant at low and intermediate T_{pol} values, whereas at higher T_{pol} ($\geq$185 °C) differences are less and less significant. Moreover, postpolymerization thermal treatment strongly reduces differences among PCL samples prepared from the various activators, thus emphasizing the minor role of different polymer structures on PCL x_c, as compared to the major differences arising from T_{pol} values. In other words, the dawning morphology of the various PCL samples strongly depends on the specific T_{pol} used, which governs the degree of crystallinity. Minor effects, linked to the specific activator used, almost completely disappear on second heating. Superposition of Figures 2 and 3 makes the above statements strikingly evident.

WAXS Structural Investigations. For a more detailed comparison among the various structures originated by the four activators, x_c of all as-polymerized samples has been evaluated also by the WAXS technique, X-ray diffraction being a powerful method[7,8] to determine the crystallinity in semicrystalline materials. The x_c values of the investigated samples, measured (between 5° and 35° of 2θ) according to the Hermans–Weidinger method,[9] are shown in Figure 4. x_c varies in a rather wide range (10–40%) and shows a regular trend with the polymerization temperature.

There is a rather good agreement with the analogous trend of x_c obtained by DSC analysis on first heating, although all WAXS data are shifted to lower values. Differences between the two methods are commonly found[10–12] and are easily predictable because of the different sensitivity of the two techniques. The good correspondence between the two sets of data supports the general conclusions drawn above on the influence of the various process parameters on x_c.

To a first approximation, the crystallinity x_c is given by

$$x_c\,(\%) = \frac{A_c}{A_a + A_c} \times 100$$

where A_a is the area due to amorphous diffusion and A_c is the area of the crystalline peaks. As an example,

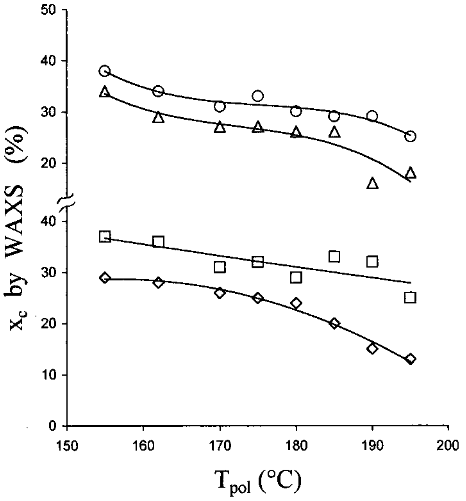

Figure 4. Crystallinity degree, x_c, of PCL samples by WAXS. Activator: ◇, HDCL; □, CCCL; △, IDCL; ○, MCCL.

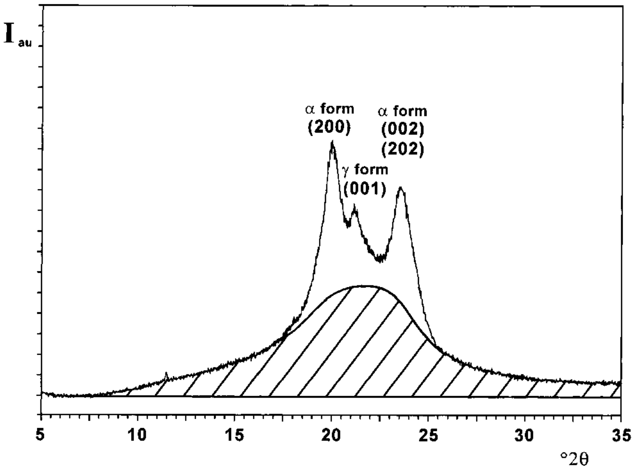

Figure 5. WAXS intensity profile of an as-polymerized PCL sample. Under the spectrum, in the range 5–35° of 2θ, the amorphous halo (shaded) of a quenched sample and the baseline (background scattering) are reported.

in Figure 5, under the spectrum of an as-polymerized PCL sample, the amorphous halo (shaded) of a completely amorphous sample, obtained by quenching, and the baseline indicating the background scattering are reported. A_a is the area under the amorphous halo, and (A_a + A_c) is the total area under the spectrum.

Indeed, it is difficult to resolve the WAXS intensity profiles into areas attributed to crystalline and amorphous phases; a more sophisticated analysis[13] to resolve the profile in Figure 5 into four distinct components, three crystalline peaks and one amorphous halo lying on the same baseline, only yielded little improvement.

The reciprocal of the width at half-height (A) for the α form (200) reflection has been chosen as an index of the order level[14] attained by our PCL samples at the different conditions of synthesis. Indeed, for a powder composed of relatively perfect crystalline particles, the mean crystallite size (L) can be determined by the Scherrer[7] equation, in which L is inversely related to the width at half-height of the reflection. However, at this stage, we prefer[14] to use the $1/A$ parameter instead of L because, for less perfect crystals, the intensity profile is also affected by lattice distortions. This parameter, i.e., the sharpness of a crystalline reflection in the WAXS intensity profile, is directly related to the

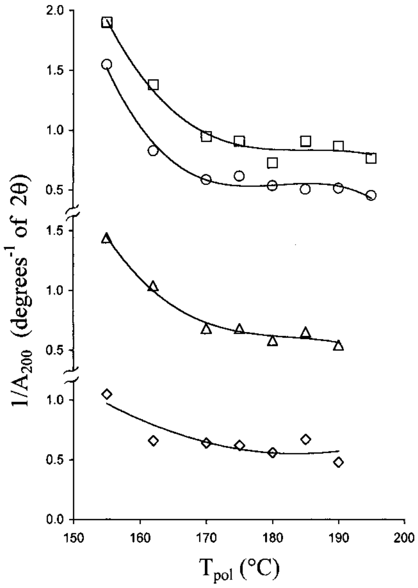

Figure 6. Sharpness, $1/A_{200}$ (deg^{-1} of 2θ), of α form (200) reflection for all PCL samples. Activator: ◇, HDCL; □, CCCL; △, IDCL; ○, MCCL.

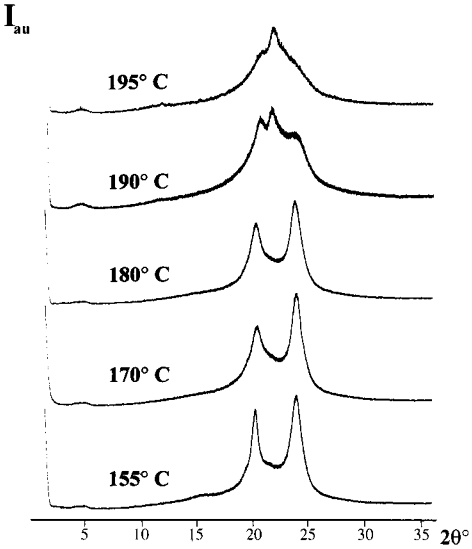

Figure 7. WAXS intensity profiles of PCL samples (activator HDCL) at different T_{pol}.

size and/or perfection of the crystallites and increases with the increasing structural order of the investigated material. The $1/A$ values (deg^{-1} of 2θ) for all PCL samples[15–17] are shown in Figure 6 as functions of polymerization temperature and show a trend very similar to that of crystallinity degree, decreasing with increasing T_{pol}, thus indicating a reduction of the crystal size and/or a loss of crystalline perfection.

As regards polymorphism, Figure 7 (as an example) shows some WAXS intensity profiles of anionic PCL samples polymerized by HDCL at five different temperatures: at low T_{pol}, the crystalline regions give the two characteristic peaks of PCL α form at $2\theta = 20.5°$ and $2\theta = 23°$, corresponding to the reflections of the crystalline planes (200) and (002) + (202), respectively. A careful observation of the intensity profile leads to the identification of a very small percent of PCL γ form, as a scarcely evident shoulder between the two α-peaks. Instead, at the highest T_{pol}'s used (190 and 195 °C), a relevant presence of γ form is evident, with a sharp peak at $2\theta = 21.5°$, corresponding to the reflection of the crystalline plane (001), which at $T_{pol} = 195$ °C almost completely hides the α trace.

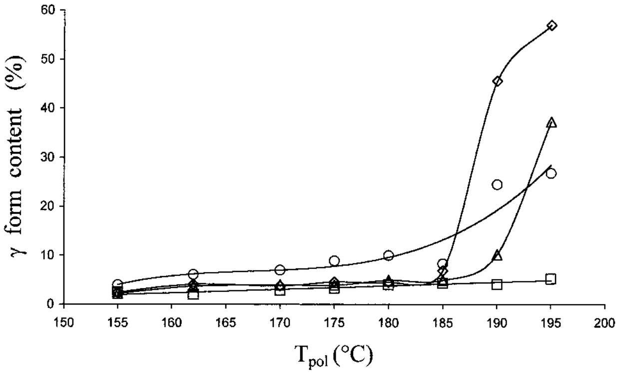

Figure 8. Plots of γ form content for all PCL samples as a function of T_{pol}. Activator: ◇, HDCL; □, CCCL; △, IDCL; ○, MCCL.

The composition of PCL crystalline regions in terms of γ form percent has been evaluated quantitatively by using (see Figure 5) the following Kyotani equation:[18]

$$\gamma\ (\%) = \frac{I_2}{I_1 + I_2 + I_3} \times 100$$

where I_1 and I_3 are the intensities of the (200) and (002) + (202) crystalline reflections of α form and I_2 is the intensity of the (001) crystalline reflection of γ form.

In Figure 8 the content of γ form for all PCL samples is plotted as a function of polymerization temperature: it can be observed that, at lower polymerization temperatures ($T_{pol} \leq 185$ °C), all samples almost exclusively present the α form, with very little or no content, if any, of γ form, only slightly dependent on the experimental conditions chosen: namely, a T_{pol} increase causes a small increase of γ form, while the kind of activation agent has no influence on it. At the highest values of T_{pol} (190 and 195 °C) there are much greater differences among the various samples as functions of the activator used: only CCCL keeps a very small content of γ form, in line with the values at lower T_{pol}'s, while the difunctional activators seem to favor the formation of this crystalline form at the above temperatures, especially in samples PCL 15 and PCL 16 (activator: HDCL).

The formation of relevant amounts of γ form at the highest temperatures by the use of some difunctional activators may not be easily explained. In a previous paper,[1] the content of γ form in anionic PCL samples has been empirically correlated with their degree of cross-linking: in particular, on increasing the extent of cross-linking, a reduced content of γ form has been found. However, the present data show a different behavior, without any possible correlation between γ form content and degree of cross-linking. IDCL-originated samples, characterized by very high levels of cross-linking, behave similarly to CCCL-derived samples, with no extent of cross-linking whatsoever.

Conclusions

On the basis of the above results, the following conclusions can be drawn: anionic PCL, in high yields and almost completely free of structural defects, can be synthesized by using $T_{pol} \leq 170$ °C, isothermal conditions, and very fast activators such as cyclohexylcarbamoylcaprolactam. The above PCL has T_g and T_m values very close to those of hydrolytic PCL, is exempt of cross-linked structures, and has a high degree of dawning crystallinity and a very low content of γ form. All these properties favorably compare to those of hydrolytic PCL and may provide interesting new perspectives of application in various fields. Detailed data on MW, MWD, residual monomer, and higher oligomer content, as functions of T_{pol} and activators chosen, will be given elsewhere.[6]

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