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The fast activation of ε-caprolactam polymerization in quasi-adiabatic conditions

Dedicated to the memory of Prof. *Mario Farina*

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SUMMARY:

Two carbamoyl-type activators of ε-caprolactam (CL) anionic polymerization have been used in *quasi*-adiabatic conditions with sodium caprolactamate as initiator, at different concentrations and relative ratios. The reaction products have been characterized in terms of high-polymer content and extent of crosslinking. Correlations between the various polymerization parameters on one side, and amount of crosslinked fraction and resultant polymer properties on the other side, have been found. Potential implications on a fine control of PCL properties, exerted by the experimental conditions chosen for the anionic synthesis, are envisaged.

Introduction

Our long-term research on the anionic synthesis of poly(ε-caprolactam) (PCL) has shown some interesting results, worth to be analyzed in terms of potential improvements of PCL reaction injection molding (RIM) technology and related applications[1,2]. Namely, two classes of carbamoyl-type activators — monofunctional and difunctional ones — have been extensively investigated in various experimental conditions (*quasi*-adiabatic, isothermal, RIM, and suspension polymerization).

Indeed, one of the examined difunctional activators, hexamethylene-1,6-dicarbamoyl-caprolactam (HDCL), is commonly and successfully employed in the industrial synthesis of PCL-based materials by the RIM process, whereas the other, its 2,2,4-tri-

In the present paper a full account on our results, related to the use of the above activators in the anionic synthesis of PCL performed *quasi*-adiabatically, is given. In these experimental conditions, formation of crosslinked polymer structures in variable amounts has been found. The detailed evaluation of how the various reaction parameters control the polymerization kinetics as well as the extent of crosslinking is of primary importance inasmuch as the latter strongly affects end properties of the resulting materials. *Quasi*-adiabatic processes seem a necessary prerequisite to induce relevant crosslinking, whereas usual RIM conditions are too close to isothermal processes to cause crosslinking to an appreciable extent[2]. Indeed, the temperature profile during polymerization seems to be the controlling factor in the formation of PCL branching and crosslinking, through its influence on the rheokinetic parameters of the polymerization reaction. The latter will, in turn, strongly affect the side reactions responsible for the network formation.

A detailed knowledge of the phenomenon can provide a full range of useful experimental conditions, also in terms of modified RIM technology, capable of affording the desired PCL properties.

Experimental part

Materials

CL has been kindly supplied by Enichem, Porto Marghera, Italy; sodium caprolactamate in CL and HDCL by DSM Research, Geleen, the Netherland. THDCL was a laboratory preparation, obtained by blocking the corresponding diisocyanate with CL in toluene and removing the solvent by vacuum distillation.

Polymerization

General information on the polymerization procedure is given elsewhere[2–4]. In the double-walled reaction vessel monomer, activator and initiator are sequentially added with stirring. Temperature rise is monitored as described in ref.[5].

Product characterization

The evaluation of monomer conversion, amount of cyclic oligomers and low molecular weight side products, and high polymer yield has been performed following already described methods[4]. Soxhlet extraction by trifluoroethanol has been utilized for the gravimetric determination of PCL crosslinked fraction. Swelling experiments have been performed exposing PCL samples to vapours of formic acid followed by gravimetric evaluation. Wide angle X-ray scattering measurements have been carried out by a PHILIPS powder diffractometer (mod. PW1050; Cu K_α Ni-filtered radiation).

Results and discussion

Polymerization runs based on HDCL as activator gave the results listed in Tab. 1, where the polymerization time, the high polymer yield and the monomer conversion for different sodium caprolactamate and activator concentrations are given. In the last column the percentage of the polymer fraction insoluble in trifluoroethanol is reported.

Tab. 1. Dependence of polymerization time t_p, monomer conversion, high-polymer yield and crosslinked fraction on [I] and [HDCL] [a)]

[HDCL] mol/mol CL in %	[I] mol/mol CL in %	t_p/s	High-polymer yield in %	Monomer conversion in %	CF_3CH_2OH insoluble fraction in %
0.15	0.30	210	94.9	97.7	13.5
0.25	0.30	120	96.3	—	50.8
0.30	0.30	72	95.8	97.8	67.2
0.40	0.30	60	96.1	—	(72.6)
0.45	0.30	50	96.0	98.1	(69.7)
0.60	0.30	43	94.7	97.2	85.5
0.90	0.30	60	92.5	—	—
0.15	0.60	600	93.3	97.0	3.5
0.20	0.60	480	94.4	97.4	7.5
0.25	0.60	276	94.6	98.3	27.7
0.30	0.60	60	95.9	98.2	60.4
0.40	0.60	50	95.5	98.4	75.9
0.50	0.60	42	96.3	98.3	79.1
0.60	0.60	30	96.0	—	82.0
0.80	0.60	27	95.6	98.4	83.0
0.90	0.60	24	96.5	98.4	80.3
0.15	0.75	365	95.1	—	6.9
0.37	0.75	40	95.9	—	70.7
0.40	0.75	36	96.4	—	63.7
0.15	0.90	155	92.6	—	5.6
0.30	0.90	84	95.6	98.2	6.7
0.45	0.90	24	98.2	—	9.7
0.60	0.90	24	96.4	98.3	63.1
0.90	0.90	18	96.4	—	—

[a)] Activator: hexamethylene-1,6-dicarbamoylcaprolactam (HDCL), initiator: sodium caprolactamate (I).

The concentration of HDCL has been varied from 0.15 to 0.9% (mol/mol of CL) at four fixed concentrations of I (0.3, 0.6, 0.75, 0.9%, mol/mol of CL).

When THDCL was used, only one initiator concentration ([I] = 0.6%) was explored (Tab. 2).

The most relevant kinetic result obtained by using these fast activators is the impressive reduction of t_p to values shorter than 60 s, in comparison with 300–600 s typical of the *cast nylon* technology, promoted by 'slow' activators (e.g., *N*-acetyl-CL)[1–5]. The overall polymerization time sharply decreases as the activator concentration increases, in the whole range of initiator concentrations explored. At the

Tab. 2. Dependence of polymerization time t_p, monomer conversion, high-polymer yield and crosslinked fraction on [I] and [THDCL][a)]

[THDCL] mol/mol CL in %	[I] mol/mol CL in %	t_p/s	High-polymer yield in %	Monomer conversion in %	CF_3CH_2OH insoluble fraction in %
0.30	0.60	54	96.3	97.9	39.1
0.40	0.60	36	96.6	98.4	63.7
0.50	0.60	26	96.0	97.6	(57.5)
0.60	0.60	28	96.4	—	75.1
0.85	0.60	18	96.4	98.1	70.9
0.90	0.60	28	96.6	—	—

a) Activator: 2,2,4-trimethylhexamethylene-1,6-dicarbamoylcaprolactam (THDCL), initiator: sodium caprolactamate (I).

mer conversions >98%. Accordingly, the amount of low molecular weight cyclic oligomers and side products is lower than 2%.

A comparison between the two activators in terms of t_p *vs.* [A] (for [I] = 0.6 mol-%) is shown in Fig. 1. It is evidenced that better results are always given by THDCL activation, with polymerization times that are *ca.* 25% lower than those derived from HDCL activation. The shortest t_p value, obtained with THDCL (0.85 mol.-%), is only 18 s.

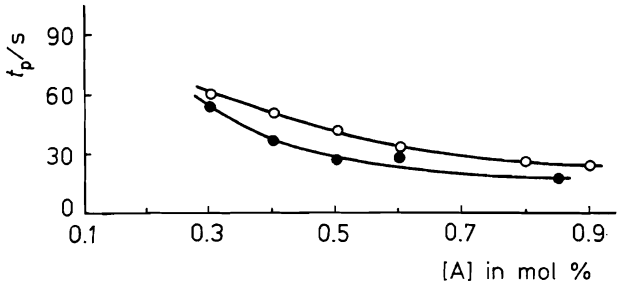

Fig. 1. Polymerization time (t_p) vs. activator (A) concentration curves ((○) HDCL, (●) THDCL; [I] = 0.6 mol-%)

In our opinion, the above t_p reduction, when THDCL is used, should somehow be linked to the rather high viscosity of that liquid activator which, when syringed into the reaction vessel, can initially form heterogeneous microdomains slow to homogenize, despite the stirring, with the other components of the reacting system. Consequently, a locally higher concentration of growing chains is formed, as compared to HDCL, which is predissolved in an aliquot of CL and very quickly homogenizes with the remaining fraction of it. Chemical differences in reactivity between THDCL and HDCL, if any, should play a much minor role in this respect.

A peculiar effect derived by the use of HDCL and THDCL in the *quasi*-adiabatic anionic polymerization of CL is the considerable formation of crosslinked polyamide. From the data given in the last column of Tabs. 1 and 2, the amount of crosslinked PCL

results strongly dependent on both the concentration and type of the activators used. The experimental data show a marked effect of these catalytic species on the network formation. The branching and crosslinking interchain reactions are indeed originated by the acylation of the active sites (carbanions and amidic anions) present in the macromolecules[6] and can by no means be considered a secondary phenomenon, as they are major characteristics of anionic PCL syntheses in *quasi*-adiabatic conditions, even in such extremely fast processes. Namely, in any specific system, complex kinetic, thermodynamic and rheological factors are able to strongly affect both the interchain exchange and polymerization reactions, giving eventually rise to the network.

As an example, in Fig. 2 the amount of the crosslinked fraction as a function of [A] for the two activators at [I] = 0.6 mol.-% is reported. For HDCL, a large increment

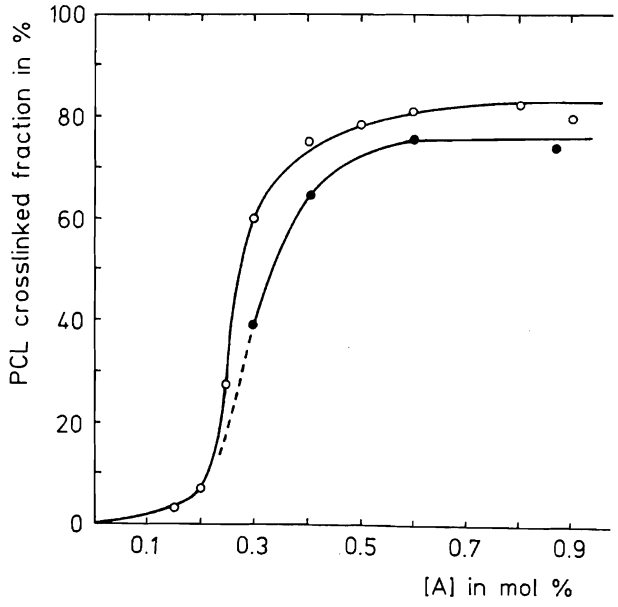

Fig. 2. PCL crosslinked fraction as a function of [A] ((○) HDCL, (●) THDCL; [I] = 0.6 mol-%)

of the crosslinked fraction for an activator concentration higher than 0.2–0.25% can be observed. A further increment of [HDCL] from 0.4% on does not seem to be particularly relevant in this respect. A similar sigmoid behavior is also shown by the percentage of PCL crosslinked fraction as a function of [THDCL]. However, it should be noticed that, in the latter case, extensive crosslinking occurs at higher [A] and reaches limiting values lower than those pertaining to HDCL. Shorter polymerization times for THDCL, as compared to HDCL (Tabs. 1 and 2), and a consequent, more rapid increase of medium viscosity can fully account for the above data.

A qualitative comparison among the various sodium caprolactamate concentrations and their role on the crosslinking extent is also possible, although only for HDCL. From the data of the last column of Tab. 1, it can be inferred that also other PCL

On the whole, the aforementioned complexity of kinetic, thermodynamic and chemo-rheological factors on the amount of crosslinking is confirmed.

The swelling data of various deoligomerized PCL samples synthesized at fixed [I] (=0.6 mol.-%) and exposed to formic acid vapours are reported in Tab. 3. It can be seen that by increasing the activator concentration, *i. e.* the fraction of crosslinked product, the polyamide swelling ratio obviously decreases. The interpolated degree of swelling at fixed crosslinking content is higher with HDCL than with THDCL, and this result should be linked to a higher number of crosslinking points per chain in the latter case and/or to steric hindrance effects.

Tab. 3. Data of PCL swelling in formic acid

Activator used	[A]/[I]	Degree of crosslinking in %	α [a] in %
HDCL	0.30/0.60	60.4	388.1
HDCL	0.40/0.60	75.9	370.8
HDCL	0.50/0.60	79.1	340.5
THDCL	0.30/0.60	39.1	340.7
THDCL	0.40/0.60	63.7	327.3
THDCL	0.85/0.60	70.9	297.2

[a] $\alpha = 100\ (m-m_0)/(m_0\ d)$, where: m = weight of the swollen sample; m_0 = original weight of the sample; d = density of formic acid at 20 °C.

The above PCL samples show a crystallization rate lower than that of linear ones. The data concerning the isothermal crystallization of the crosslinked fraction (at 460 K) are reported in Tab. 4. The crystallization rate is expressed as the Avrami constant K. This value decreases as the crosslinked fraction increases.

Tab. 4. Isothermal crystallization data (T_c = 460 K)[a]

Activator used	[A]/[I]	ΔH_c / J/g	n	K / min^{-n}	Sample type
HDCL	0.30/0.60	44.7	3.8	0.0043	insoluble fraction
HDCL	0.40/0.60	41.4	3.9	0.0038	
HDCl	0.80/0.60	46.4	3.4	0.0019	
THDCL	0.30/0.60	52.7	3.3	0.0689	insoluble fraction
THDCL	0.40/0.60	49.7	3.7	0.0104	
THDCl	0.80/0.60	26.8	3.3	0.0008	

[a] T_c: crystallization temp.; ΔH_c: crystallization enthalpy; n, K: Avrami exponent and constant.

X-ray measurements, reported in Tab. 5 on demonomerized samples, allow to point out the presence of γ-form crystalline domains, unusual for PCL samples prepared in our experimental conditions. The amount of γ-type polyamide is related to the percentage of crosslinked fraction and decreases as the gel fraction increases.

Indeed, from these data, a nice correlation can be envisaged between the amount of γ form (Tab. 5) and length of the segments between two neighbouring crosslinking points (Tab. 3) for the two sets of PCL samples. At higher crosslinking densities (activator THDCL), the γ-form content is reduced accordingly.

Tab. 5. X-ray analysis

Activator used	[A]/[I]	Degree of crosslinking in %	γ-form content in %
HDCL	0.40/0.60	75.9	25.5
HDCL	0.80/0.60	83.1	6.6
THDCL	0.30/0.60	39.1	41.7
THDCL	0.40/0.60	63.7	36.6
THDCL	0.85/0.60	70.9	20.6

Conclusions

Depending on the experimental conditions, complex rheokinetic factors, responsible for the relative importance of main and side reactions, give rise to a variety of PCL chains, characterized by branching and crosslinking to a variable extent. It is therefore possible to envisage a large choice of experimental conditions able to orient the anionic PCL synthesis in order to produce end materials with the desired properties and performances.

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