

The beneficial influence of ultrasound in the polymerization of ϵ -caprolactam to polyamide-6 (Nylon 6). Part II: Additional experiment to understand the “pre-sonication effect”

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Abstract

Ultrasound (US) “pre-sonication effect” is the beneficial effect of US in the hydrolytic polymerization of ϵ -caprolactam (CL) mixtures with very low water concentrations (about 0.1–1 wt%). It appears after a mild initial treatment of the mixtures with US [17.5–20 kHz, short times (5–15 min), low temperatures (70–110 °C)] followed by heating at 220–260 °C. An explanation is proposed on the basis of the formation in mild conditions (100 °C) of low concentrations of cyclic oligomers never detected in the literature at those conditions. These, under US irradiation, produce linear amino acid oligomers, which are strong activators of polymerization when the mixture of CL and water, after US irradiation, is heated at the suitable polymerization temperature indicated above.

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1. Introduction

In Part I of this paper, it was shown how ultrasonic irradiation (around 20 kHz) of ϵ -caprolactam mixtures with water, either with or without activators, can help the polymerization of CL to polyamide-6 (Nylon-6). The topical question to be understood from these results is: why does the mixture of CL and water after US irradiation for very short times (5–15 min) at low temperatures (70–110 °C) give higher molecular weight polymers, (with respect to silent conditions, i.e. no use of US at the same conditions), when this mixture is heated, at the polymerization temperature (260 °C), after US irradiation? This phenomenon constitutes a “pre-sonication effect” and in order to give it a plausible explanation, a series of additional experiments was performed with respect to those in Part I.

2. Experimental

Apparatus. An improved reactor (Fig. 1) has been used for the runs of Part II. This reactor is equipped with an efficient magnetic stirrer and with the same US emitter (at 17.5 kHz, 0.07 kW (kg CL)⁻¹) as in Part I.

Materials. Azobisisobutyronitrile (AIBN), ϵ -aminocaproic acid (ACA), ϵ -caprolactam (CL) are Fluka products.

Analyses. GC analysis for the determination of CL conversion was described in Part I. HPLC analysis of cyclic oligomers (CY) was performed according to a method developed and used at Rhodia Co. Laboratories [1]: instrument Varian Pro Star, mobile phase water, trifluoroethanol (50/50 volume), flux 1 ml min⁻¹, column H-Sil C8 (Hamilton) 250 × 4.6 mm, pore diameter 5 μ m, internal standard phenol. In both methods the samples to be analyzed were dissolved in 2 ml of a mixture of phenol (373 mg in 250 cc of TFE) and trifluoroethanol.

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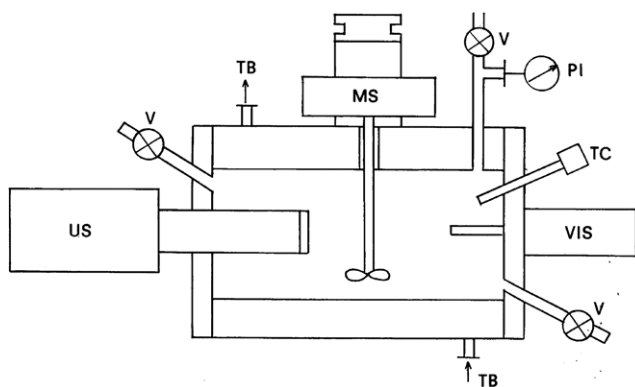


Fig. 1. Magnetically stirred (MS) reactor (total volume 400 ml) equipped with US (17.5 kHz) and a vibrational viscosimeter (VIS). V, valve; TC, thermocouple; PI, pressure indicator; TB, connection to thermostatic bath.

GC analyses were performed in a Packard 438 instrument as described in Part I.

3. Results

(If not otherwise indicated all the percentages are on weight base).

ACA is well known as a promoter of CL polymerization since this amino acid is the first product in the hydrolytic ring-opening reaction between CL and water [2,3]. For this reason some runs were done at different molar concentrations of ACA and water in CL with and without the use of US in the initial step, as described in the caption of Fig. 2a–b; the molar concentrations of water and ACA are the same. Another series of experiments was performed in order to study the range of ACA concentration in CL

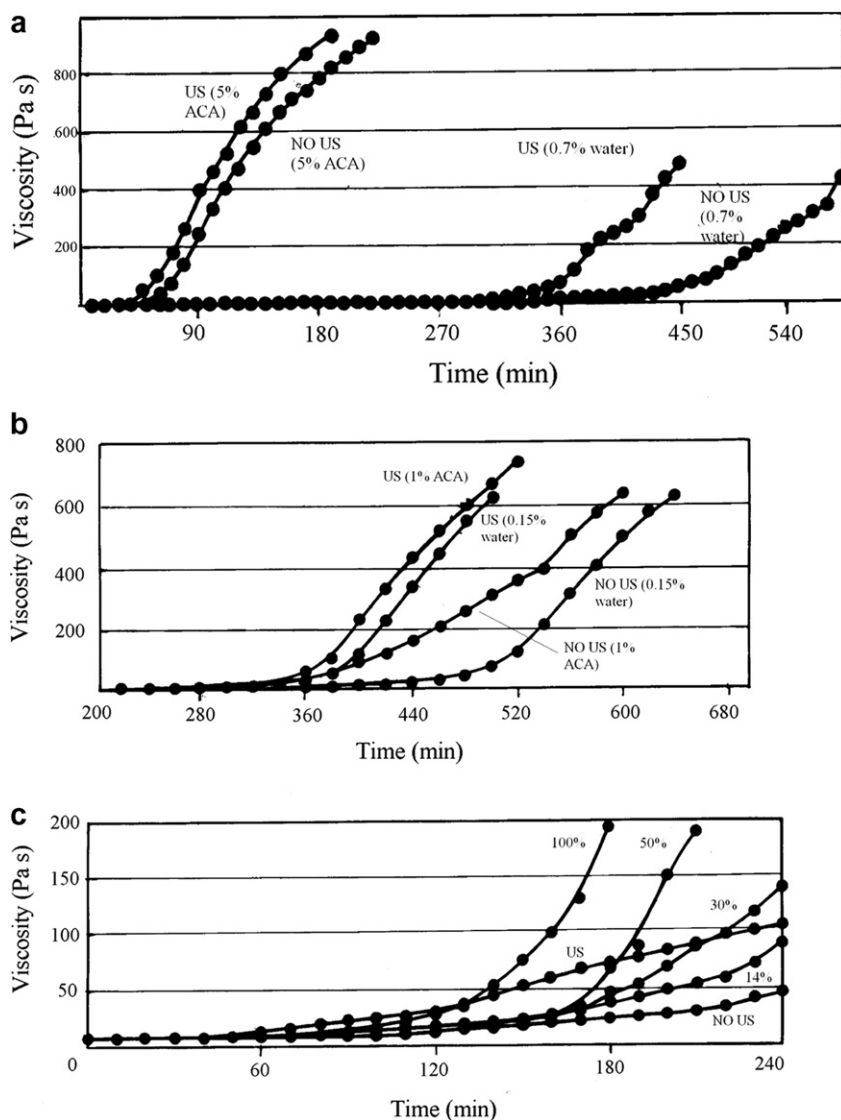


Fig. 2. Viscosity vs. reaction time (t_R) of different mixtures of CL with ACA or water; $t_S = 5$ min; $T_S = 101$ °C a and b ($T_R = 250$ °C); molar concentration of ACA or water in CL: A = 4.38%; B = 0.86% corresponding, respectively, to (a): ACA = 5 wt%, water 0.7 wt%; (b): ACA = 1 wt%; water 0.15 wt%. (c) ($T_R = 220$ °C): Curves US, NO-US: 0.5 wt% water in CL, corresponding to 3.1% molar. Curve 100%: 3.1% molar of ACA in CL; curves 50%, 30%, 14% refer to the indicated percentage of 3.1% molar of ACA in CL. Curve with US: $t_S = 5$ min, $T_S = 101$ °C.

necessary to promote the same increase of CL polymerization in the mixture with water, in the absence of US pre-treatment as was obtained using US at the beginning of the run ($t_S = 5$ min, $T_S = 101$ °C). The experiments with water were made at 0.5% of water in CL (corresponding to a molar percentage of 3.1) with and without US; the concentration of ACA was changed from 100% to 14% in moles, Fig. 2c, which shows the viscosities of the different mixtures vs. the reaction time ($t_R = 240$ min; $T_R = 220$ °C).

The formation in the CL/water mixture of radical species, that could act as activators of polymerization during US irradiation, was also analyzed by adding to CL the typical radical generator AIBN. A mixture of dry CL and 0.5% of AIBN was subjected to US and the results were compared with those of the runs with and without the initial use of US (Fig. 3).

In order to verify the beneficial effect of US, as previously described, a number of mixtures of CL and water were heated, after US irradiation, at temperatures ranging from 160 to 235 °C, i.e. below those used industrially for the polymerization of CL (250–280 °C). The results are reported in Table 1, where CL conversions after US irradiation are compared with those in silent conditions. The particular activity of ACA and water in promoting both CL polymerization (Fig. 2) and conversion (Table 1) suggested the performance of a careful analysis of the presence of cyclic oligomers (CY) when CL/water mixture reaches the temperature of US irradiation (70–110 °C) but before beginning US irradiation itself. Furthermore, the mixture composition was studied after different times of US irradiation or of silent conditions. Fig. 4 shows the ratio of CY concentration, from dimer to hexamer, with respect to the initial concentration ($t = 0$, corresponding to the reaching of 100 °C) in silent or US conditions, with the initial water concentration in CL of 0.55%. Similar results are reported in Table 2 in order to compare the total CY concentration

Table 1

Ratio, R , of CL conversion, C , with and without US at different temperatures (T_R) of polymerization T or $T_S = 101$ °C; t or $t_S = 5$ min; 0.5% H₂O

T_R (°C)	$R = C_{US}/C_{NO-US}$
160 ^a	11 (4)
190 ^a	3 (4); 4.9 (5)
205	1.16 (4)
220	1.12 (4)
235	1.07 (4)

In parentheses the reaction time t_R (h).

^a Data partially reported in Table 2 of Part I.

at 110 and 70 °C. The last series of experiments was made using a mixture of CL to which an industrial mixture (Rhodia Co.) of CY and CL was added; such mixture contains 0.4% dimer (CD); 0.34% trimer (CT); 0.3% tetramer (CTH), the balance being CL. As a result, the composition fed to the reactor was: 300 g CL, 1.4 g water (0.5% of CL), 4.8 g of the mixture of cyclic oligomers (1.5% of CL). The reactor was heated to 100 °C under stirring and maintained at this temperature for 15 min in silent or US irradiated conditions, then samples for analysis were withdrawn. The ratio $[(CY)^{US}/(CY)^{NO-US}]$ was: dimer, 0.72; trimer, 0.93; tetramer, 0.50; neither pentamer nor hexamer CY were found.

4. Discussion

The experimental evidence of the beneficial action of US in promoting CL hydrolytic polymerization (as shown in Part I of this paper) shows a topical “pre-sonication effect” which needs to be understood.

The run using AIBN (Fig. 3) indicates that the influence of US is not connected with the formation of radical species. In fact no significant difference is shown between the

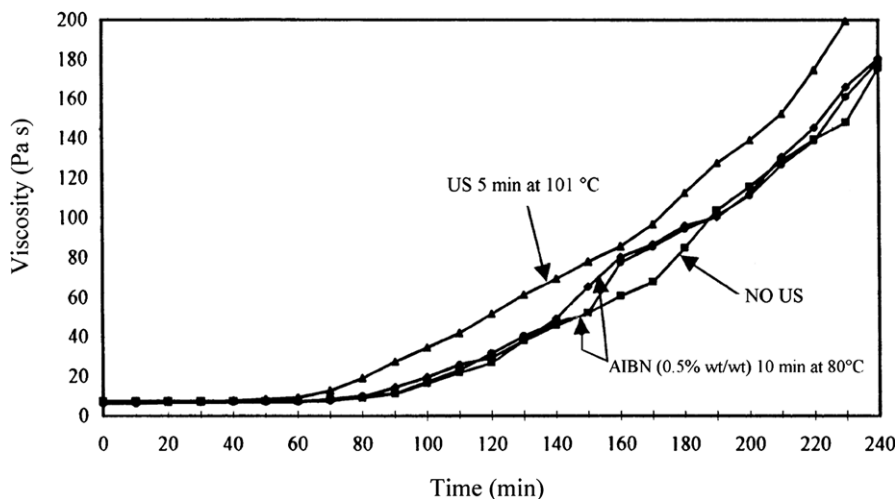


Fig. 3. Comparison of viscosities vs. reaction time of different mixture: CL with water (1.55%); CL with AIBN (0.5%); experimental conditions: $t_S = 5$ min, $T_S = 101$ °C, $t_R = 240$ min, $T_R = 235$ °C.

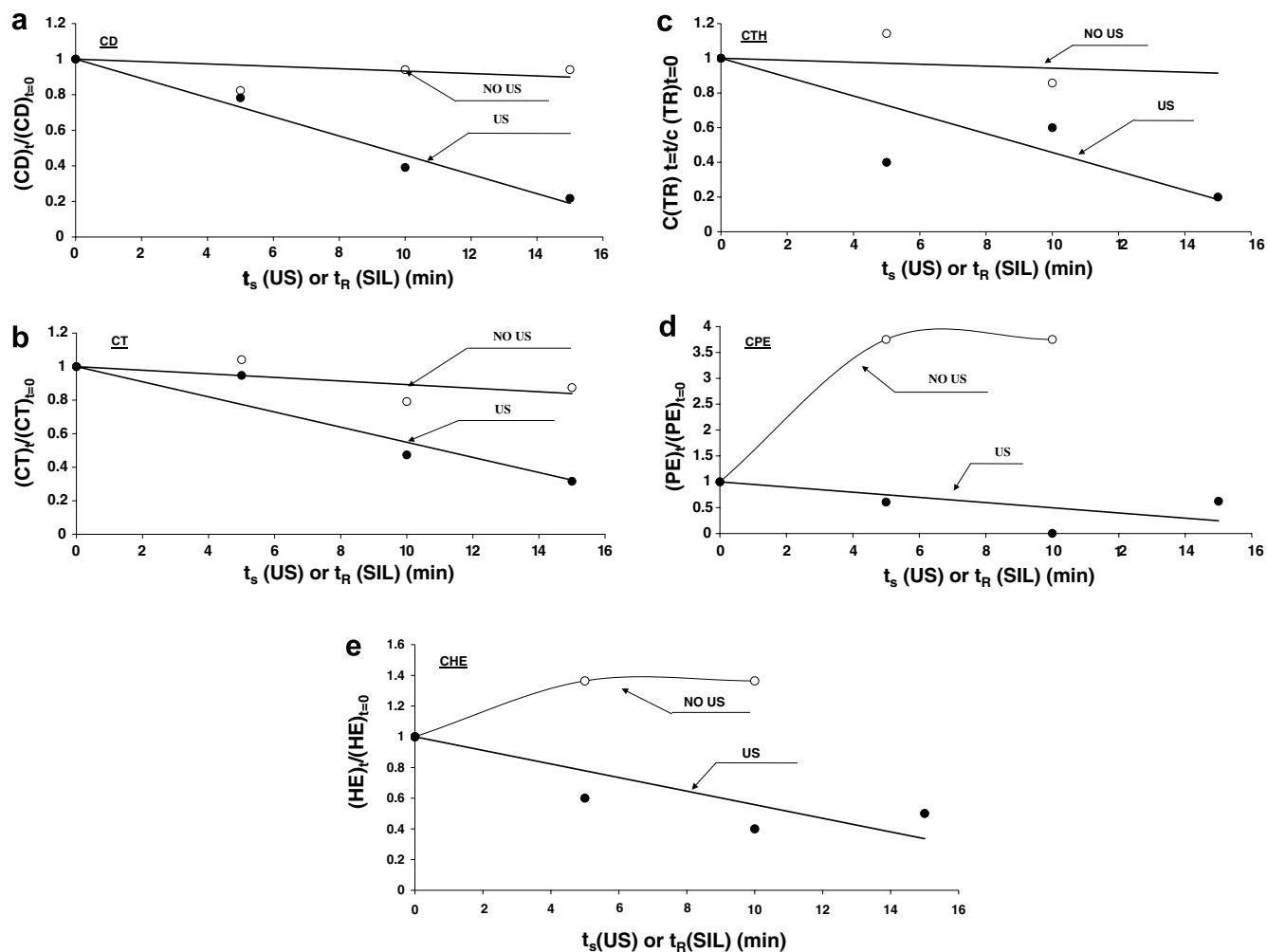


Fig. 4. Ratio of the concentrations of cyclic oligomers (CY) at different times to the initial concentration ($t = 0$) in runs with or without US at $t = 0$ –15 min and T or $T_s = 100$ °C. (a) Dimer (CD); (b) trimer (CT); (c) tetramer (CTH); (d) pentamer (CPE); (e) hexamer (CHE).

Table 2

Total cyclic oligomer concentration (%) (dimer–hexamer) formed in silent (NO-US) or ultrasonic (US) conditions in a mixture of CL and 0.5% water

t total (min)	$T = 110$ °C		$T = 70$ °C	
	NO-US	NO-US (10 min) followed by US	NO-US (10 min)	NO-US (10 min) followed by US
0	0.29	0.29	0.65	0.65
15	1.58	0	0.51	0.27
20	1.48	0.12	0.42	0.12

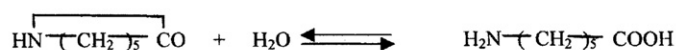
use of AIBN and silent conditions; it should be remembered that no mechanism of CL hydrolytic polymerization which involves radical species is reported in literature [2–6].

Table 1 gives an indication that after US irradiation some reactions involving CL occur already at temperatures (160–190 °C) at which the polymerization rate is very low. The indications of this table together with those reported in Fig. 7 and Table 2 of Part I, confirm that the beneficial effect of US is more evident the lower is the initial percentage of water and that the conversion of CL is more evident, with respect to silent conditions, at a low temperature. The

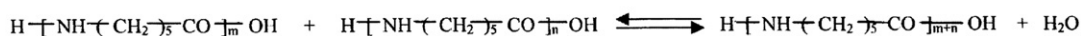
formation and transformation of cyclic oligomers (CY) from CL at 100 °C, as shown in Fig. 4, is a new result in literature and is very useful in understanding the “pre-sonication effect” when one considers the detailed mechanism of CL hydrolytic polymerization, as proposed by Arai et al. [6] (Scheme 1). Cyclic oligomers have been found at low temperature, 150 °C, by Ueda et al. [8] in the anionic polymerization of CL.

Usually the mathematical elaboration of the experimental data for CL hydrolytic polymerization is based on the first three reactions of Scheme 1, i.e. the reaction RO, PC, PA [2–5]. Only in a subsequent paper of Arai et al. [6] was the presence of cyclic dimer (CD) considered in the reaction scheme and from a mathematical point of view in the kinetic equations. The presence of CY, formed by intra- or inter-molecular transacylation or intermolecular transamidation, has been discussed by many authors since 1952 ([3] and reference therein); their concentration in the polymer is a function of the hydrolytic polymerization temperature; from 220 to 250 °C the total percentage at equilibrium of dimer to hexamer in the polymer increases from 2.52 to 3.29 wt% [3], p. 106.

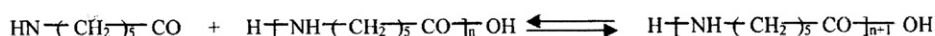
Ring Opening of CL ($\Delta H = 2240 \text{ cal (mol)}^{-1}$) (RO)



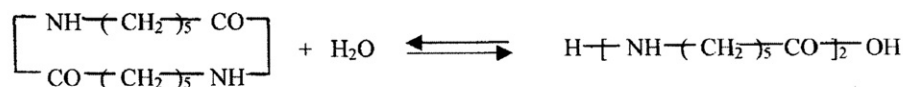
Polycondensation ($\Delta H = -614.4 \text{ cal (mol)}^{-1}$) (PC)



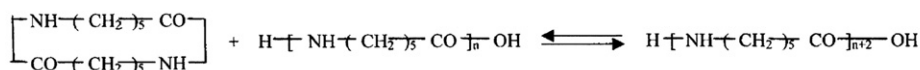
Polyaddition of CL ($\Delta H = -4823.3 \text{ cal (mol)}^{-1}$) (PA)



Ring-opening of CD (Endothermic)



Polyaddition of CD (Exothermic)



Scheme 1. Reactions involved in CL hydrolytic polymerization according Arai et al. [6].

The novelty is that cyclic oligomers are formed also at low temperatures (around 100°C); moreover such compounds decompose under the action of US more rapidly than in silent conditions (Fig. 4 and Table 2). According to Scheme 1 the decomposition of CY takes place by the action of water or linear aminoacid oligomers to give molecules of aminoacids which are strong activators of CL polymerization through the polyaddition reaction (PA). According to this reaction scheme, after the initial step of CL ring opening, this molecule is mainly converted to polymers ([3], p. 91; [8]). Wiloth [9] demonstrated that, especially at low content of water in CL, the addition of aminoacid monomer on CL is extremely rapid. For Nylon 6, in contrast to nylon 6–6, the addition reaction of Scheme 1 is the major growth mechanism [10].

The above-mentioned activity of amino acid molecules in CL polymerization has been confirmed, both in the presence and in the absence of US in the initial step. In fact ACA at high concentration (5%) competes with US to increase the viscosity (Fig. 2a) (i.e. the runs with or without US but with 5% of ACA give quite similar results), but at lower concentration (1%) the effect of US prevails (Fig. 2b). The amount of ACA added to CL which simulates the action of US is reported in Fig. 2c. Considering that 0.5 wt% of water in CL corresponds to a molar percentage of 3.1%, mixtures of CL-ACA have been prepared with the following molar percentages of ACA: upper curve (100%) in Fig. 2c (100% means the same molar concentration of

water at 0.5 wt%/wt%, i.e. 3.1 molar%) Curves 50%, 30%, 14% are in the same proportion. It is interesting to observe that an amount of ACA between 14% and 30% gives the same results as US applied to the mixture of CL and water at 0.5 wt%.

The above results, combined with those of literature ([3,6–8]) strongly support our explanation of the

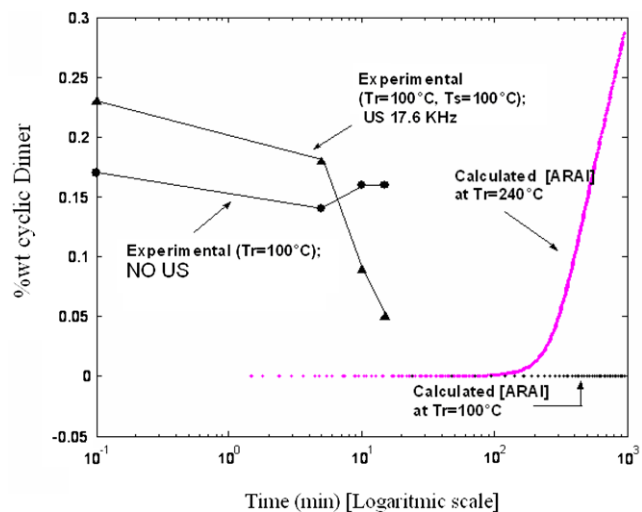


Fig. 5. Calculated and experimental concentration of cyclic dimer as a function of time t (logarithmic scale). The initial time $t=0$ for the experimental results correspond to 5 min after reaching the temperature of 100°C .

“pre-sonication effect”. It is based on the initial formation of cyclic oligomers at low temperatures (70–110 °C) and then with their decomposition, by the action of US, to light aminoacid oligomers; such compounds strongly enhance the reaction rate of polymerization when the mixture is heated at a higher temperature (around 250 °C). Moreover the results of the runs using a mixture of CL and water with a mixture of cyclic oligomers support such an explanation of the “pre-sonication effect”, the ratio $(CY)^{US}/(CY)^{NO-US}$ being always less than one after t or t_S of 15 min or 10 min at T or T_S of 100 °C (Fig. 4).

The presence of cyclic oligomers at a low temperature, as found experimentally in the work of this paper, is a new result which should be compared with the one calculated by applying the mathematical model and the parameters proposed by Arai et al. [6]; for this computational work a MATLAB program was used. The concentration of cyclic dimer (CD) was calculated at $T_R = 220$ and 100 °C and compared with the experimental results at 100 °C in silent or US conditions as described in the caption of Fig. 5; the small decrease of CD in silent conditions (from about 0.17% to 0.15%) results from the uncertainty of the experimental results at such a low concentration. It is clear that Arai’s mathematical model is not able to predict the behavior of the system at 100 °C; this is obviously due to the kinetic and equilibrium parameters which are optimized on the experimental data in the range 230–280 °C [6].

5. Conclusions

All the data presented in Part II of this paper, considering also the relevant literature [3–8], are consistent with an explanation of the “pre-sonication effect” of US, as shown in Part I and in the introduction of Part II. This explanation involves the formation of cyclic oligomers at a low

temperature and their decomposition, under the action of US, to linear aminoacid oligomers, which are strong activators of the hydrolytic polymerization of CL when the mixture is heated at the appropriate polymerization temperature.

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