Solution Polymerization of *N*-vinylcaprolactam in 1,4-dioxane. Kinetic Dependence on Temperature, Monomer, and Initiator Concentrations

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ABSTRACT: The kinetics of the solution free radical polymerization of *N*-vinylcaprolactam, in 1,4-dioxane and under various polymerization conditions was studied. Azobisisobutyronitrile and 3-mercaptopropionic acid were used as initiator and as chain transfer agent (CTA), respectively. The influence of monomer and initiator concentrations and polymerization temperature on the rate of polymerizations (R_p) was investigated. In general, high conversions were obtained. The order with respect to initiator was consistent with the classical kinetic rate equation, while the order with respect to the monomer was greater than unity. The overall activation energy of 53.6 kJ mol^{-1} was obtained in the temperature range 60–80 °C. The decreasing of the absolute molecular weights when increasing the CTA concentration was confirmed by GPC/SEC/LALS analyses. It was confirmed by UV-visible analyses the effect of molecular weights on the lower critical solution temperature of the polymers. It was also verified that the addition of the CTA influenced the kinetic of the polymerizations. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 229–240, 2010

Key words: *N*-vinylcaprolactam; solution polymerization; kinetics; LCST; absolute molecular weights

INTRODUCTION

Stimuli-responsive polymers with properties such as biocompatibility, functionality, and nontoxicity are potential biomedical materials.[1,2] These intelligent materials respond to small external stimuli (temperature, pH, ionic force, and magnetic fields) with changes in its form and volume.[3] Thus, stimuli-responsive polymers have attracted much attention due to its large range of applications as a carrier in controlled release of drugs.[4,5] The most important stimulus in these studies is temperature.[6] Thermally responsive polymers and their use in biomedical applications are widely investigated nowadays.[7] Aqueous solutions of thermo-responsive polymers exhibit a phase separation in the transition temperature, known as the lower critical solution temperature (LCST)[8] responding with large reversible change in hydrophilicity and showing the phase transition of the polymer chains from solvated coiled to dehydrated globular states when the temperature is increased above LCST.[9] An example of temperature-responsive and biocompatible polymer that has been studied for therapeutic purposes is poly(*N*-vinylcaprolactam) (PNVCL).[7] This polymer shows the LCST in water close to physiological temperature, which opens perspectives for applications in biochemistry and medicine.[4] The LCST is sensitive to changes in the polymer concentration, molecular weight, and the composition of the solution.[5] PNVCL is composed of amide group that render the polymer as a whole "hydrophilic."[10] Because hydrolysis of the amide group of PNVCL will not produce small amide compounds, this polymer is suitable for biomedical applications.[8] Presently, several studies have reported on the phase behavior of PNVCL in water.[11–14] Applications of PNVCL in the area of biomedical materials, in stabilization of proteases and in controlled drug delivery have been published for example by Peng and Wu,[13] Markvicheva et al.,[15] and Vihola et al.[7] The first work with this monomer was published in 1968. In this work, Solomon et al.[16] studied the kinetic of the bulk polymerization of *N*-

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vinylcaprolactam (NVCL). In 1969, Solomon et al.[17] studied the kinetic of the polymerization of NVCL in toluene. However, nowadays, the interest in the thermo-responsive behavior of PNVCL is increasing. Interest in the physical behavior of PNVCL originates largely from its biocompatibility and low toxicity.[5,18] Vihola et al.[7] studied the citotoxicity of PNVCL of various molecular weights, and the results revealed that the polymers were well tolerated at lower molecular weights. Therefore, in these last years, the synthesis of PNVCL with lower molecular weights has attracted significant attention in the biomedical and pharmaceutical fields.[19]

Mercaptan derivatives compounds, such as the 3-mercaptopropionic acid used in this work, are commonly used to synthesize NVCL-based polymers with lower molecular weights via radical polymerization. A relatively new and attractive chemical route that can be applied in the synthesis of PNVCL with controlled molecular weight is the living radical polymerization (LRP). Living radical polymerization has gained importance in polymer control in terms of molecular weight, molecular weight distribution (MWD), and architecture control. *N*-vinylcaprolactam is a typical unconjugated monomer, just like its analogs, vinyl acetate and *N*-vinylpyrrolidone. It is well known that LRP of unconjugated monomers is not an easy task. The high reactivity of the radical species derived from such monomers, which results in significant retardation and/or complete inhibition, is the main reason for the limitations concerning their polymerization via LRP. For this reason, in the literature, there is a lack of information concerning the synthesis of PNVCL via LRP. In the open literature, only two articles reporting the synthesis of NVCL-based polymers by RAFT/MADIX mechanisms have been found.[20,21] Despite all the efforts recently made to overcome these limitations, the whole livingness characteristic in the LRP of NVCL has not been achieved. Moreover, for this specific monomer, there is an additional unsolved and unexplained problem, that is, the problem related to limited conversions. When PNVCL is synthesized to be used as a carrier in drug release systems, the choice of the reagents is crucial. In general, the chain transfer agents used in RAFT/MADIX polymerizations (xanthates and dithiocarbamates, for the specific case of NVCL polymerizations) present high toxicity. Thus, the preparation of PNVCL for biological applications via these mechanisms, could be viable only if an additional step is performed, that is, the degradation of the terminal thiocarbonylthio groups from the chain transfer agent. Spruell et al.,[22] proposed an elegant procedure to remove the dithiobenzoate end groups from polymers synthesized via RAFT polymerizations. In their one-pot procedure, that is, on the basis of Michael addition reactions, it was possible to achieve simultaneously the removal of the thiocarbonylthio moiety and the introduction of functional groups to a polystyrene chain.

To determine values of elemental kinetic coefficients in free radical polymerizations, some studies of vinyl monomers have used nonsteady state methods. Theses studies revealed that, in some cases, the results contradicted the classical kinetic assumptions.[23] Therefore, it is important to know the reason for these anomalous results, that is, a monomer reaction order higher than unity or a variation of $k_p/k_t^{0.5}$ with monomer concentration. One important factor to be analyzed when changing the polymerization parameters such as initiator and initial monomer concentrations and temperature is the viscosity, as was observed by Foroutan et al.[24] With the variation of the viscosity, we can observe a deviation from the normal kinetic and significant changes of mass and heat transfer and mainly changes of the termination rate constant k_t, that is, the decrease of the mobility of macroradicals leads to a decrease of k_t values, resulting in an autoacceleration of the reaction and an increase of the polymerization degree (gel effect).[25] The propagation rate constant k_p is also dependent of the reactions conditions but it is less sensitive to the diffusion because of the mobility of the monomer molecules.

Among the factors leading to changes in the viscosity, the mobility of macroradicals, and the k_t constant, we can emphasize the initiator and initial monomer concentrations and temperature. When the polymerization is carried out at lower temperatures, for example, a transition state might be reached at a certain conversion, which means that the polymerization temperature equals the glass transition of the polymer–monomer mixture (glass effect).[25]

The goal of this work is to show the advantages of synthesizing PNVCL through a simpler route, in which it is possible to obtain polymers with low molecular weights. The thermo-responsive polymers obtained are available to be used as a carrier in drug release systems, without any additional and laborious step of purification for the final polymers. Moreover, there are no studies in the literature describing the effect of the molecular weight on the thermoproperty of PNVCL. In this article, we could observe that the LCST changed when increasing the molecular weight. Because the LCST will influence the kinetics of drug release, the control of molecular weight in the synthesis of PNVCL is also of interest for biomedical applications in targeted drug delivery.

To produce tailored thermo-responsive polymers, it is important to know the kinetic of their polymerizations. In this sense, ^{1}H-NMR technique was used to study the dependence of polymerization rate on

temperature, as well as on initiator and monomer concentrations for the solution polymerization of NVCL in 1,4-dioxane, using azobisisobutyronitrile (AIBN) as initiator and 3-mercaptopropionic acid as chain transfer agent. The number-average molecular weights ($\overline{M}_n$) and the MWD of the polymers were determined using a gel permeation chromatography (GPC) instrument coupled with a triple detector, including a refractive index, a viscometer and a low- and high-angle light scattering detectors. This equipment gives the absolute molecular weight, and this is very interesting due to the fact that the use of standard calibration, such as polystyrene (PS), can leads to false results in the analyses of molecular weight of PNVCL. Finally, the influence of the molecular weight on the LCST of the polymers was verified by UV-visible analyses.

EXPERIMENTAL

Materials

N-vinylcaprolactam (98%, Aldrich, São Paulo, state of São Paulo, Brazil) was distilled under vacuum to remove the inhibitor. 2,2′-azobisisobutyronitrile—AIBN (kindly furnished by BASF, Guaratinguetá, state of São Paulo, Brazil) was purified by recrystallization from ethanol. The chain transfer agent (CTA), 3-mercaptopropionic acid (MPA) (99%, Aldrich), and trioxane (99%, Aldrich) were utilized without further purification. 1,4-dioxane (99.8%, Aldrich) was distilled over $LiAlH_4$ under vacuum. Chloroform-d (99.8%, Aldrich) was utilized for determination of the monomer conversion by ^{1}H NMR analyses (Varian, 300 MHz) (Laboratório de Química Fina, Engineering School of Lorena, University of São Paulo, Brazil).

Polymerization procedure

The PNVCL polymers were synthesized by free radical polymerization in 1,4-dioxane at 70°C. The reactions were carried out in a 50 mL glass double-wall reactor under nitrogen atmosphere. First, the desired amount of *N*-vinylcaprolactam was transferred to the reactor with an appropriate amount of internal standard (trioxane) and CTA. Then, 75% of the solvent was added, and the mixture was flushed with argon for 20 minutes at a moderate gas flow rate. A solution with AIBN and 25% of the solvent was prepared and flushed also with argon for 20 minutes. When the temperature reached 70°C, the polymerization was initiated through the addition of the AIBN solution. A syringe was used to transfer the solution containing the initiator into the reactor. At this time, one sample was withdrawn from the reaction medium. The polymerization was carried out for 3 hours. For the UV/visible analyses, the polymers were purified by precipitation, under stirring in hot water (45°C) above the LCST of PNVCL. After sedimentation, the aqueous phase was separated, and the precipitated polymer was solubilized again in cold water using an ice bath. This procedure was repeated three times. Then, the polymers were dried at 45°C in a vacuum oven during 24 hours.[26,27]

Kinetic study

The monomer conversion was determined by ^{1}H-NMR. Samples were withdrawn from the polymerization mixture at different reaction times, introduced into vials containing hydroquinone, and placed in ice to stop polymerization. The ^{1}H-NMR analyses were performed without evaporation of the polymerization solvent by mixing 0.2 mL of each sample with $CDCl_3$ (1 : 3 v/v). Monomer conversion was determined by comparison of vinyl protons of NVCL with protons of Trioxane as reference, according to eq. (1).

$$x(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 is the integral for the monomer vinylic proton at the beginning of the reaction (zero time) and A_t is the integral for the vinylic proton at the time of the sample withdrawn. With the conversion values at different polymerization times, the initial polymerization rate, R_p, was obtained from the slope of the linear part of the conversion-versus-time curves and the relationship of polymerization rate with initial monomer and initiator concentrations was obtained by plotting the ln R_p versus ln $[M]_0$ and ln $[I]_0$. The order of polymerization with respect to monomer and initiator concentrations was obtained from the slope of the linear plots.

To investigate the effect of monomer and CTA concentrations and polymerization temperature on R_p, the same method used by McKenna et al.[28,29] was applied here. In this method, the rate of reaction in a batch polymerization is given by the following expression:

$$R_p = -\frac{[M]_0 d(1-x)}{dt} = k_p[M]_0(1-x)[R^*] \quad (2)$$

where $[M]_0$ is the initial monomer concentration, x, the conversion, and $[R^*]$, the instantaneous concentration of polymeric free radicals, which assuming pseudo-steady state hypothesis, can be calculated by:

$$[R^*] = \sqrt{\frac{2fk_d[I]}{k_t}} \quad (3)$$

where f is the initiator efficiency, k_d and k_t are the initiator decomposition and termination rate constants, respectively. The solution to eq. (2) is

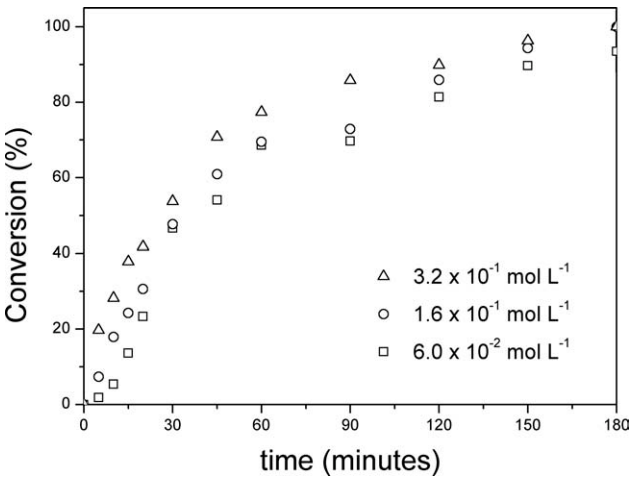

Figure 1 Effect of the initial monomer concentration on the conversion of NVCL. $[I]_0 = 2.3 \times 10^{-2}$ mol L^{-1}, [CTA] $= 6.4 \times 10^{-3}$ mol L^{-1} and $T = 70°C$.

$$\ln(1-x) = -\frac{k_p}{\sqrt{k_t}}\sqrt{\frac{8f[I]_0}{k_d}}\left(1-e^{-k_d t/2}\right) \quad (4)$$

Thus, assuming that f, k_d, and $[I]_0$ are known and with measurements of conversion as a function of time, $x(t)$, it was possible to obtain an estimate of $k_p/k_t^{0.5}$ constant by regressing the data of a graph of $\ln(1-x)$ versus $-(8f[I]_0/k_d)^{0.5}$ $[(1-\exp(-k_d t/2)]$.

LCST measurements

The transmittance for each polymer aqueous solution was measured with an UV-visible spectrophotometer (Genesys 10 Series Spectrophotometers) at 570 nm. The concentration of each polymer solution was 5 mg mL^{-1}. The light intensity through the solution was measured as a function of temperature. The transmittance measurements were performed from 28 to 42°C with the temperature increased with increments of 1°C every 5 minutes. The transition temperature (LCST) was defined as the temperature in which the transmittance is 50% of the initial value obtained at room temperature.[5]

Absolute molecular weights and molecular weights distribution

GPC analyses were performed in a Waters GPC device equipped with a 1515 Waters HPLC pump, a 2414 Waters differential refractometer, and a 717 Plus Waters autosampler. The GPC apparatus is coupled with a 302 Viscotek dual detector, including a viscometer, a low angle/LALS (7°) and a high angle/RALS (90°) light scattering detectors in a wavelength of 670 nm. Polystyrene standards ($\overline{M}_w$ = 99,448 g mol^{-1}, viscosity index = 0.477 and $\overline{M}_w$ = 273,773 g mol^{-1}, viscosity index = 0.894) were used for the calibration of the dual detector. A set of three Phenogel columns (Phenomenex), with porosities of 10^3, 10^4, and 10^6Å, was used. A solution of tetrabutylammonium bromide in Tetrahydrofuran (2.5 g $L^{-1)}$ was used as eluent at the flow rate of 1.0 mL min^{-1}. The *dn/dC* obtained for PNVCL in this eluent was 0.1349 mL g^{-1}.

RESULTS AND DISCUSSION

Influence of monomer concentration

The influence of *N*-vinylcaprolactam concentration on the polymerization rate was studied for monomer concentrations 6.0×10^{-2}, 1.6×10^{-1}, and 3.2×10^{-1} mol L^{-1}. The initiator and CTA concentrations were kept at constant values, 2.3×10^{-2} and 6.4×10^{-3} mol L^{-1}, respectively. Figure 1 shows the conversion versus polymerization time with variation of monomer concentration.

As the radical mobility, and, hence, the nature and extent of the gel effect, vary with solution concentration, the kinetic features of the polymerization depend strongly on initial monomer concentration. The initial rate of heat release depends on initial monomer concentration. The rate profiles for the polymerizations performed with different initial monomer concentrations are compared in Figure 2.

Figures 1 and 2 show that the value of the initial monomer concentration strongly affects the kinetics of the polymerization. It is possible to observe that the conversion increased as the polymerization proceeded and the polymerization rate is faster at the first hour. Figure 2 shows that those polymerizations carried out at higher monomer concentrations achieve higher values of R_p, R_{max}. On the other hand, if we observe the conversion corresponding to R_p, R_{max}, we can see that this parameter also increased as the initial monomer concentration

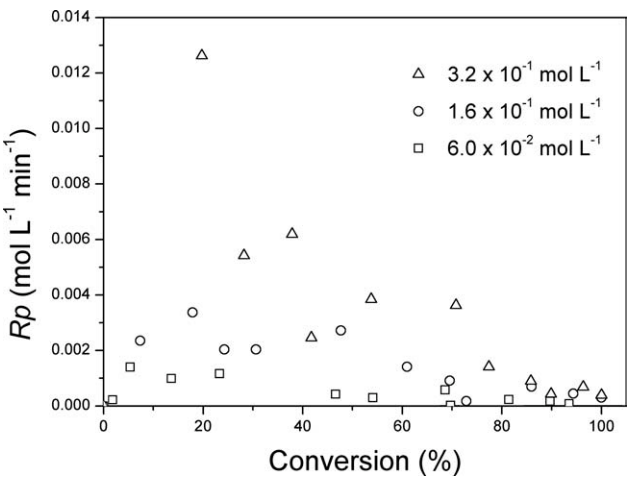

Figure 2 Dependence of polymerization rate on the NVCL conversion at different initial monomer concentrations.

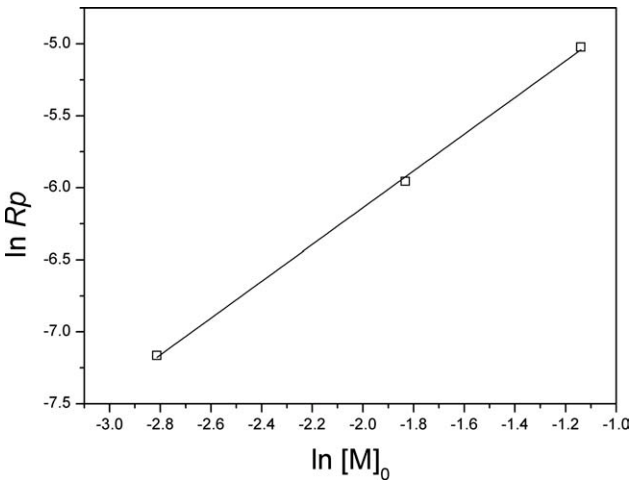

Figure 3 Polymerization rate as a function of the initial monomer concentration.

increased. This fact can be attributed to the acceleration of the decomposition of the initiator in the presence of higher monomer-to-solvent ratios leading to the increase of initiation rate.[30] The relationship between the AIBN decomposition rate constant and the monomer concentration was observed by Szafko and Feist.[31] These authors interpreted this result on the basis of solvation of the initiator molecules. Moreover, R_p is also dependent on the viscosity of the polymerization medium and another important factor to be considered is the greater importance of diffusional parameters when $[M]_0$ is increased.[32] We can also observe from Figures 1 and 2 that the higher values of R_p were obtained until 30 minute and that after 120 minute there is no significant difference in the polymerization rate. This fact could be explained by the higher concentration of polymeric chains at higher conversions. In such conditions, the shorter chains can diffuse more easily and consequently they will have a significant effect on the termination constant.[33]

The polymerization rate for each initial monomer concentration, R_p, was obtained from the slopes of the linear part of conversion-versus-time plots, considering low polymerization data, until 20 minute of reaction (Fig. 1). Figure 3 provides plots of R_p as a function of $[M]_0$.

R_p increases linearly with the initial monomer concentration. The slope of the linear ln R_p versus ln $[M]_0$ curve is a measure of the order of the reaction with respect to monomer concentration. In this case, the slope of the linear curve in Figure 3 is 1.32. Thus, the relationship of polymerization rate with monomer concentration was $R_p \propto [M]_0^{1.32}$. The correlation coefficient was 0.999. This result differs from that obtained by Kalugin et al.[34] These authors observed that the polymerization is of first order with respect to the monomer. The fact that the dependence of the overall polymerization rate on monomer concentration is greater than first order can be associated with the dependence of the initiation rate on the monomer concentration and the greater impact of the gel effect at higher monomer concentrations, as explained by Scott and Peppas.[32] If the initiator concentration does not vary much during the course of polymerization, and the initiator efficiency is independent of monomer concentration, polymerization proceeds by first-order kinetics, that is, the polymerization rate is proportional to monomer concentration.[35] However, the polymerization of certain monomers in concentrated solution is accompanied by a marked deviation from first-order kinetics, and this unusual dependence arises due to an increase in reaction rate and molecular weight termed autoacceleration or gel effect. This effect is independent of initiator type, and it is due to the diffusion-controlled termination, that is, a decrease in the rate at which the polymer molecules diffuse through the viscous medium, thus, lowering the ability of two long-chain radicals to come together and terminate. Because termination is diffusion controlled for most liquid-phase polymerizations, even at low conversion, the dependence of diffusion rate on the viscosity of the medium leads to the gel effect at high polymer concentrations. The decrease in termination rate leads to an increase in overall polymerization rate and in molecular weight. We can observe that the polymerization rate was greater than first order in monomer concentration. This result is also indicated by other studies like Lin et al.[33] using acrylamide as monomer, and it is in a good agreement with studies by Riggs and Rodiguez[36] for acrylonitrile and methyl acrylate and Ishige and Hamielec[37] for acrylamide. Lin et al.[33] explained the abnormality of order with respect to the acrylamide concentration by the solvent-transfer, complex, and cage-effect theories.

However, if we consider the classical representation of free radical polymerization kinetics, the rate of reaction in a batch reactor is given by the eq. (4) and the hypothesis underlying this equation (quasi-steady state for radical formation, independence of rate constants on monomer concentration, etc.) leads to an expression where monomer conversion-versus-time curves are independent of $[M]_0$. Thus, we had estimated the value of the pseudo rate constant, $k_p/k_t^{0.5}$, for each initial monomer concentration and for this purpose, it was necessary to choose the values of the parameters f and k_d. It has been suggested that the initiator efficiency, f, is a function of monomer type and concentration.[28,29] However, no reliable information is available on exact values of f in the systems of interest here and the general consensus seems to be to take $f = 0.6$, which is what we did in this work, though any error can be introduced by doing so will be incorporated into the estimated

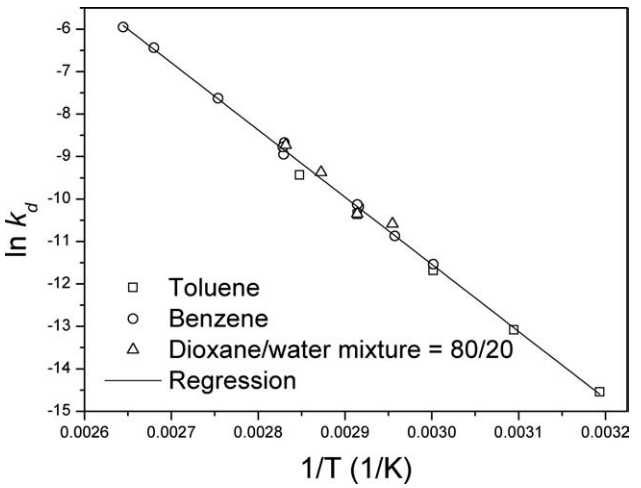

Figure 4 Regression of literature data for decomposition constant of AIBN as a function of temperature.

value of $k_p/k_t^{0.5}$. To estimate k_d for AIBN and to choose the value best adapted to the experimental conditions of this work, data of k_d in toluene, benzene and a dioxane/water mixture, obtained in the Polymer Handbook,[38] were plotted as a function of the inverse of absolute temperature which ranged between 40 and 105°C (Fig. 4) and regressed to obtain a reasonable estimation. The result of the regression is:

$$k_d = 4.032 \times 10^{15} \exp\left(\frac{-15,824}{T}\right) \quad (5)$$

$$r^2 = 0.996$$

The value of k_d obtained at 70°C was 3.789×10^{-5} s^{-1} (2.273×10^{-3} min^{-1}), and it is in good agreement with the data available in the Polymer Handbook for a 80/20 (v/v) dioxane/water mixture (3.20×10^{-5} s^{-1}).[38]

Then, the values of f and k_d were used to solve eq. (4) and to obtain the values of $k_p/k_t^{0.5}$ for different initial monomer concentrations, as shown in Figure 5.

Contrarily to what one would expect from eq. (4), but in line with the different kinetic curves shown in Figures 1 and 2, it appears in Figure 5 that the value of $k_p/k_t^{0.5}$ is somehow correlated with the initial monomer concentration. It is interesting to note the relatively linear nature of the variation of $k_p/k_t^{0.5}$ with the concentration of monomer for each $[M]_0$. However, we can observe that the lumped constant $k_p/k_t^{0.5}$ varies with the changes on the initial monomer concentration.

The values of $k_p/k_t^{0.5}$ obtained from Figure 5 as a function of the initial monomer concentration are shown in Figure 6.

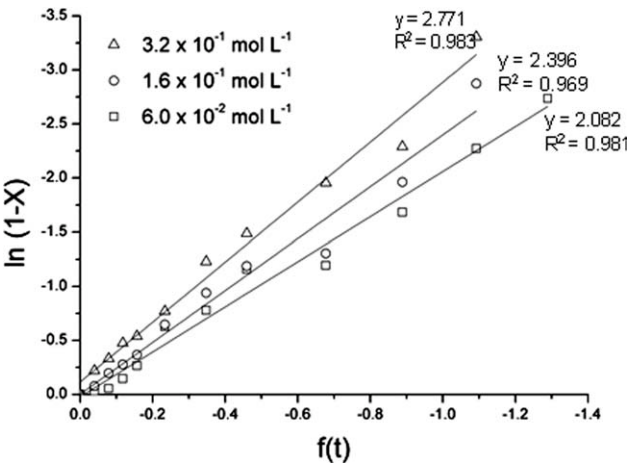

Figure 5 Determination of the values of the lumped constant $k_p/k_t^{0.5}$ at different initial monomer concentrations from the plot of ln(1−X) as a function of $f(t) = -(8f[I]_0/k_d)^{0.5}[(1-\exp(-k_d t/2)]$.

Figure 6 shows the increase of $k_p/k_t^{0.5}$ with the increasing of the initial monomer concentration. Russel et al.[39] suggested that, if the real value of k_t for a macroradical is controlled by its center of mass diffusion, then longer chains should have a lower value of k_t than shorter chains, and therefore, conditions that favor the growth of long chains should have smaller values of k_t, and, consequently, higher values of $k_p/k_t^{0.5}$ From this concept, it seems reasonable to expect that in cases where the increasing of the solvent concentration leads to the increasing of chain transfer to small molecules, and this would create significant populations of short, highly mobile radicals, and, thus, lead to an increase in the overall value of k_t.

Similar results were obtained by McKenna et al.[28,29] for the solution polymerization of butyl acrylate. In their work, a dependence of $k_p/k_t^{0.5}$ on the

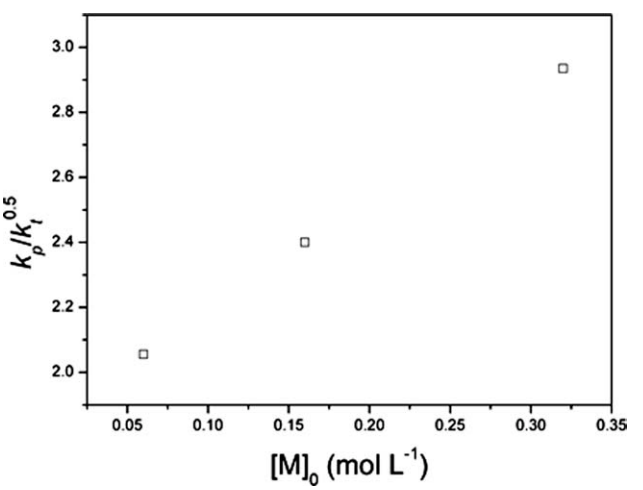

Figure 6 NVCL homopolymerizations with different initial monomer concentrations: changes in the $k_p/k_t^{0.5}$.

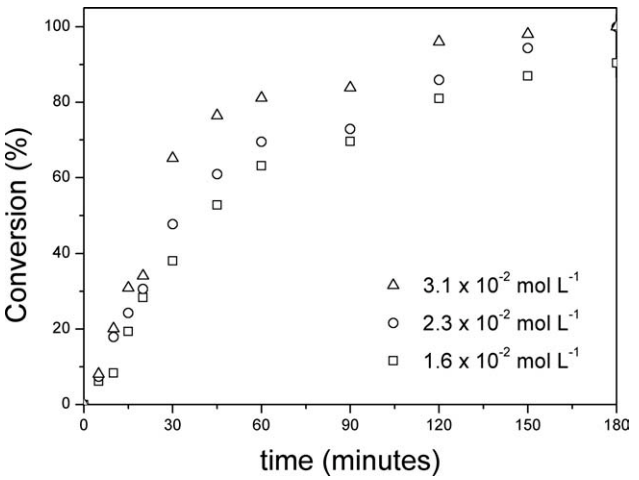

Figure 7 Effect of the initiator concentration on the conversion of NVCL. $[M]_0 = 1.6 \times 10^{-1}$ mol L^{-1}, [CTA]/[M] = 0.04 and $T = 70°C$.

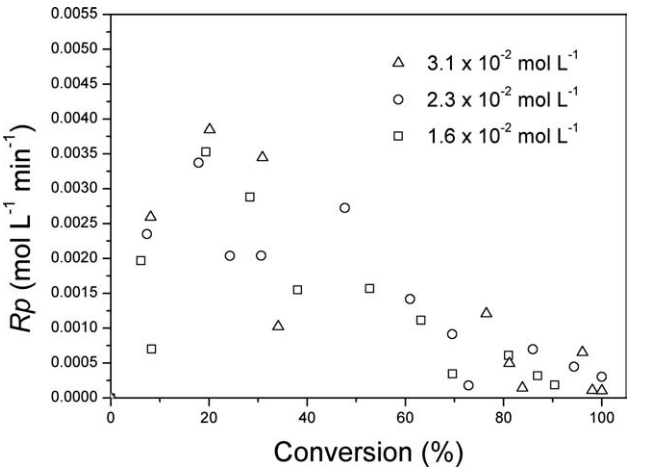

Figure 8 Dependence of the polymerization rate on the NVCL conversion for different initiator concentrations.

monomer concentration was also observed. These authors explained that the increase of $k_p/k_t^{0.5}$ with the increasing of the initial monomer concentration is equivalent to decreasing the amount of solvent, and, consequently, the fraction of short radicals in solution. They still mentioned that this effect could also explain why the reactions "slow down" occurs more than expected at long times. In this last instance, the ratio of monomer-to-solvent decreases as the monomer is consumed, leading to a situation similar to changing the initial monomer concentration.

Therefore, we can assume that the termination rate in the NVCL polymerization is chain length controlled, even at low conversions. In other words, if the individual rate constants of the terminating macro-radicals are a function of the diffusion rate constants, then they will be a function of chain length as well.[40] Thus, the termination rate constant, k_t, is diffusion controlled, and, consequently, the initial monomer concentration will have influence on the $k_p/k_t^{0.5}$ parameter.

Influence of initiator concentration

The influence of initiator concentration on the polymerization rate was studied for initiator concentrations of 1.6×10^{-2}, 2.3×10^{-2}, and 3.1×10^{-2} mol L^{-1}. The monomer concentration and CTA-to-monomer molar ratio were kept at constant values, 1.6×10^{-1} mol L^{-1} and 0.04, respectively. Figure 7 shows the conversion-versus-time curves for different initiator concentrations, and the average rate profiles are provided in Figure 8.

Figures 7 and 8 show that the conversion increases with the increase of the initiator concentration, which would be obviously explained by the increase of the radical concentration in the reaction media. The fact that the polymerization rate depends on $[AIBN]^{1/2}$ was demonstrated by plotting ln R_p as a function of ln $[AIBN]_0$.

Figure 9 shows that R_p increases linearly with initiator concentration. The R_p values were obtained from the linear part of the curve plotted in Figure 7, at low conversions. The slope of the line drawn through the data points was 0.52, with a correlation coefficient of 0.999. In this way, the dependence of polymerization rate on the initiator concentration was found to be $R_p \propto [I]^{0.52}$. This result indicates that termination occurs through bimolecular interaction of growing chain radicals.[31–46] The polymerization rate with respect to initiator concentration in this study is consistent with the classical kinetic theory, which predicts that the polymerization rate depends on the square root of the initiator

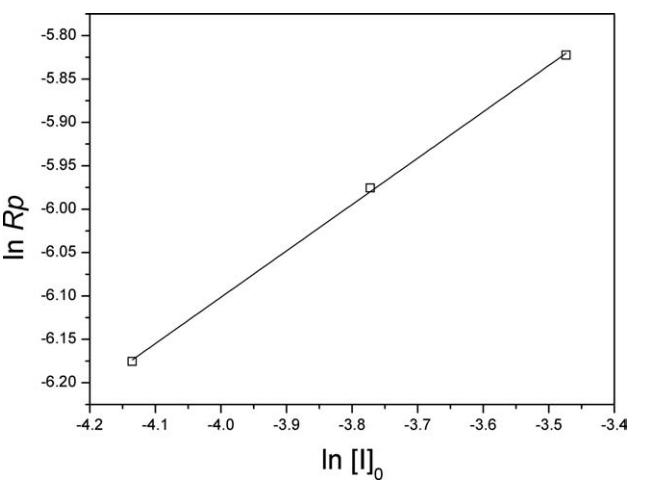

Figure 9 Polymerization rate as a function of initiator concentration.

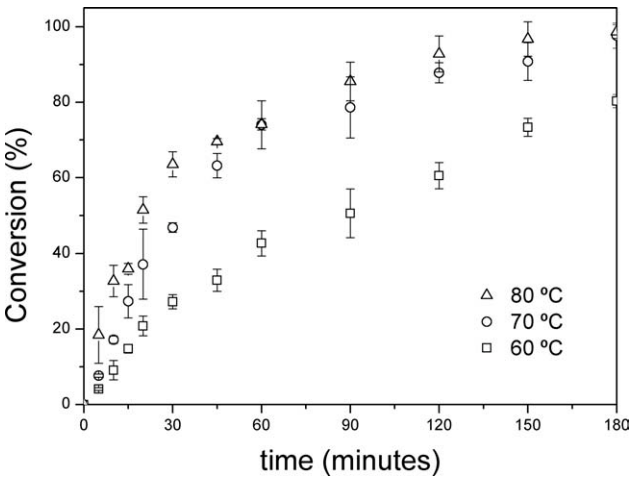

Figure 10 Effect of the polymerization temperature on the conversion of NVCL. $[M]_0 = 1.6 \times 10^{-1}$, $[I]_0 = 2.3 \times 10^{-2}$ and [CTA]/[M] = 0.04.

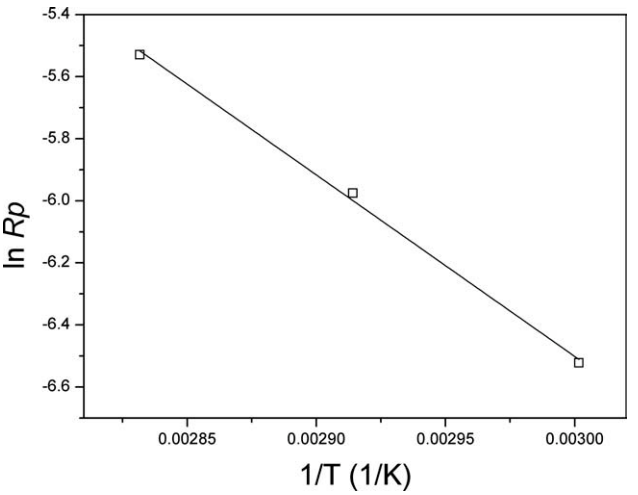

Figure 12 Dependence of R_p on the polymerization temperature.

concentration, as also indicated by some previous works.[33,47–49]

Influence of polymerization temperature

The influence of temperature on the polymerization rate was studied at 60, 70, and 80°C, as shown in Figure 10. The monomer and initiator concentrations as well as the CTA-to-monomer molar ratio were kept constants at 1.6×10^{-1}mol L^{-1}, 2.3×10^{-2} mol L^{-1}, and 0.04, respectively. Figures 11 and 12 show that the polymerization rate is strongly dependent of the polymerization temperature.

As it is well known, the dependence of the kinetics of free radical polymerizations on the temperature of polymerization is described by Arrhenius relationship for the kinetic constants k_p, k_t, and k_d.[50] It is obvious that the polymerization reaction initiates earlier by increasing the reaction temperature and less time is needed to achieve higher conversions at higher temperatures. The dependence of R_p on the polymerization temperature is shown in Figure 12. The R_p values were obtained from the linear part of the curves showed in Figure 10.

Figure 12 shows the linear dependence of ln R_p on (1/T), with $r^2 = 0.997$. This result was not surprising, because for an Arrhenius-type dependence of the kinetic constants on temperature, a linear dependence is expected, and the overall activation energy E_A is given by the slope of the plots as shown in Figure 12. E_A contains contributions from the activation energies for propagation, initiator dissociation, and termination.[51]

The measured slope in Figure 12 gives a value of 53.6 kJ mol^{-1}, which is lower than the typical values for overall activation energies in polymerizations initiated by a thermally decomposing initiator.[38] For example, Tinker et al.[52] found a value of activation energy for AIBN in 1,4-dioxane of 84.0 kJ mol^{-1}. If we compare these values, it is obvious that the activation energy obtained in our work is lower than the value of the literature. However, it is known that E_A can be altered by the complex formation between monomer and initiator, that is, if the complexation takes place, the activation energy will be higher. However, due to the very close proximity of the generated radicals, not all of them can eventually escape from their "cage" to react with monomer molecules. According on the cage-effect theory, some primary radicals will either self-terminate or react with other nearest-neighboring molecules before diffusing out of the cage. Thus, we can conclude that the controlling mechanism in our study is in accordance with the cage-effect theory.

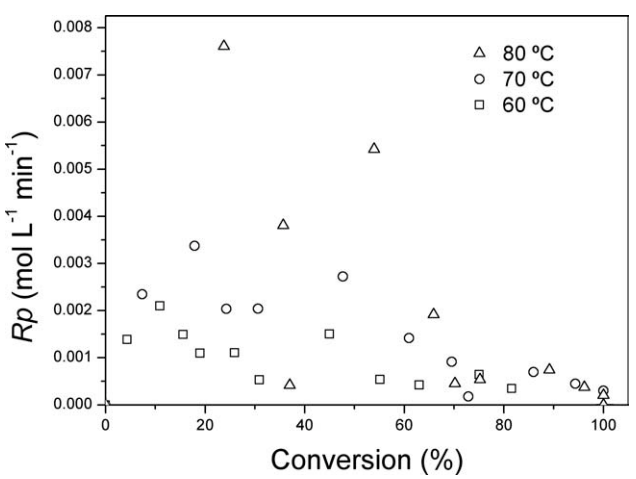

Figure 11 Dependence of the polymerization rate on the NVCL conversion for different polymerization temperatures.

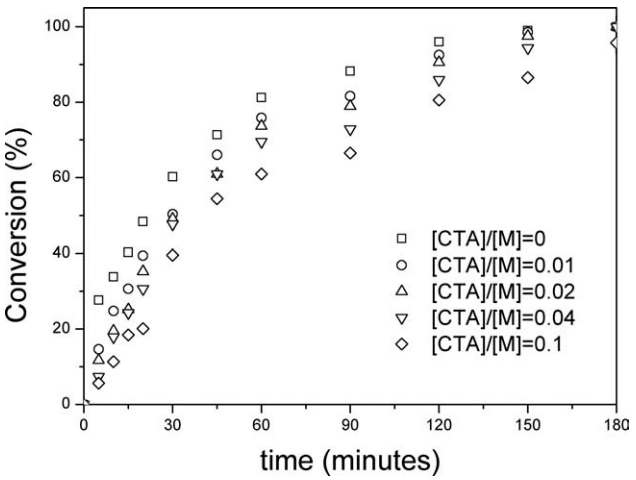

Figure 13 Effect of CTA (3-mercaptopropionic acid) concentration on the conversion of NVCL. $[M]_0 = 1.6 \times 10^{-1}$ mol L^{-1}, $[I]_0 = 2.3 \times 10^{-2}$ mol L^{-1} and T = 70°C.

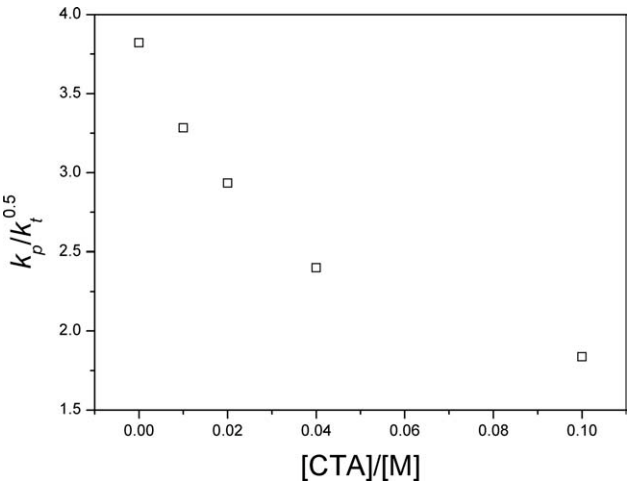

Figure 14 NVCL homopolymerizations with different CTA-to-monomer molar ratios: changes in the lumped constant $k_p/k_t^{0.5}$.

There are no results of activation energy in the literature for *N*-vinylcaprolactam at the same experimental conditions of this work. However, this result is similar to others obtained by Lin[33] and Mahdavian et al.[53] for acrylamide. Mahdavian et al.[53] also attributed this abnormality to the cage-effect.

Influence of the chain transfer agent/CTA (3-mercaptopropionic acid) on the polymerization kinetic, molecular weight and molecular weight distribution

The influence of CTA concentration on the polymerization rate, number-average molecular weight, and MWD was studied using the following CTA-to-monomer molar ratios: 0, 0.01, 0.02, 0.04, and 0.1. The initial monomer and initiator concentrations were kept constant at 1.6×10^{-1} and 2.3×10^{-2} mol L^{-1}, respectively. All the polymerizations were carried out at 70°C. Figure 13 shows the influence of the addition of the CTA on the conversion-versus-time curves.

Figure 13 show that the addition of CTA, in these concentrations, may affect the rate of polymerization. Traditionally, it is believed that the presence of CTA affects only the molecular weight and not the rate of polymerization.[54] However, if the k_t chain-length dependence is valid, some effects on R_p are also possible. To verify the influence of CTA concentration on k_t, eq. (4) was also used to obtain the values of $k_p/k_t^{0.5}$ for different CTA-to-monomer molar ratios (Fig. 14).

Figure 14 shows that the increase on the CTA-to-monomer molar ratio leads to a decrease in the $k_p/k_t^{0.5}$ constant. There is a combination of CTA and solvent concentrations at which their effects on R_p becomes significant. In other words, for experiments performed with higher CTA concentrations, the CTA leads to an increase of short chains. This increase is becoming so significant that the effect of CTA is expressed not only on the molecular weight but also on k_t.

The effect of CTA concentration on the number-average molecular weight and MWD is presented in Table I. As was expected, the CTA reduced significantly the molecular weight of the polymers. However, there is no significant effect on the MWD.

By plotting the ratio of $(k_p/k_t^{0.5})/(k_p/k_t^{0.5})_{CTA=0}$ and the ratio of $M_n/M_{n,CTA=0}$ (Fig. 15), both as a function of [CTA]/[M], we find that both these ratios follow the same behavior. This also means that the lumped constant $k_p/k_t^{0.5}$ varies almost linearly with the number-average molecular weight, which is confirmed by the results in Figure 16.

From the analysis of the data shown in Table I, it is possible to estimate the value of the ratio between the rate constant of transfer to CTA and the propagation rate constant, $C = k_f/k_p$ as the slope of the plot of the inverse of the number-average molecular weight as a function of [CTA]/[M]. Figure 17

TABLE I
Effect of the CTA-to-Monomer Molar Ratio on the Number-Average Molecular Weight ($\overline{M}_n$) and Molecular Weight Distribution

[CTA]/[M] (molar)	Conversion (%)	Number-average molecular weight ($\overline{M}_n$) $\times 10^{-3}$ (g mol^{-1})	MWD
0	100	59.03	1.81
0.01	100	52.03	1.67
0.02	100	47.47	1.79
0.04	100	34.11	1.65
0.1	95.8	24.87	1.98

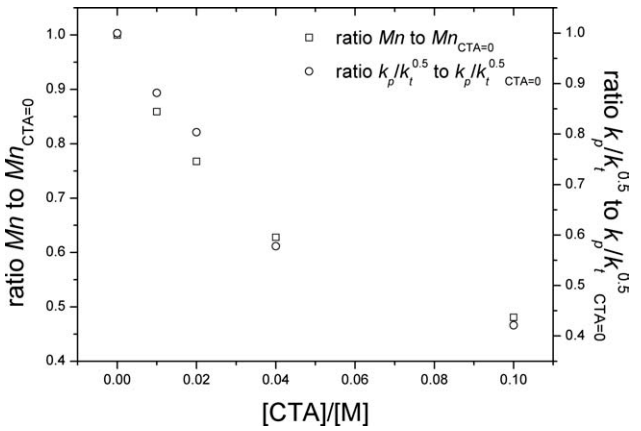

Figure 15 The effect of [CTA]/[M] on the ratio $(k_p/k_t^{0.5})/(k_p/k_t^{0.5})_{CTA=0}$ and on the ratio $M_n/M_{n,CTA=0}$.

presents this plot, from which one can estimate $C = k_f / k_p = 2.0 \times 10^{-4}$.

Effect of molecular weight on the LCST

It is well known that the LCST of PNVCL shifts to higher values when decreasing the molecular weight of the polymer.[55] This phenomenon is ascribed to the fact that the solution behavior of the PNVCL/water system corresponds to a typical Flory-Huggins demixing behavior with LCST, also called Type I behavior.[5] As shown in Table I, higher ratios of CTA-to-monomer resulted in polymers with lower molecular weights. Figure 18 shows a definite effect of the molecular weight on the LCST of PNVCL in aqueous solution at 5 g L^{-1}. The LCST decreased as the molecular weight of the polymer increased. The variation of the number-average molecular weight of PNVCL from 24.97 $\times$ 10^3 to 59.03 $\times$ 10^3 g mol^{-1} leaded to the variation of the LCST from 36 to 34°C, respectively. This result is explained by the fact that

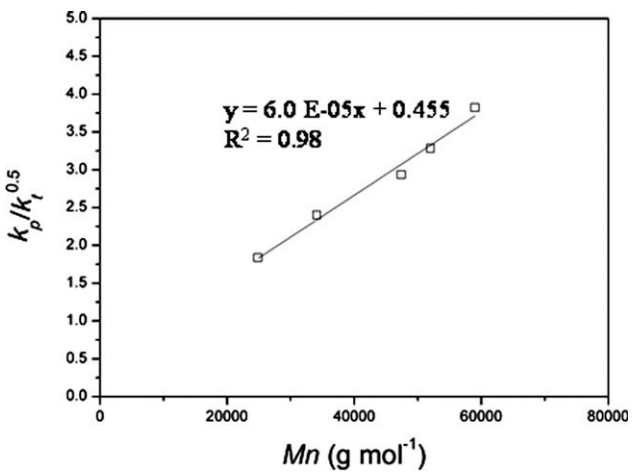

Figure 16 Effect of the number-average molecular weight on the lumped parameter $(k_p/k_t^{0.5})$.

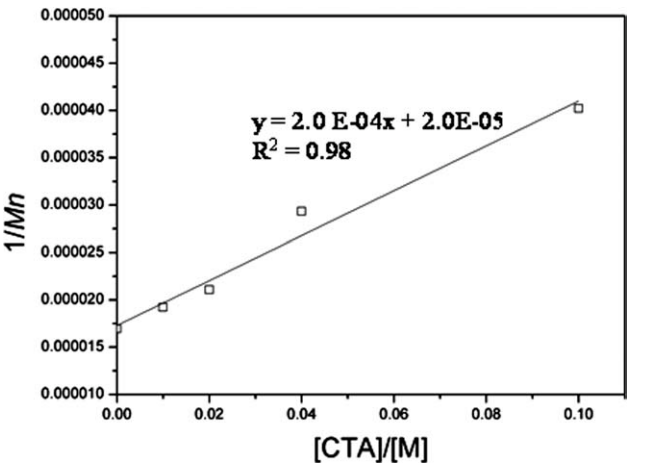

Figure 17 Plot of the inverse of the number-average molecular weight versus [CTA]/[M].

the decrease of the molecular weight leads to an increase of the polymer hydrophilicity. Moreover, the increase of the hydrophilicity would also be explained by the contribution of the carboxyl end group from the CTA as was evidenced by Tadaaki et al.[19] for PNVCL with molecular weights between 650 and 6040 g mol^{-1}. As the molecular weights obtained in this work were in general much higher than those obtained by Tadaaki et al.,[19] the influence of the carboxyl end group was not evidenced. Therefore, the increase of molecular weight seems to have a more effective influence on the LCST, even if we consider that no high difference on the LCST values was observed in the range of molecular weights studied in this work.

CONCLUSION

In this work, we have demonstrated that the kinetic for the solution polymerization of NVCL in 1,4-

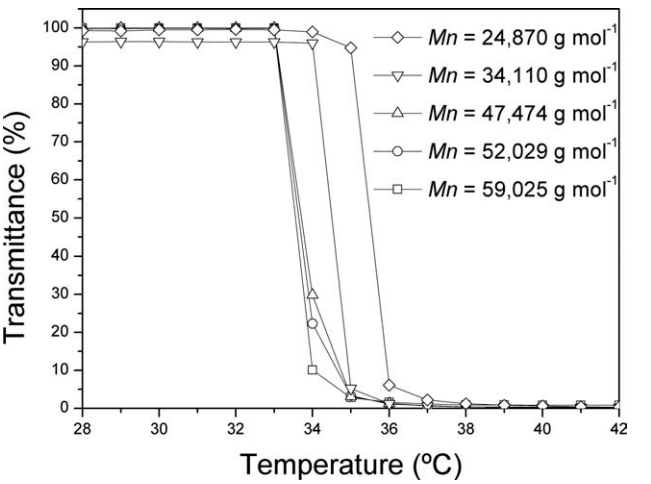

Figure 18 Effect of molecular weight on the LCST of PNVCL.

dioxane is highly dependent on polymerization conditions. The kinetic of *N*-vinylcaprolactam solution polymerization depends strongly on the initial NVCL and AIBN concentrations and the polymerization temperature. It has been shown that the value of $k_p/k_t^{0.5}$ depends not only on the initial monomer concentration at fixed initiator concentrations but also on the CTA-to-monomer molar ratio. The high degree of chain transfer reactions when increasing the CTA-to-monomer molar ratio might indeed have an enhancing effect on the chain length dependence of k_t at low conversions by creating large populations of small and highly mobile radicals.

The polymerization rate was greater than first order in monomer concentration, probably due to chain-length dependence of k_t. This result agreed well with polymerization initiated by others initiators where the apparent order for monomer was always greater than unity. The dependence of initiator concentration on polymerization rate followed the classical kinetic theory.

Increases in the polymerization temperature led to faster polymerizations. The overall energy of activation was found to be 53.6 kJ mol^{-1}.

The ratio of the rate constant for chain transfer to CTA (3-mercaptopropionic acid) and the propagation rate constant was estimated to be $C = k_f/k_p = 2.0 \times 10^{-4}$.

The LCST increased as the molecular weight of the polymers decreased. This fact was mainly explained by the increase of PNVCL hydrophilicity when reducing the molecular weight of the polymer. Some effect could also be attributed to the presence of the carboxyl end group from the CTA. However, no significant difference on the LCST values was observed for the range of molecular weights studied in this work. As was expected, for the polymers of higher molecular weights synthesized in this work the effect of the carboxyl end group was not evidenced.

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