

# Radical Polymerization of *N*-Vinylcaprolactam in the Presence of Chain-Transfer Agents

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Free-radical polymerization of *N*-vinylcaprolactam (VCL) in the presence of chain-transfer agents has been studied to obtain polyvinylcaprolactam possessing a predetermined relative molecular mass. Allyl compounds have been used as chain-transfer agents. Free-radical polymerization kinetics of VCL in the presence of allylbenzene and allylcaprolactam has been investigated as well as free-radical polymerization of VCL in isopropyl alcohol solution. The effect of reaction mixture composition on the rate and degree of polymerization has been studied, too. Possibility of synthesis of vinylcaprolactam oligomers with terminal hydroxyl groups has been demonstrated. Influence of a series of substituents at allylic compounds on kinetics of chain transfer has been investigated using quantum-chemical methods.

It is well known that polyvinylcaprolactam (PVCL) in aqueous solutions has lower critical solution temperature that lies in the temperature range characteristic of living systems [1]. This unique property offers an opportunity to develop novel technologies for drugs, enzymes, and living cells encapsulation. This might contribute to development of certain areas of biotechnology, microbiology, and medicine.

It is a well-documented fact that lower critical solution temperature of PVCL with low degrees of polymerization depends on relative molecular mass of the polymer. Therefore, development of new approaches to relative molecular mass control represents a very critical issue. Usually reactions of weak inhibition and chain transfer are used to obtain polymers possessing predetermined molecular characteristics. Recently, radical polymerization of vinylpyrrolidone (VP) has been extensively studied [1]. Polymerization of VP in the presence of hydrogen peroxide, ammonium hydroxide, and iron ions in aqueous solution is one of the most widely used methods of control of molecular mass of poly(vinyl lactams) in radical polymerization. In spite of an apparent simplicity of realization, carrying out of this reaction needs the careful check of conditions of its execution since the reaction process is accompanied by certain side reactions with hydrazine formation and subsequent deterioration of the reaction product quality. For this reason, much attention

is being paid to searching of alternative ways of synthesis. A large number of compounds used for control of the molecular mass of poly(*N*-vinyl amides), in particular polyvinylpyrrolidone, can be divided into two groups.

The first group comprises organic compounds which are good chain-transfer agents such as isopropanethiol, phenylmethanethiol, benzenethiol, sulfanylacetic acid, and isobutyl and isopropyl alcohols. Polymerization rate in the presence of one of these chain-transfer agents is almost constant because a radical formed in the result of chain transfer can continue chain propagation.

The second group includes allyl compounds. Polymerization of VP in the presence of allyl acetate, allyl glycidyl ether, and allylpyrrolidone has been studied [1, 2]. In these conditions, the main reaction restricting molecular mass of polymer is the degradation chain transfer. In this paper, some new approaches to control relative molecular mass of PVCL obtained during a process of radical polymerization are suggested.

## EXPERIMENTAL

VCL monomer was manufactured at the Institute of Polymer Chemistry and Physics, Academy of Sciences of Uzbekistan, using acetylation of caprolactam. The obtained monomer was rectified by two vacuum

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distillations. Purity of the distilled VCL was tested using the method of reverse-phase thin-layer chromatography. The isopropyl alcohol — water mixture (volume ratio 50 : 50) was used as a mobile phase. Visualization with iodine vapour showed only one chromatographic zone with  $R_f = 0.66$ . This fact together with the determined values of density ( $n_d^{20} = 1.5131$ ) and refraction index ( $d_4^{20} = 1.028$ ) that were in accordance with the literature data testified the complete purification of the monomer. All other reagents used were of chemical or analytical purity grade and were purchased from REAKHIM, Russia. Allyl compounds were subjected to vacuum distillation immediately prior to utilization. All solvents used were purified by a single distillation.

PVCL was synthesized in dioxane solution in the presence of azobis(isobutyronitrile) (AIBN) initiator at 60 °C. Allylbenzene (AB), allylcaprolactam (ACL), allyl phenyl ether (APE), allyl alcohol (AA), and allyl glycidyl ether (AGE) were used as chain-transfer agents. Radical polymerization of VCL in isopropyl alcohol was also performed in order to obtain PVCL possessing predetermined molecular characteristics. The synthesis was carried out in the ampoules degassed by freezing and thawing in vacuum at residual pressure of 0.13 Pa. Reprecipitation of the polymers was performed with diethyl ether. Kinetics of radical polymerization has been studied using a dilatometric method, and initiation rate in the presence of a stable 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) radical has been determined. IR spectra have been recorded using Specord 75 IR spectrometer. Quantitative determination of terminal hydroxyl groups has been performed by the acetylation method based on interaction of the polymer hydroxyl groups with acetic anhydride in the presence of pyridine. Number-average relative molecular mass of PVCL has been calculated basing on assumption that macromolecule contained only one terminal hydroxyl group [1]. Intrinsic viscosities of polymer solution were measured by using Ubbelohde viscosimeter in dimethylformamide solution at 25 °C. The experimental results were treated by using coordinates of the Huggins and Kramer's equation. The sum of Huggins and Kramer's constants is  $K_H + K_K \approx 0.5$  for all samples.

## RESULTS AND DISCUSSION

Previously constants of chain transfer ( $C_s$ ) for VCL polymerization in the presence of several allyl compounds have been determined [3]. It has been established that  $C_s$  values are decreasing in series AB, ACL, APE, AA, AGE in the indicated order [3]. It has been concluded that AB and ACL are the most suitable for control of PVCL relative molecular mass, and hence in the present work we investigated kinetics of VCL polymerization in the presence of AB and ACL. As can be seen from Fig. 1, VCL polymerization rate is

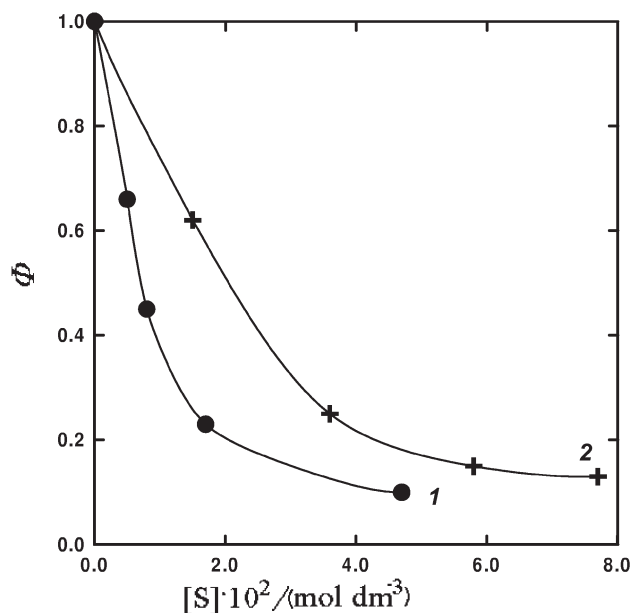


Fig. 1. Dependence of inhibition coefficient  $\Phi$  on concentrations of AB (1) and ACL (2) in the reaction mixture.

decreasing when concentration of allyl compounds in the reaction mixture increases. Inhibition coefficient  $\Phi$  is equal to the ratio of polymerization rates in the presence and absence of allyl compounds ( $R_{p(s)}$  and  $R_{p(0)}$ , respectively).

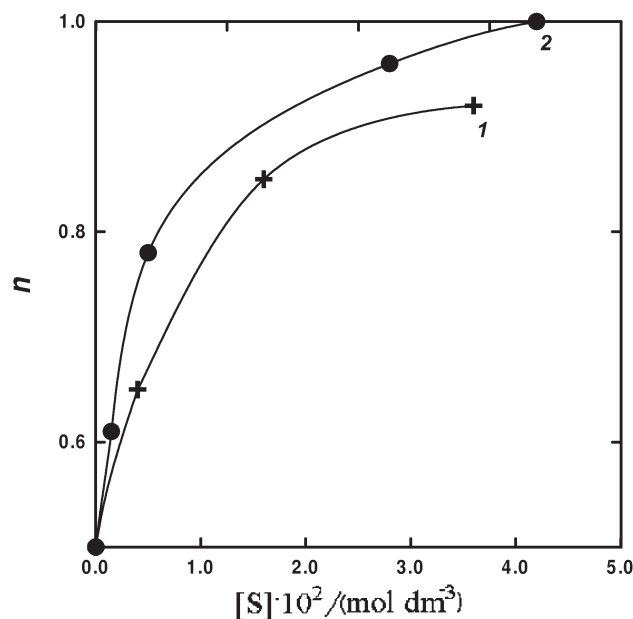
$$\Phi = \frac{R_{p(s)}}{R_{p(0)}} \quad (1)$$

Thus, weak inhibition (or retardation) takes place due to degradation chain transfer on allyl compound.

It is well known that labile hydrogen atom located in  $\alpha$ -position to a double bond in allyl compounds easily interacts with active radicals and allyl radical is obtained as a result of such interaction.

The resulting allyl radical is subsequently stabilized by conjugation and is practically incapable to continue the chain reaction. The chain transfer is in such a case equivalent to a monomolecular termination reaction. These circumstances influence the overall kinetics. In a classical case of radical polymerization, reaction order with respect to the initiator concentration is equal to 0.5 in accordance with the bimolecular mechanism of chain-break process. We have established the same value of initiator reaction order in the absence of allyl compounds. However, if allyl compounds are added to reaction mixture, reaction order with respect to the initiator concentration is gradually increased up to 1, as can be seen from Fig. 2.

Shape of the curves 1 and 2 in Fig. 2 can be explained in the following manner. If AB and ACL concentrations are increased, the extent of monomolecular chain termination characterized by the first reaction order with respect to the initiator concentration



**Fig. 2.** Dependence of polymerization reaction order on initiator concentration, on concentrations of AB (1) and ACL (2).

**Table 1.** Dependence of PVCL Relative Molecular Mass on Allyl Compound Concentrations

Agent	$[S] \cdot 10^2$ mol dm <sup>-3</sup>	$[\eta] \cdot 10^2$ m <sup>3</sup> kg <sup>-1</sup>	$M_r \cdot 10^{-3}$
AB	0.37	3.3	166
	1.85	2.6	110
	3.72	2.1	76
	5.54	1.5	42
ACL	9.2	2.2	82
	9.7	1.7	52
	16.0	1.0	18

is increased, too. In this way, one can control relative molecular masses of synthesized polymers by changing concentrations of allyl compounds (Table 1).

As can be seen from Table 1, PVCL relative molecular mass ( $M_r$ ) decreases at increased concentrations of AB (1) and ACL (2) (Fig. 1). It can be also observed that AB more effectively reduces relative molecular mass of PVCL than ACL.

Degree of polydispersity is an important parameter of the synthesized polymer. It is known that  $M_m/M_N$  value for polymers synthesized in the presence of chain-transfer agents is controlled by chain-break mechanisms at least at the initial stages of the process. The value can be calculated using the following equation

$$M_m/M_N = \{[3 - \lambda + 2(\beta + \gamma)][1 + \lambda + 2(\beta + \gamma)]\} / 2(1 + \beta + \gamma)^2 \quad (2)$$

where  $\beta = R_{ts}/R_{t0}$ ,  $R_{ts}$  is the rate of monomolecular

termination reaction (degradation chain transfer),  $R_{t0}$  rate of bimolecular termination reaction,  $\lambda$  the ratio of disproportionation reaction in bimolecular chain termination reaction,  $\gamma = R_{ts}^{\sim}/R_{t0}$ , where  $R_{ts}^{\sim}$  is the rate of reaction of allyl radical stabilized by conjugation with the chain growth radical [4]. With the increase of allyl compounds concentration, the  $R_{ts}$  value grows and, as a result, polymerization rate is reduced while the order of the reaction with respect to the initiator concentration increases up to 1 (Figs. 1 and 2).

Eqn (2) implies that in this case  $M_m/M_N$  value has to be close to 2. In a previous work we have experimentally determined polydispersity parameters of PVCL samples synthesized in the presence of AB by a method of high-speed sedimentation, applying graphic fractionation procedure [5]. It was shown that the  $M_m/M_N$  values of polymers were indeed close to 2. This result is in agreement with the above-mentioned results of the study of polymerization kinetics. Taking into account all these facts, a conclusion can be made that AB is a more effective chain-transfer reactant than ACL.

Reactivity of allyl compounds in chain-transfer reactions depends on a nature of a substituent at an allyl bond. In order to explain the differences in reactivity of a series of allyl compounds, we have performed quantum-chemical calculations. According to the generally accepted ideas [6], radical formation by hydrogen atom abstraction from an allyl monomer is the slowest step of radical polymerization. Thus, relative reactivity of different allyl monomers and of hydrogen atoms at different sites is defined by velocity of the abstraction of such hydrogen atoms. This velocity, in agreement with the Bell—Evans—Polanyi principle, is the larger the lower is the energy of the bond breaking and the more stable is the formed radical.

In order to estimate the energies of C—H bond scission at  $\alpha$ -positions of allylbenzene and allylcaprolactam, we have performed quantum-chemical calculations with full geometry optimizations for monomers and the corresponding radicals. Energy of the chosen C—H bond was calculated as a difference between binding energies of an allyl monomer and the corresponding radical. The quantum-chemical calculations have been performed using the semiempirical PM3 method [7] applying the restricted Hartree—Fock (RHF) method to compute geometrical and energy characteristics of allyl monomers, and unrestricted Hartree—Fock (UHF) method to compute those for corresponding allyl radicals. All quantum-chemical calculations have been performed using a quantum-chemical program HyperChem [8]. We have found that dissociation energies of  $\alpha$ -C—H bonds in AB and ACL equal to 273.105 kJ mol<sup>-1</sup> and 276.036 kJ mol<sup>-1</sup>, respectively. Thus,  $\alpha$ -C—H bond energy in AB is slightly smaller than that in ACL. This result can be explained by higher stability of AB radical in comparison with that of ACL radical due to unpaired

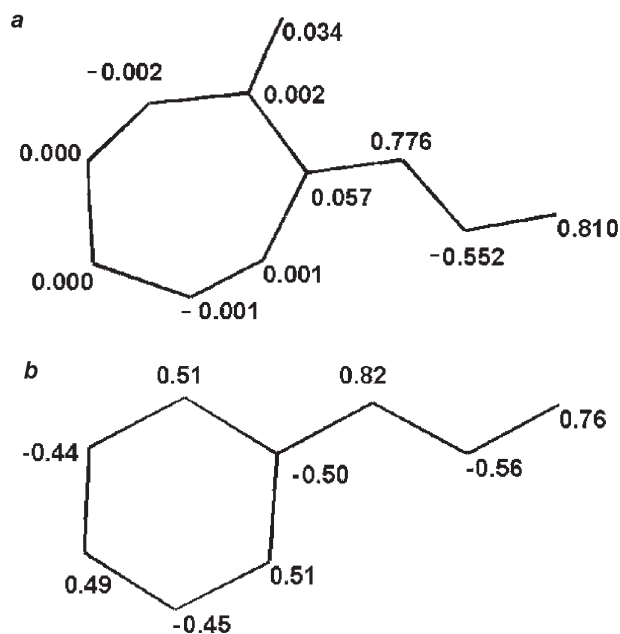


Fig. 3. Spin population for ACL radical atoms (a), for AB radical atoms (b).

electron delocalization within conjugated system. As can be seen in Figs. 3a and 3b, unpaired electron of AB radical is delocalized on 8 atoms, whereas that of ACL is delocalized mainly on 3 atoms, and therefore, AB radical is more stable.

A significant drawback of utilization of allyl compounds as chain-transfer agents is copolymerization ability of allyl compounds and problems associated with purification of the obtained polymers. Isopropyl alcohol (IPA) can be used as an alternative chain-transfer agent at polymerization of VP [1], while sometimes it is also used as a molecular mass controller of choice. For this reason, we have studied kinetics of radical polymerization of VCL in IPA solution. In order to experimentally determine the reaction order on initiator, the dependence of polymerization rate with respect to the initiator concentration has been

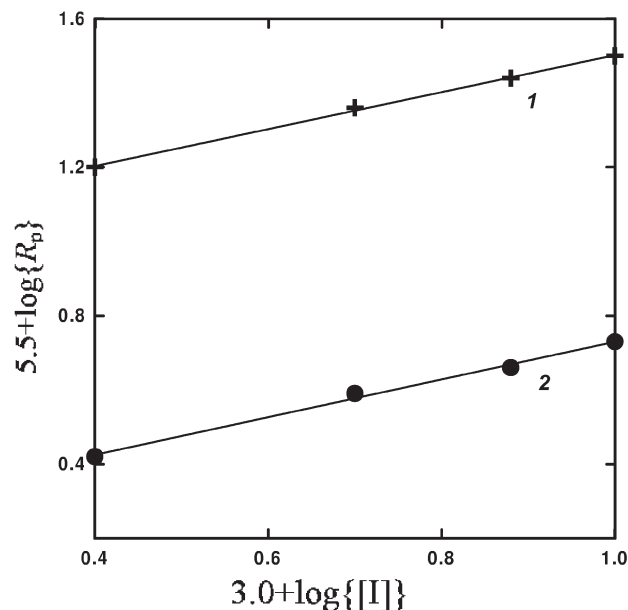


Fig. 4. Logarithmic dependence of VCL polymerization rate in isopropyl alcohol with respect to the initiator concentration ( $[I]$ ).  $[VCL] = 3.7 \text{ mol dm}^{-3}$  (1),  $[VCL] = 37 \text{ mol dm}^{-3}$  (2).

investigated (Fig. 4). We observed that reaction order with respect to the initiator concentration was close to 0.5 independently of the  $m(VCL)/m(IPA)$  ratio. This result corresponds to the bimolecular mechanism of chain termination.

A complex relationship was discovered at examination of dependence of rate of polymerization on a concentration of monomer (Table 2). It is known that in classical radical polymerization the kinetics of reaction is described by an equation of the first order with respect to the concentration of monomer. In this case, 15-fold decrease of monomer concentration in a reaction mixture at a constant concentration of AIBN =  $10^{-2} \text{ mol dm}^{-3}$  results in 7.9-fold decrease of the rate of a polymerization.

Thus, the increase of the ratio of polymerization rate to monomer concentration ( $R_p [VCL]^{-1}$ ) is ob-

Table 2. Kinetic Parameters of Polymerization of VCL in IPA

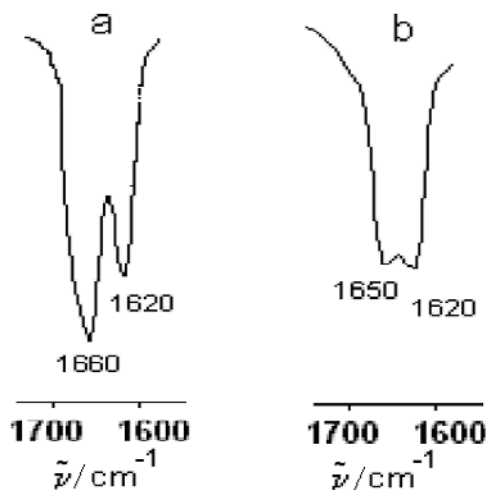
Sample	Concentration		Rate of reactions		$(R_p/[M]) \cdot 10^5$ s <sup>-1</sup>	$K_p/K_t^{5*}$	$[\eta] \cdot 10^2$ m <sup>3</sup> kg <sup>-1</sup>
	mol dm <sup>-3</sup>		mol dm <sup>-3</sup> s <sup>-1</sup>				
	IPA	VCL	Polymerization { $R_p$ } · 10 <sup>5</sup>	Initiation { $R_i$ } · 10 <sup>8</sup>			
1	12.4	37	1.41	2.9	3.83	23	<1.0
2	11.7	74	2.7	3.3	3.65	20	1.1
3	15	1.48	5.7	4.5	3.85	18	1.6
4	9.8	1.85	6.3	5.9	3.40	14	2.0
5	6.5	3.71	13	7.6	2.82	10	2.5
6	3.3	5.55	11.0	14	2.10	7	4.1

\* $K_p$  and  $K_t$  are propagation and termination constants, respectively.

**Table 3.** Dependence of PVCL Relative Molecular Masses and Concentration of Terminal Hydroxyl Groups on Polymerization Conditions,  $\theta = 60^\circ\text{C}$ ,  $[\text{AIBN}] = 10^{-2} \text{ mol dm}^{-3}$ 

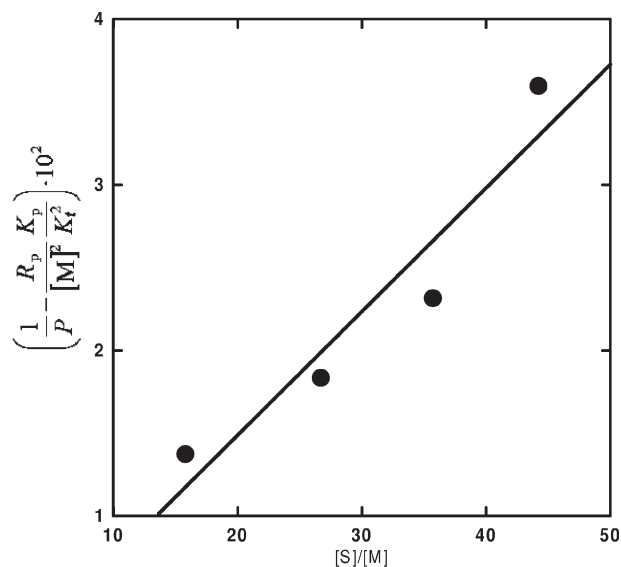
Sample	[VCL]	[IPA]	$w(\text{OH})$	$M_N$
	$\text{mol dm}^{-3}$	$\text{mol dm}^{-3}$	%	
1	24	12.7	65	2600
2	29	12.6	47	3600
3	35	12.5	31	5500
4	46	12.3	25	6800
5	74	11.7	18	9500
6*	1.48	15	—	25000

\*The relative molecular mass of sample 6 has been obtained from the measurement of intrinsic viscosity.



**Fig. 5.** IR spectra of VCL (a) and VCL and IPA mixture ( $m(\text{VCL})/m(\text{IPA}) = 1 : 3$ ) (b).

served with increasing IPA concentration in the reaction mixture. Such dependence documents a significant influence of IPA on polymerization kinetics. Similar dependences have been observed earlier at radical polymerization of VP in aqueous and ethanol solutions [1]. It is known that the formation of a hydrogen bridge between solvent and monomer molecules can occur in the mixtures of vinyl lactams with protic solvents. In this case the polarity of a double bond is increased because of its conjugation with C=O group through nitrogen atom. This phenomenon is characteristic of polymerization processes of both VP and VCL [1]. Apparently IPA is also capable to form hydrogen bridges with VCL molecules. These circumstances make the system more complicated because of probable simultaneous copolymerization of the "free" and solvated monomers differing in double bond polarization [9]. IR-spectroscopic investigations of the systems have been carried out for experimental confirmation of the interaction between VCL and IPA. An absorption band at  $1660 \text{ cm}^{-1}$  that is characteristic of carbonyl groups and the one at  $1620 \text{ cm}^{-1}$  characteristic of a double bond have been observed in VCL spectrum. The intensity of the for-



**Fig. 6.** Dependence between the coordinates of Mayo's equation.  $P$  is number-average degree of polymerization,  $[M]$  is monomer concentration.

mer absorption band is higher than that of the latter.

IR absorption band of carbonyl in VCL—IPA mixtures is shifted towards lower wavenumbers by about  $8\text{--}10 \text{ cm}^{-1}$  and IR absorption band intensity of the double bond is increased in comparison with that of carbonyl group as can be seen from Fig. 5. The similar results have been obtained previously for VCL in protic solvents by IR spectroscopy [1]. These phenomena can be explained in a following manner: formation of solvation layer due to hydrogen bonds results in an increase of double bond polarity because of its conjugation with C=O group through nitrogen atom. One can assume that solvated form of VCL has higher reactivity in a radical polymerization. With the increased dilution of reaction mixture the content of solvated form grew, which resulted in increase of the ratio of polymerization rate to monomer concentration ( $R_p/[\text{VCL}]^{-1}$ ). In the diluted solutions of VCL in IPA limitation of  $M_n$  is provided by a chain transfer to IPA.

This reaction leads to formation of terminal hydroxyl groups in PVCL macromolecules. We have synthesized VCL oligomers with terminal hydroxyl groups (Table 3). As can be seen from Table 3, radical polymerization in diluted solutions of VCL in IPA provides VCL oligomers with terminal hydroxyl groups.

On the basis of the data obtained (Fig. 6), we have determined constants of chain transfer on IPA ( $C_s = 8 \times 10^{-4}$ ). This value is close to that obtained previously for the VP—IPA system [1], that testifies that the radicals of VCL and VP have similar reactivity.

## CONCLUSION

Both described approaches allow to obtain PVCL with low  $M_r$ , although mechanisms of its control may vary. In the case of use of allylbenzene and allylcaprolactam, the basic reaction restricting  $M_r$  of PVCL is degradation chain transfer. Allyl radical formed as a result of chain transfer is stabilized by conjugation, it is relatively inactive and practically it is not capable to react with double bond of a monomer. This chain transfer is essentially equivalent to monomolecular process of termination. A substituent at allyl group significantly affects the activity of chemical compound during the chain transfer. This effect is probably associated with more effective conjugation of AB radical.

VCL polymerization in IPA solution is characterized by ordinary mechanism of chain transfer and bimolecular process of termination. Major disadvantage of IPA as  $M_r$ -controlling agent is a significantly lower value of the chain-transfer constant in comparison with AB and ACL. Therefore, PVCL of low  $M_r$  can be obtained only by using dilute solutions of monomer in IPA. On the other hand, IPA in contrast to  $M_r$  controllers of allyl type, can be easily removed from reaction mixture upon completion of polymerization process. It is especially interesting to note that oligomers with terminal hydroxyl groups can be synthesized by

VCL polymerization in IPA solutions. In the recent years much attention has been paid to the synthesis of biodegradable polymers. It is known that poly(vinyl lactams) as carbon-chain polymers are only hardly subjected to biodegradation. This problem can be solved if the basic polymer chain would contain groups susceptible to chemical or enzymatic hydrolysis. We suggest that one of the possible ways of synthesis of such polymers could be application of VCL oligomers with terminal hydroxyl groups as macromonomers capable to interact with bifunctional compounds with formation of polymers with heteroatoms in a main chain.

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