Propagation Rate Coefficient for Radical Polymerization of *N*-Vinyl Pyrrolidone in Aqueous Solution Obtained by PLP−SEC

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ABSTRACT: Propagation rate coefficients, k_p, of *N*-vinyl pyrrolidone (NVP) radical polymerization in aqueous solution have been measured via the pulsed-laser polymerization - size exclusion chromatography method (PLP−SEC) over an extended concentration range from 1.8 to 100 wt % NVP at temperatures between 2 and 60 °C. The SEC analyses have been carried out by a modified procedure using dimethyl acetamide as the eluent. An about 20-fold increase of k_p is observed in passing from NVP bulk polymerization to reaction in dilute aqueous solution. As with nonionized methacrylic acid (MAA), for which a similarly strong change in k_p has recently been reported, the large solvent effect in NVP polymerization is assigned to intermolecular interactions resulting in a significant hindrance of internal rotational motion in the transition state structure for propagation. Some contribution from a minor change in activation energy may however not be ruled out. PLP−SEC studies carried out on aqueous NVP solutions to which either polyNVP or *N*-ethyl-2-pyrrolidone (NEP), the saturated analogue of NVP, have been added, demonstrate that k_p depends on the molecular environment at the reactive site, which is affected by NVP (or NEP) content, but not by the polyNVP content. The lowering of monomer concentration during NVP polymerization to higher degrees of monomer conversion results in an increase of k_p. Variation of p*H* in the range 3 to 10 does not affect k_p.

Introduction

Radical polymerizations in aqueous solution are of eminent technical importance. In order to model and optimize such processes, accurate kinetic data are needed. The most important types of water-soluble monomers are (meth)acrylic acid, (meth)acrylamides and *N*-vinyl amides. Whereas considerable recent interest has focused on detailed kinetic investigations into the first two groups,[1–11] *N*-vinyl amide kinetics has not been studied by any of the novel laser-assisted techniques. In an attempt to improve this situation, the present paper is devoted to the measurement of the propagation rate coefficient, k_p, of *N*-vinyl pyrrolidone (NVP) in aqueous solution at widely differing NVP concentrations, c_{NVP}. NVP is a hydrophilic nonionic monomer which readily polymerizes to polyNVP, the technically most important member of the family of poly(*N*-vinyl amides). These polymeric materials exhibit various interesting properties, as they are composed of both a polar amide group and a nonpolar substructure.[12] The aspects of synthesis, properties and applications of poly(*N*-vinyl amides) are outlined in the comprehensive survey by Kirsh.[13] The extensive use of poly(*N*-vinyl amides) is essentially due to their favorable interactions with hydrogen-bonded, dipolar, and hydrophobic compounds. Because of the solubility in most conventional solvents, the adhesive and binding power, film forming ability, affinity to hydrophobic and hydrophilic surfaces (thus acting as a compatibilizer), the ability to form complexes, and the thickening properties, polyNVP is extensively used in the pharmaceutical industry.[14] PolyNVP is a valuable material for medicine, cosmetics, food and textile applications, and in several other areas where advantage is taken of the sorbent properties, the protection of colloids, the modification of membrane surfaces, and carrier properties for biologically active compounds.[13]

PolyNVP is primarily prepared by radical polymerization, although NVP can also be produced by cationic polymerization.[15,16] Since its first use, around 70 years ago,[13] studies were devoted to obtain a better understanding of the mechanism of NVP polymerization by correlating kinetic data,[17–21] especially the ones measured in aqueous phase, to solution properties of NVP[22] and polyNVP.[22–26] It was found that the polymerization rate for NVP in aqueous solutions was higher than in organic solvents, a characteristic feature for polymerization of water-soluble monomers.[27] The increased rate of polymerization in aqueous solutions was assigned to strong hydration of NVP and polyNVP by water molecules,[22–24,26] via hydrogen-bonding interactions between water and the oxygen atom of the carbonyl group, thus affecting the electronic charge density on the vinyl group.[24] In the pioneering work by Karaputadze et al.,[20] the degree of hydration of NVP was related to an effective rate coefficient, which increased by about a factor of 5 between the bulk reaction and polymerization of 2 wt % NVP in aqueous solution. However, this effective rate coefficient does not represent a suitable kinetic quantity to be used for modeling purposes, as it was composed of initiation, propagation, and termination rate coefficients.

It is by now well accepted that the understanding of radical polymerization kinetics requires accurate individual rate coefficients to be known. Pulsed-laser assisted techniques have become the standard tool for obtaining rate coefficients for homo- and copolymerizations.[28] Only until recently, measurements of propagation rate coefficients, k_p, by the IUPAC-recommended method of pulsed-laser polymerization in conjunction with size-exclusion chromatography (PLP−SEC)[29]

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have been carried out for homopolymerizations in aqueous solution of methacrylic acid (MAA),[1,5–8] acrylic acid (AA),[1–4] *N*-isopropyl acrylamide,[9] and acrylamide.[10] These studies revealed specific features that largely differ from what is encountered in radical polymerization in organic solvents. In particular, a huge solvent effect on k_p has been found. Nonionized methacrylic acid (MAA) has been extensively studied within the entire concentration range from bulk to dilute aqueous solution.[5] Hydrogen-bonded interactions between the propagating MAA macroradical and an environment that, depending on the particular MAA concentration, consists of different relative amounts of MAA and water molecules do not significantly affect the activation energy for propagation reaction, $E_A(k_p)$, but largely influence the pre-exponential factor, $A(k_p)$. The observed decrease in $A(k_p)$, by about a factor of 10, in passing from dilute aqueous MAA solution to bulk MAA polymerization, is assigned to the increased friction that the relevant degrees of rotational motion of the transition state structure experience[30] upon replacing H_2O by MAA molecules.[5] This finding for MAA appears to be a general kinetic effect for hydrogen-bonded monomers in aqueous solution. For this reason, the PLP−SEC-derived propagation rate coefficients may be looked upon as "true" k_p values.[5] They do not reflect a deviation in local monomer concentration at the site of the propagating radical from the preselected overall monomer concentration (which does not significantly change during the PLP−SEC experiment, as pulsed-laser-induced monomer conversion does not exceed a few percent). Recent PLP−SEC experiments on aqueous solutions of nonionized MAA, to which either the saturated analogue of MAA, isobutyric acid, or polyMAA have been added, demonstrated that k_p is determined by the actual monomer concentration and not by the overall content of MAA units (contained in both monomer and polymer). Hence k_p of MAA increases with monomer conversion during polymerization at constant overall content of MAA moieties.[7] Polymerizations of MAA at different degrees of ionic dissociation revealed that ionization also strongly affects k_p.[6] The entire body of data obtained for MAA propagation in widely differing aqueous environments could be adequately described by the above-mentioned entropic effect, which primarily acts on the Arrhenius pre-exponential factor.

It appeared to be of interest to see whether the picture that has evolved for MAA also applies to propagation kinetics of other monomers in aqueous phase. NVP should be well suited for this purpose, as the structure is completely different from the one of MAA. NVP bears no hydrogen atom for interaction via hydrogen bonds, but has a large dipole moment, perhaps even exceeding 4 Debye units, which is the dipole moment reported for *N*-methyl pyrrolidone.[31] Strong intermolecular interactions are expected to occur in both pure NVP and in NVP-water mixtures. The interactions will be essentially of dipolar origin in NVP - poly(NVP) systems with contributions of hydrogen bonding coming into play in aqueous solution.[22–24,26,32,33] Moreover, in view of the technical importance of NVP polymerization, the lack of reliable rate coefficients for this monomer appears to be inadequate. The k_p values which were available so far, have been deduced by combining data from chemically initiated and from photoinitiated polymerization. The resulting k_p values are as follows: $\sim$1000 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ for bulk polymerization at 20 °C[18] and $\sim$22 000 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ for 0.5 $\text{mol}\cdot\text{L}^{-1}$ NVP in aqueous solution at 25 °C.[21]

The primary task was to identify suitable PLP conditions that lead to PLP-structured MWDs and to find SEC conditions allowing for high-quality molecular weight analysis for polyNVP. This paper presents the collaborative work involving PLP polymerization experiments carried out at the University of Göttingen, at Queen's University, and at the Polymer Institute in Bratislava accompanied by SEC characterization of polyNVP samples at the Polymer Institute in Bratislava. This imparts, at least partially, a benchmark character to the obtained data. The experiments are performed over an extended NVP concentration range, from dilute solution to bulk NVP polymerization, and within a broad temperature range, following the approach taken in the PLP−SEC studies into MAA propagation kinetics.[5] Additional PLP−SEC studies have been carried out using NVP of different purity, but also on NVP solutions to which the saturated analogue of NVP, *N*-ethyl pyrrolidone (NEP), or polyNVP have been added. Moreover k_p of NVP has been determined for a range of p*H* values.

Experimental Section

Chemicals. Three grades of *N*-vinyl pyrrolidone, NVP, were used for PLP experiments: NVP > 99% stabilized with 0.01 wt % NaOH (Aldrich), NVP > 97% stabilized with 0.001 wt % *N,N'*-di-*sec*-butyl-*p*-phenylenediamine (Fluka), both used as received, and NVP distilled at reduced pressure and 51 °C. The photoinitiators, DMPA (2,2-dimethoxy-2-phenyl acetophenone, Aldrich, 99%) and D1173 (2-hydroxy-2,2-dimethyl acetophenone, Ciba Specialty Chemicals Inc., 97%), were used as supplied as were the commercially available polyNVPs (Aldrich) with weight average molecular weights reported by the supplier to be 24 000 and 360 000 $\text{g}\cdot\text{mol}^{-1}$, respectively, and *N*-ethyl-2-pyrrolidone (NEP, Aldrich, 98%). Demineralized water was used for preparation of the polymerization solutions.

Preparation of NVP Solutions for the PLP Experiments. Solutions of different NVP and photoinitiator concentrations, c_{NVP} and c_{I}, respectively, were prepared by diluting a stock solution of the photoinitiator in NVP with NVP and water to yield the desired monomer and initiator concentrations. The NVP concentrations used for the PLP experiments ranged from 1.8 to 100 wt % and c_{I} was typically around 10^{-3} $\text{mol}\cdot\text{L}^{-1}$. The densities of NVP[34] and water[35] were estimated from the following relations: $\rho_{\text{NVP}}/\text{g}\cdot\text{cm}^{-3} = 1.0592 - 7.7772 \times 10^{-4}\,(T/°\text{C}) - 4.6649 \times 10^{-7}\,(T/°\text{C})^2$ and $\rho_{\text{water}}/\text{g}\cdot\text{cm}^{-3} = 0.9999 + 2.3109 \times 10^{-5}\,(T/°\text{C}) - 5.44807 \times 10^{-6}\,(T/°\text{C})^2$, respectively. Under the assumption of ideal mixing of NVP and water, the so-obtained densities were used to transform concentrations by weight into molar concentrations for different polymerization temperatures.

Aqueous NVP solutions containing NEP or polyNVP were prepared by adding NEP or polyNVP to aqueous NVP−photoinitiator solutions.

Pulsed-Laser Polymerization. Pulsed-laser polymerizations were carried out using three different pulsed-laser setups as are available at the participating institutes. At the University of Göttingen, PLP was performed using an excimer laser (LPX 210i, Lambda Physik) operated on the 351 nm XeF line. Pulse repetition rates of 20 and 40 Hz were used at an incident laser energy of about 10 mJ per pulse. At Queen's University, a SpectraPhysics QuantaRay 100 Hz Nd:YAG Laser was employed producing 355 nm laser light with incident energy of about 10 mJ per pulse at pulse repetition rates of 20 and 50 Hz. A Solar LQ129 (Minsk, Belarus) lamp-pumped Nd:YAG laser employing second and third harmonics for operation at 355 nm with an energy of 3 mJ per pulse and pulse repetition rates of 10, 20, and 30 Hz was used in Bratislava.

Polymerizations were carried out using either QS165 cells equipped with a jacket for temperature control or in a QS110 cell with 10 mm path length. In both cells (Hellma-Worldwide) the monomer solution was purged with nitrogen for 2−4 min. The cell was sealed with a PTFE stopper. Prior to pulsing, the polymerization cell was thermostatted for about 20 min. Several hundred laser pulses were typically applied to reach a monomer conversion of about 5%. Postpolymerization was suppressed by pouring the polymerization mixture into a sample vial containing hydroquinone monomethyl ether. For removing residual NVP, which is difficult to perform due to its high boiling temperature, different methods were used including high-vacuum drying, freeze-drying, precipitation in various solvents, and air drying. The protocol used for aqueous solution polymerizations involved the removal of the majority of water under high vacuum at ambient temperature followed by addition of *n*-hexane to precipitate polyNVP and extract residual NVP. After several addition and decanting steps with *n*-hexane, polyNVP was dried under vacuum at room temperature to constant weight. On the resulting product, the degree of monomer conversion was determined gravimetrically. For samples obtained by bulk polymerization, polyNVP was precipitated in *n*-hexane followed by drying in vacuum at ambient temperature to constant weight.

Size-Exclusion Chromatography. SEC analysis of the molecular weight distributions (MWDs) was performed with the eluent dimethyl acetamide (DMAc) containing 0.1 wt % LiBr on a Polymer Standards Service (PSS) column setup (Mainz, Germany) consisting of an 8 × 50 mm PSS GRAM 10 μm guard column and three 8 × 300 mm PSS GRAM 10 μm columns with pore sizes of 100, 1000 and 3000 Å placed in a column heater set to 45 °C. The flow rate of 0.8 $\mathrm{mL \cdot min^{-1}}$ was controlled by toluene as the flow rate marker in a Waters SEC system (degasser, autosampler 717 with loop volume 100 μL, 515 pump, column heater). Other than with the PLP–SEC studies into k_p of MAA, where direct calibration of SEC columns was employed,[5] the nonavailability of narrow polyNVP calibration standards required the use of MALLS-RI detection. A MALLS absolute detector PSS SLD7000 (PSS, Mainz, Germany) in conjunction with a Waters 2410 DRI detector provided absolute molecular weights.[36] The values of the refractive index increment, d*n*/d*c*, were determined on a Brice-Phoenix 2000-V differential refractometer to be 0.093 and 0.165 mL/g for polyNVP and polystyrene (PS), respectively. These numbers were estimated,[37] from the values measured at 436 nm (0.098 and 0.174 mL/g for polyNVP and PS, respectively) and 546 nm (0.096 and 0.169 mL/g for polyNVP and PS, respectively), for 633 nm which is the wavelength at which the MALLS detector works. A narrow PS calibration standard of 67 500 $\mathrm{g \cdot mol^{-1}}$ molecular mass (PSS, Mainz, Germany) was used as the isotropic scatterer. Effective calibration was made using PS standards, each of narrow molecular mass distribution, for the mass range 376 to 2 300 000 $\mathrm{g \cdot mol^{-1}}$ (PSS, Mainz, Germany). PSS WinGPC7 was used for data acquisition and evaluation. The factor which correlates the positions of primary and secondary points of inflection (POI) obtained by absolute (MALLS-RI detection) and by effective (RI detection) calibrations was found to be: $M_{\mathrm{i,MALLS\text{-}RI}}/M_{\mathrm{i,RI}} = 1.53 \pm 0.10$ in the range of molecular weights of polyNVP from 20 000 to 200 000 $\mathrm{g \cdot mol^{-1}}$. This correction factor was used for obtaining POI positions and thus k_p values in the few cases (marked in the tables) where the MALLS detector signal was insufficient for precise MWD analysis. The calibration curves for PS standards (RI detection) and polyNVP samples (MALLS–RI detection) are parallel in this molecular weight range, which indicates that the Mark–Houwink–Sakurada exponents are the same for PS and polyNVP at the particular SEC conditions of eluent composition and temperature. This observation further validates k_p evaluation from the polystyrene calibration curve.[38]

It should be noted the above SEC conditions were found to be suitable for characterization of the MWDs of polyNVP. Our decision for selecting these conditions was based on recent work of the Pasch group as well as on discussions with Polymer Standards Service proposing the versatility of GRAM columns for characterization of polymers (including hydrophilic ones) and using DMAc containing lithium salts as the eluent.[39–41] The SEC conditions are advantageous for characterization of polyNVP samples in terms of high resolution, excellent reproducibility, complete recovery of the injected sample and of fixed sample peak positions, irrespective of polymer concentration (at least in the injected sample concentration range from 1 to 20 mg/mL as has been tested for a sample with M_w of 58 000 $\mathrm{g \cdot mol^{-1}}$). The SEC analysis of polyNVP samples used in this work extends the existing SEC work on polyNVP.[42–44]

p*H* Adjustment of Aqueous NVP Solutions. The p*H* of aqueous NVP solutions was adjusted to values between 3 and 11 by adding acetic acid and NaOH, respectively, just before carrying out the PLP experiment. An EcoScan p*H* 5 instrument (Eutech Instruments Singapore PTE) was used for p*H* measurement.

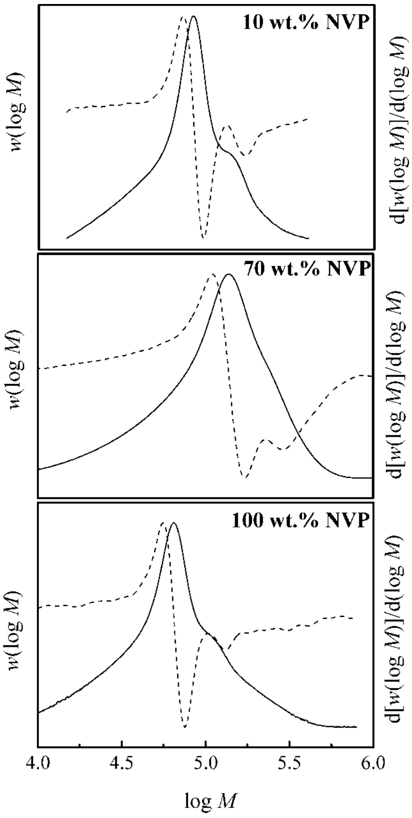


Figure 1. Molecular weight distributions (solid lines) and associated first-derivative curves (dashed lines) of polyNVP obtained by polymerizations of *N*-vinyl pyrrolidone in aqueous solution at 25 °C and different NVP concentrations. Laser repetition rate: 20 Hz.

Results and Discussion

The pulsed-laser polymerizations were carried at NVP concentrations between 1.8 and 100 wt % and temperatures between 2 and 60 °C. Special care was taken to demonstrate that the IUPAC consistency criteria for reliable k_p measurement are fulfilled.[45] The polymerizations were carried out using different PLP setups, two types of photoinitiator, different initiator concentrations as well as pulse repetition rates. Moreover, it was checked whether the purity of NVP affects k_p.

Shown in Figure 1 are MWDs of polyNVP obtained by PLP at 25 °C for aqueous solutions containing 10 and 70 wt % NVP as well as for bulk NVP polymerization together with the associated first-derivative curves that exhibit well-resolved primary and secondary POIs to be used for k_p determination. Similarly, the MWDs and first-derivative curves in Figure 2 for 10 wt % NVP and temperatures between 15 and 60 °C demonstrate the suitability of PLP–SEC for k_p analysis on these systems. The structured MWDs indicate that, unlike with acrylate monomers,[46] intramolecular hydrogen transfer plays no major role in NVP radical polymerization. As compared to the ester moiety, the amide structure is less capable of activating α-hydrogen atoms on the backbone of NVP macroradicals and of polyNVP. As a consequence, NVP behaves like the "classical" monomers subjected to PLP–SEC analysis, *i.e.*, styrene[45] and several methacrylates.[47–49]

The experimental conditions of the large set of PLP–SEC measurements are listed in Tables 1 and 2. The ratio of the molecular weights at the first and second overtone positions of the MWD, which were determined from the maxima of the

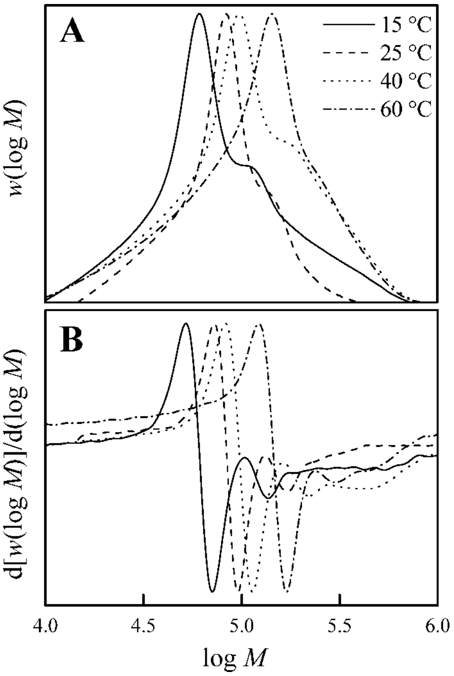


Figure 2. Molecular weight distributions (A) and associated first-derivative curves (B) of polyNVP obtained by radical polymerization in aqueous solution of 10 wt % *N*-vinyl pyrrolidone at various temperatures. Pulse repetition rate: 20 Hz.

associated first-derivate curves, is mostly close to 0.5 thus fulfilling the important consistency criterion for reliable k_p analysis. In a few cases, the second point of inflection could be identified only as a shoulder (SH). The resulting k_p values were nevertheless considered to be reliable, as experiments under ostensibly the same conditions, in which both POIs were clearly seen, yielded similar k_p values. A few experiments, mostly at lower NVP concentration, were run up to relatively high degrees of monomer conversion, up to 20%, to obtain sufficient amounts of polymer for SEC analysis. The actual NVP concentration, c_{NVP}, that is used for estimating k_p via eq 1, was selected to be the arithmetic mean of the initial NVP concentration and of the one after PLP. The simple formula which correlates the degree of polymerization at the first POI, L_1, with k_p, c_{NVP} and time t_0 between two successive pulses reads: $L_1 = k_p c_{NVP} t_0$, which expression may be rewritten as follows:

$$k_p = M_1 \nu_{rep}/(M_0 c_{NVP}) \qquad (1)$$

where M_0 is the molecular mass of one NVP repeat unit. The entire set of k_p values listed in the last column of Tables 1 and 2 is determined from the measured position of the first POI, M_1, according to eq 1.

Inspection of the entries in Tables 1 and 2 demonstrates that k_p is not dependent on photoinitiator concentration and on pulse repetition rate, which is in fulfillment of further consistency criteria for reliable PLP−SEC studies. The k_p values obtained for the different grades of NVP are more or less identical, although the different monomer qualities differ in absorption, between 0.1 and 0.6, at the laser wavelength. Blank PLP experiments without photoinitiator on nonpurified NVP showing significant laser light absorbance due to the stabilizing agent for NVP resulted in no polymer formation even after applying 300 pulses at ambient temperature. Hence, no special precaution needs to be taken for purifying NVP, contrary, e.g., to polymerization of *N*-vinyl carbazole where significant PLP-induced polymerization occurred in the absence of photoinitiator.[50]

As can be seen from the entries in Table 1, k_p varies enormously with the NVP content of the aqueous solution, from about 1000 L·mol^{-1}·s^{-1} for bulk polymerization up to about 20 000 L·mol^{-1}·s^{-1} for an NVP concentration of 1.8 wt %. It should be noted that the two literature values ($k_p \sim 1000$ L·mol^{-1}·s^{-1} at 20 °C in bulk and $k_p \sim 22\,000$ L·mol^{-1}·s^{-1} for 0.5 mol·L^{-1} NVP) determined 50 years ago,[18,21] are remarkably close to our PLP−SEC data.

Plotted in Figure 3 are the experimental k_p values (circles) as a function of NVP concentration for 25 °C. The cross symbols in Figure 3 represent the arithmetic mean of k_p values determined for each set of independent k_p measurements at a particular NVP content. With the exception of the data for 10 wt % NVP, the individual k_p data are very close to the arithmetic mean value. Inspection of the data for 10 wt % NVP reveals no systematic effect on k_p of either photoinitiator concentration, pulse repetition rate, or the number of applied laser pulses, but indicates an uncertainty of about ±15% for k_p determination. Such an uncertainty is typical for PLP−SEC experiments.

The NVP propagation rate coefficient decreases by slightly more than 1 order of magnitude in passing from dilute solution to bulk polymerization. A similar strong effect has been seen with k_p of nonionized methacrylic acid in aqueous solution.[5]

Listed in Table 2 are the k_p values measured between 15 and 60 °C for NVP contents in aqueous phase from 5 up to 100 wt %. Presented in Figure 4 is the entire k_p information contained in Tables 1 and 2. Reduced propagation rate coefficients, $k_p/k_{p,max}$, are plotted vs NVP concentration; $k_{p,max}$ refers to the k_p value obtained from extrapolation of k_p data at identical temperature to zero NVP concentration. Within the limits of experimental accuracy, the reduced propagation rate coefficients for the experimental temperatures may be fitted (eq 2) by an expression with an exponential and a linear term in monomer concentration, c_{NVP}:

$$k_p/k_{p,max} = 0.36 + 0.64\exp(-0.092(c_{NVP}/\text{wt }\%)) - 0.0031(c_{NVP}/\text{wt }\%) \qquad (2)$$

Absolute $k_p(c_{NVP},T)$ values may be estimated via an Arrhenius expression for $k_{p,max}$ with activation energy $E_A(k_p) = 17.6$ kJ·mol^{-1} (obtained as the arithmetic mean of the $E_A(k_p)$s in Table 3, see below) and with frequency factor $A(k_p) = 2.57 \times 10^7$ L·mol^{-1}·s^{-1}.

That $k_p/k_{p,max}$ may be fitted exclusively as a function of c_{NVP}, irrespective of temperature (Figure 4), is equivalent to saying that the activation energy, $E_A(k_p)$, is insensitive toward NVP concentration. This type of behavior has also been observed for k_p of methacrylic acid in aqueous solution. The pronounced variation of k_p with c_{MAA} has been identified as a genuine kinetic effect that primarily influences the pre-exponential term,[5] whereas attempts to assign the pronounced changes in PLP−SEC-derived k_p of MAA to specific local monomer concentrations at the free-radical site or to monomer association, e.g., to dimer formation, turned out to be not successful.

In case of NVP, the limited number of data points, the relatively narrow temperature range, from 15 to 60 °C, and the experimental uncertainty, do not allow for a firm decision whether it is the pre-exponential factor or the activation energy, which changes, or whether both $A(k_p)$ and $E_A(k_p)$ change. Presented in Table 3 are the results of linear Arrhenius fitting of k_p values measured on both aqueous solutions differing in NVP content and on bulk NVP. The mean values of k_p estimated from each series of individual k_p data obtained at identical c_{NVP} and identical polymerization temperature have been subjected to the fitting procedure. The temperature range and the number of different temperature levels of the underlying experiments are also listed in Table 3. The activation energy exhibits no systematic trend toward increasing NVP concentration, although the activation energy for bulk NVP polymerization appears to be slightly above $E_A(k_p)$ for polymerizations in aqueous solution.

Table 1. Propagation Rate Coefficients, k_p, Obtained from PLP−SEC Experiments on *N*-Vinyl Pyrrolidone (NVP) at 25 °C in Aqueous Solution and in Bulk[a]

	c_{NVP}								
NVP grade	wt %	mol·L^{-1}	$c_I \times 10^3$ (mol·L^{-1})	ν_{rep} (Hz)	N_P	fract convn	$M_1 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2[e]	k_p (L·mol^{-1}·s^{-1})[f]
>97%	1.8	0.16	1.8[b]	10	300	0.05	31.6	0.54	18 229
				10	600	0.12	36.7	0.58	21 974
>97%	3.0	0.27	2.0[b]	10	300	0.09	49.9	0.41	17 366
				10	600	0.17	44.8	0.44	16 199
				20	600	0.14	29.0	0.57	20 765
>97%	5.2	0.47	0.5[c]	40	50	0.01	20.3[d]	0.52	16 094
				40	300	0.01	20.8[d]	0.51	16 432
>97%	6.1	0.55	2.1[b]	10	300	0.09	84.3	0.50	14 561
				10	600	0.21	86.3	0.52	15 902
				20	300	0.06	43.7	0.57	14 901
				20	600	0.17	43.7	0.52	15 706
>97%	10.0	0.90	2.5[b]	10	300	0.05	138.0	0.53	14 123
				10	600	0.07	118.6	0.53	12 304
				20	300	0.02	72.8	0.55	14 735
				20	600	0.04	57.8	0.50	11 790
>97%	10.4	0.94	2.4[b]	10	300	0.08	128.5	0.63	12 810
				10	600	0.18	133.0	0.58	14 018
				20	300	0.11	84.3	0.68	*17 089*
				20	600	0.18	55.3	0.54	11 695
distilled	10.3	0.93	2.1[b]	10	300	0.09	104.0	0.52	10 534
				10	600	0.20	95.3	0.45	10 236
				20	300	0.12	47.8	0.54	*9840*
				20	600	0.19	60.0	0.49	12 007
>97%	20	1.79	0.5[c]	20	50	0.01	88.9	0.55	9179
>99%	25	2.27	2.5[c]	20	1800	0.11	81.8	0.47	6871
			5.0[c]	50	500	0.11	36.8	*SH*	7739
				50	1000	0.10	35.1	0.50	7343
>97%	30	2.75	2.2[b]	10	300	0.07	190.1	0.54	6461
				10	600	0.14	204.6	0.56	7211
				20	300	0.08	96.8	0.59	6621
				20	600	0.17	90.0	0.45	6443
distilled	30	2.75	2.7[b]	10	300	0.09	174.6	0.48	6069
				10	600	0.18	175.4	0.51	6374
				20	300	0.09	99.8	0.59	6928
				20	600	0.20	95.5	0.52	7031
>97%	39	3.57	0.5[c]	20	300	0.01	123.0[d]	0.52	6230
				40	300	0.01	55.8[d]	0.44	5656
	40	3.65	2.0[b]	30	300	0.04	66.4	0.51	5021
				30	600	0.22	70.0	0.52	5813
>99%	50	4.58	2.5[c]	20	1800	0.20	97.7	0.53	4259
			5.0[c]	50	1000	0.08	48.6	0.49	4965
>97%	60	5.52	2.0[b]	10	600	0.06	342.0	0.50	*5737*
				20	600	0.06	143.5	0.53	*4830*
				10	300	0.05	200.0	0.52	3347
				10	600	0.11	189.2	0.44	3278
				20	300	0.06	112.0	0.56	3782
				20	600	0.12	110.2	0.49	3830
distilled	60	5.52	2.5[b]	10	300	0.07	191.9	0.49	3250
				10	600	0.14	176.2	*SH*	3089
				20	300	0.07	109.4	0.51	3708
				20	600	0.15	101.0	*SH*	3571
>97%	70	6.46	2.1[b]	10	300	0.04	182.8	0.42	2595
				10	600	0.09	203.7	0.49	2962
				20	600	0.10	110.2	0.48	3226
			4.8[b]	30	300	0.05	78.5	0.54	3371
				30	600	0.09	62.8	0.51	2748
>97%	90	8.38	5.0[b]	20	300	0.06	76.0	*SH*	1681
				30	300	0.03	47.3	0.46	1550
				30	600	0.08	52.4	0.42	1755
			2.0[b]	10	300	0.02	138.0	*SH*	1548
				10	600	0.04	151.7	*SH*	1765
				20	300	0.03	89.1	0.56	1702
				20	600	0.06	82.0	0.46	1807
>97%	100	9.35	5.0[b]	20	300	0.02	78.5	0.41	*1529*
				20	600	0.06	61.7	0.43	*1222*
				30	300	0.02	39.2	0.54	*1142*
			2.2[b]	10	300	0.01	118.3	*SH*	900
				10	600	0.03	108.9	0.58	910
				20	300	0.02	52.5	0.54	950
				20	600	0.04	49.4	0.50	967
distilled	100	9.35	1.9[b]	10	300	0.03	90.2	0.54	893
				10	600	0.04	103.3	0.49	999
				20	300	0.02	50.0	0.54	894

Table 1. Continued

NVP grade	c_{NVP} wt %	c_{NVP} mol·L^{-1}	$c_I \times 10^3$ (mol·L^{-1})	ν_{rep} (Hz)	N_P	fract convn	$M_1 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2[e]	k_p (L·mol^{-1}·s^{-1})[f]
				20	600	0.04	52.0	0.48	881
>97%	100	9.35	2.4[b]	10	300	0.01	97.1	0.50	937
				10	600	0.01	100.7	0.49	975
				20	300	0.01	46.3	0.45	894
				20	600	0.01	56.0	0.54	1082
>99%	100	9.35	2.5[c]	20	1800	0.05	42.7	0.45	844
>97%	100	9.35	20.0[b]	30	300	0.03	31.1	0.58	910
				30	600	0.06	28.2	*SH*	840

[a] Also given are the experimental conditions and parameters: the grade of NVP subjected to PLP−SEC analysis, the weight and molar concentration of NVP, c_{NVP}, photoinitiator concentration, c_I, laser pulse repetition rate, ν_{rep}, number of applied laser pulses, N_P, fractional monomer conversion, molecular weight at the first point of inflection (POI) of the MWD, M_1, and ratio of molecular weights at the first and second POI, M_1/M_2. [b] D1173 used as the photoinitiator. [c] DMPA used as the photoinitiator. [d] M_1 values obtained by calibration against narrow polystyrene standards and subsequent multiplication by a factor of 1.53 (see Experimental Section). [e] SH: The second overtone position only shows up as a shoulder in the first-derivative curve of the MWD. [f] k_p values given in *italics* were not considered in the subsequent data evaluation. These (very few) k_p data differ by more than 20% from the associated arithmetic mean k_p value for the particular NVP concentration and temperature.

The two parameters, $E_A(k_p)$ and $A(k_p)$, are correlated by the Arrhenius fitting procedure. Larger uncertainties in $E_A(k_p)$ are associated with larger uncertainties in $A(k_p)$, as is illustrated by the second and third columns in Table 3. The k_p values for 25 °C, as estimated from the mean values of the Arrhenius parameters for each NVP concentration, are given in the last column of Table 3. They are in close agreement with the associated experimental values.

Shown in Figure 5 are the Arrhenius plots of k_p for NVP in both aqueous solution and bulk polymerization. The arithmetic mean values of k_p (deduced from k_p data sets measured at identical NVP concentration and polymerization temperature) were subjected to Arrhenius fitting. The full lines illustrate the resulting fits. The dashed lines are obtained by Arrhenius fitting under the assumption that a single (mean) activation energy, $E_A(k_p) = 17.6$ kJ·mol^{-1}, applies to the entire data, irrespective of NVP concentration. Whether the bulk NVP data also fit into this picture cannot be safely established on the basis of the available experimental material. The relatively close comparison of the full and dashed Arrhenius lines for NVP bulk polymerization, however, indicates that using the mean value of activation energy, $E_A(k_p) = 17.6$ kJ·mol^{-1}, allows for reasonable k_p estimates for the entire NVP concentration range, at least at the polymerization temperatures under investigation.

It needs to be mentioned that the alternative procedure of trying to fit measured k_p by adopting a single mean value of $A(k_p)$ and adjusting $E_A(k_p)$ also affords for an adequate representation of k_p values measured in the experimental ranges of temperature and NVP concentration. Plotted in Figure 6 are the 95% joint confidence intervals (JCIs)[51] of $E_A(k_p)$ and $A(k_p)$, as obtained from the entire k_p set in Tables 1 and 2. The JCIs indicate that both Arrhenius parameters may change with NVP concentration. Even for bulk NVP polymerization, however, where $E_A(k_p)$ appears to be above the activation energy for polymerization in aqueous solution, k_p may be estimated within experimental accuracy from the Arrhenius expression which adopts a single value of activation energy, $E_A(k_p) = 17.6$ kJ·mol^{-1}. Assigning the variations of k_p with NVP concentration entirely to $A(k_p)$ allows for using the same physical concept as with nonionized methacrylic acid to interpret the variation of k_p with monomer concentration in aqueous solution. First experiments on *N*-vinyl formamide suggest that, also with this monomer, the variation of k_p within an extended monomer concentration and temperature range may be interpreted by changes of the pre-exponential rather than of the activation energy.[52]

The results of fitting k_p for various NVP concentrations as a function of polymerization temperature may be summarized: Although effects of NVP concentration in aqueous solution on $E_A(k_p)$ may not be ruled out, it is not in conflict with experimental data to assign the observed large changes of k_p with c_{NVP} entirely to $A(k_p)$. This behavior corresponds to the one observed with nonionized methacrylic acid and further supports the concept that the experimental k_p values are *true* kinetic parameters[5] with at best minor contributions from local monomer concentration at the propagating chain-end being different from overall monomer concentration.

Illustrated in Figure 7 is the comparison of the dependence of reduced propagation rate coefficient, $k_p/k_{p,max}$, on monomer concentration (at low degrees of initial monomer conversion) for NVP and for nonionized MAA.[5] The dependencies are close to each other and are more or less identical at monomer concentrations up to 20 wt %. No full agreement is expected, as the intermolecular forces in the NVP and MAA systems are rather different. It should be recalled that even for one and the same monomer, as has been demonstrated for MAA,[6] variation of p*H* may completely change the dependence of $k_p/k_{p,max}$ on monomer concentration and even gives rise to an increase in k_p upon enhancing monomer concentration in aqueous solutions of fully ionized MAA.

The similarity of the dependence of k_p on monomer concentration for NVP and for nonionized MAA provides further support for the same physical effect being operative in both cases. According to transition state (TS) theory, the pre-exponential factor is essentially determined by the geometry of the rotating groups in the reactants and by the rotational potentials of the relevant internal (hindered) motions in the TS.[30] Large hindrance of rotational freedom is associated with a significant entropy penalty which results in a smaller $A(k_p)$ value and thus in smaller k_p. Applying this knowledge to the k_p data of MAA and NVP measured upon passing from bulk to aqueous solution polymerization, leads to the conclusion that the gradual replacement of monomer molecules by H_2O molecules changes the environment of the TS structure for addition of a monomer molecule to a macroradical such that the chain end experiences a higher degree of rotational freedom. Thus the relevant degrees of freedom in the TS for propagation experience less friction toward increasing water content resulting in an increase of k_p toward lower monomer concentration. Interestingly, the larger hindrance of internal rotational mobility in the propagation TS structure for polymerization at high monomer concentrations, including bulk polymerization, may be brought upon by both hydrogen-bonded interactions, as with nonionized MAA, and by strong dipolar interactions, as with NVP. The enhanced mobility in dilute aqueous solution may be visualized by enhanced motional freedom, which a "fish in water" may experience.[5] That dipolar interactions in NVP can induce an effect similar to the one of hydrogen bonds in MAA is probably due to the size of the NVP dipole moment, μ_{NVP}.[53] To the best of our knowledge, μ_{NVP} has not been reported so far. It appears

Table 2. Propagation Rate Coefficients, k_p, at Temperatures Other than 25 °C Obtained from PLP−SEC Experiments on *N*-Vinyl Pyrrolidone (NVP) in Aqueous Solution and in Bulk[a]

	c_{NVP}									
NVP grade	wt %	mol·L^{-1}	$c_I \times 10^3$ (mol·L^{-1})	T (°C)	ν_{rep} (Hz)	N_P	fract convn	$M_1 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2[e]	k_p (L·mol^{-1}·s^{-1})[f]
>97%	5.2	0.47	0.5[c]	15	20	300	0.01	34.1[d]	0.51	13 485
				15	40	50	0.01	16.2[d]	0.50	12 850
				15	40	300	0.01	16.4[d]	0.51	12 967
		0.47		40	20	300	0.01	48.3[d]	0.47	19 358
				40	40	50	0.01	27.4[d]	0.51	22 024
				40	40	300	0.03	24.5[d]	0.50	19 674
		0.46		60	20	50	0.01	77.7[d]	0.51	31 488
				60	40	50	0.01	42.7[d]	0.51	34 528
				60	40	300	0.03	40.2[d]	0.50	32 597
>97%	10.0	0.90	2.5[b]	15	10	300	0.04	91.8	0.46	9354
				15	10	600	0.07	98.9	0.54	10 239
				15	20	300	0.02	55.6	0.54	11 198
				15	20	600	0.03	52.1	0.50	10 572
		0.90	2.5[b]	40	10	300	0.05	161.8	0.50	16 680
				40	10	600	0.10	158.9	0.49	16 794
				40	20	300	0.04	84.7	0.50	17 342
				40	20	600	0.08	82.8	0.51	17 300
		0.89	2.5[b]	60	10	600	0.12	214.8	0.48	23 266
				60	20	300	0.04	121.3	0.51	25 224
				60	20	600	0.08	122.5	0.52	25 895
>97%	20	1.78	0.5[c]	40	40	50	0.01	51.1	0.50	10 394
				40	20	300	0.01	108.9	0.51	11 107
>97%	39	3.60	0.5[c]	2	20	300	0.01	60.0[d]	0.52	3019
				2	40	300	0.01	31.3[d]	0.53	3140
	40	3.68	2.0[b]	5	30	300	0.03	40.1	0.49	2990
	39	3.58	0.5[c]	15	40	300	0.01	36.0[d]	0.49	3629
	39	3.54	0.5[c]	40	40	300	0.01	78.7[d]	0.41	8032
	40	3.57	2.0[b]	60	30	300	0.14	123.9	*SH*	10 064
				60	30	600	0.25	138.7	*SH*	11 982
>97%	60	5.55	2.0[b]	40	20	300	0.03	179.5	0.51	5984
				40	20	600	0.06	183.7	0.49	6216
>97%	70	6.51	4.8[b]	10	30	300	0.04	50.6	0.52	2143
				10	30	600	0.05	45.6	0.53	1943
		6.50	2.1[b]	15	10	300	0.04	160.0	0.51	2260
				15	10	600	0.08	173.4	0.53	2502
				15	20	300	0.06	84.0	0.50	2396
				15	20	600	0.12	91.4	0.50	2686
		6.40		40	20	300	0.08	141.6	*SH*	4139
			4.8[b]	40	30	300	0.03	99.1	0.54	4250
				40	30	600	0.04	106.4	0.51	4597
		6.32		55	30	300	0.03	123.9	0.44	5365
				55	30	600	0.10	133.0	0.42	5975
>97%	90	8.50	5.0[b]	5	20	300	0.04	63.7	0.57	1374
				5	20	600	0.08	42.6	0.43	939
				5	30	600	0.06	34.2	0.48	1119
		8.44	2.0[b]	15	10	300	0.02	105.0	0.60	1071
				15	10	600	0.04	95.1	0.45	1088
				15	20	300	0.03	68.7	0.54	1417
				15	20	600	0.05	65.8	0.53	1386
		8.29	5.0[b]	40	20	300	0.06	125.0	*SH*	2791
				40	20	600	0.21	117.8	*SH*	2858
				40	30	600	0.02	95.3	0.60	3139
			2.0[b]	40	20	300	0.04	107.2	*SH*	2330
				40	20	600	0.08	103.8	*SH*	2315
		8.16	5.0[b]	60	30	300	0.02	112.7	*SH*	3768
				60	30	600	0.04	111.2	*SH*	3759
>97%	100	9.49	5.0[b]	5	20	300	0.02	26.7	0.54	*511*
				5	20	600	0.04	29.2	0.43	563
				5	30	300	0.01	21.4	0.57	612
			20.0[b]	5	30	300	0.03	26.8	0.52	772
				5	30	600	0.05	27.3	0.52	*796*
		9.42	2.2[b]	15	10	300	0.01	77.4	0.55	742
				15	10	600	0.02	69.5	0.53	671
				15	20	300	0.02	32.4	0.59	542
				15	20	600	0.03	37.2	0.53	593
			2.4[b]	15	10	300	0.01	75.7	0.46	724
				15	10	600	0.01	76.7	0.50	735
				15	20	300	0.01	38.1	0.45	729
				15	20	600	0.01	38.8	0.43	744
		9.24	5.0[b]	40	20	600	0.03	58.2	0.48	*1148*
				40	30	300	0.01	64.1	0.60	*1879*
				40	30	600	0.02	53.6	0.58	1580
			2.4[b]	40	10	300	0.01	142.9	*SH*	1396
				40	10	600	0.02	135.2	*SH*	1330
				40	20	300	0.01	69.8	0.44	1364
				40	20	600	0.01	84.3	0.50	1653
		9.09	5.0[b]	60	30	300	0.01	85.3	0.53	2546
				60	30	600	0.03	83.4	*SH*	2518

Table 2. Continued

NVP grade	c_{NVP} wt %	c_{NVP} mol·L^{-1}	$c_I \times 10^3$ (mol·L^{-1})	T (°C)	ν_{rep} (Hz)	N_P	fract convn	$M_1 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2[e]	k_p (L·mol^{-1}·s^{-1})[f]
			2.4[b]	60	20	300	0.01	128.8	*SH*	2555
				60	20	600	0.01	124.2	*SH*	2471
			20.0[b]	60	30	300	0.05	85.0	*SH*	2592
				60	30	600	0.10	62.8	*SH*	*1958*

[a] Also given are the experimental conditions and parameters: the grade of NVP subjected to PLP−SEC analysis, weight and molar concentration of NVP, c_{NVP}, photoinitiator concentration, c_I, temperature, T, laser pulse repetition rate, ν_{rep}, number of applied laser pulses, N_P, fractional monomer conversion, molecular weight at the first point of inflection (POI) of the MWD, M_1, and ratio of molecular weights at the first and second POI, M_1/M_2. [b] D1173 used as photoinitiator. [c] DMPA used as photoinitiator. [d] M_1 values obtained by calibration against narrow polystyrene standards and subsequent multiplication by a factor of 1.53 (see Experimental Section). [e] SH: The second overtone position only shows up as a shoulder in the first-derivative curve of the MWD. [f] k_p values given in *italics* were not considered in the subsequent data evaluation. These (very few) k_p data differ by more than 20% from the associated arithmetic mean k_p value for the particular NVP concentration and temperature.

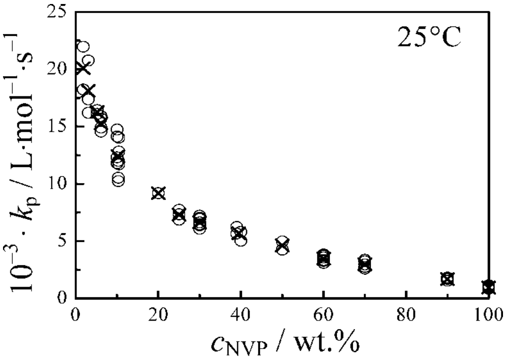


Figure 3. Variation of the propagation rate coefficient, k_p, of *N*-vinyl pyrrolidone (NVP) with monomer concentration, c_{NVP}, in aqueous solution at 25 °C (circles). The crosses represent the arithmetic mean k_p value for the individual NVP concentrations under investigation.

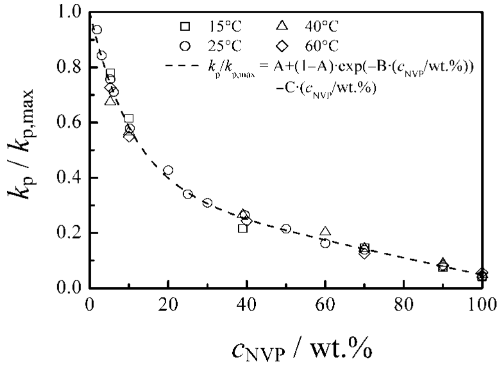


Figure 4. Dependence of the reduced propagation rate coefficient, $k_p/k_{p,max}$, on overall NVP concentration, c_{NVP}, for NVP polymerizations in aqueous solution at 15, 25, 40 and 60 °C; k_p is the arithmetic mean value deduced from experiments at identical NVP concentration and temperature and $k_{p,max}$ is the k_p value extrapolated toward zero *N*-vinyl pyrrolidone concentration, $c_{NVP} = 0$, at the same polymerization temperature. The $k_{p,max}$ values of 16 793 L·mol^{-1}·s^{-1} at 15 °C, 21 475 L·mol^{-1}·s^{-1} at 25 °C, 30 154 L·mol^{-1}·s^{-1} at 40 °C, and 45 212 L·mol^{-1}·s^{-1} at 60 °C were directly calculated from the Arrhenius parameters given in the text. The dashed line represents the fit (to the function given in the figure) of the reduced k_p values for the 15 to 60 °C range of polymerization temperature. The parameter values of the fitted function are: $A = 0.36$, $B = 0.092$, and $C = 0.0031$.

most likely that μ_{NVP} even exceeds the large dipole moment of *N*-methyl pyrrolidone, (NMP), which is $\mu_{NMP} = 4.06$ D.[31] The reason behind such large dipole moments is seen in the participation of the nitrogen lone pair electrons to resonance structures for NMP and NVP, as depicted in Scheme 1. The assumption of μ_{NVP} being even above μ_{NMP} is based on the fact that the vinyl double bond may enhance the contribution of the resonance structure with a positive charge on the nitrogen and a negative charge on the oxygen atom because of the more extended delocalization associated with these structures. The structures in Scheme 1 illustrate that the large dipole moment occurs with NVP, with polyNVP, and with NVP macroradicals.

The results for NVP and for MAA suggest that a significant decrease of k_p toward higher monomer concentration seems to be a general phenomenon with nonionized water-soluble monomers. The large solvent effects on k_p with hydrogen-bonded and highly polar monomers in aqueous solution are due to the fact that the intermolecular interactions between functional groups of the monomeric (and polymeric) species and a molecular environment consisting either of monomer or of water are strong, but are different. This difference is sufficiently large as to give rise to clearly different extents of internal friction of the TS structure for propagation and thus of k_p. In principle, solvent effects on k_p are generally occurring. Intermolecular interactions may however be too weak as to give rise to easily detectable effects on k_p and mostly the polarities of monomer and solvent will be close to each other, which results in very similar effects on the hindrance to internal friction of the TS structure. It should be noted that, in bulk polymerization, the monomer may be looked upon as a particular solvent. In solution polymerizations, the solvent is frequently chosen such as to be not too dissimilar in polarity from the monomer. Thus the differences in intermolecular interactions of TS structure with molecular environment are not sufficiently pronounced as to give rise to clearly different k_p values. After the safe detection and understanding of the strong k_p solvent effect in MAA aqueous-solution polymerization, closer inspection of acrylate and methacrylate homo- and copolymerizations[54] has revealed that basically the same entropy-related effects occur with these monomers without water being present. These effects are however less pronounced and require highly accurate PLP−SEC analyses.

The k_p data presented so far refer to polymerization at low degrees of NVP conversion, mostly below 5%, as is typical for investigations via PLP−SEC. For practical purposes, information on k_p up to much higher monomer conversions is required. For common monomers, such as styrene and alkyl methacrylates, it has been assumed that the low-conversion k_p holds over a wide range of monomer conversion including technically relevant conditions. This assumption appears to be an excellent one for monomers which exhibit no clear solvent effect on k_p. The situation is obviously different for propagation in aqueous solution. The observed strong variation of k_p with solvent concentration raises the question of how to account for the change in monomer concentration that is associated with monomer conversion. One may think of two limiting situations: (a) monomer concentration is essentially affecting k_p, which results in an increasing k_p value during the course of a polymerization to high conversion or (b) the overall content of monomer units, including both monomer and monomer units contained in the polymer, determines k_p. In this second case, more or less the same k_p value applies for polymerization of a given solution up to high degrees of monomer conversion.

Table 3. Arrhenius Activation Energy, $E_A(k_p)$, and Pre-Exponential, $A(k_p)$, Estimated from Linear Fitting of the Logarithm of the Propagation Rate Coefficient, k_p, of *N*-Vinyl Pyrrolidone in Aqueous Solutions of Different NVP Content and in Bulk[a]

c_{NVP} (wt %)	$E_A(k_p)$ (kJ·mol^{-1})	$A(k_p) \times 10^{-6}$ (L·mol^{-1}·s^{-1})	temperature interval (°C)	no. of different temperatures	k_p(25 °C) extrapolated (L·mol^{-1}·s^{-1})
5	**16.0** ± 1.4	5.8 < **10.1** < 17.6	15−60	4	16 060
10	**15.7** ± 0.5	5.9 < **7.0** < 8.4	15−60	4	12 662
40	**18.3** ± 1.4	4.8 < **8.3** < 14.6	2−60	6	5298
70	**17.3** ± 0.6	2.6 < **3.3** < 4.2	10−55	5	3032
90	**18.0** ± 1.6	1.3 < **2.5** < 4.8	15−60	5	1768
100	**20.1** ± 2.1	1.4 < **3.3** < 7.8	15−60	5	1013

[a] The indicated uncertainties are standard deviations.

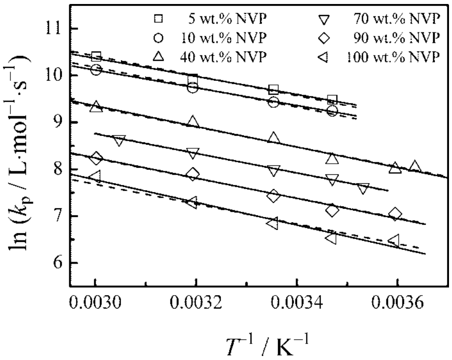


Figure 5. Arrhenius fits of the (averaged) propagation rate coefficients for *N*-vinyl pyrrolidone (NVP) polymerizations in aqueous solution between 5 and 90 wt % NVP and for bulk NVP polymerization (full lines). The dashed lines represent Arrhenius fits to the same k_p data set assuming the activation energy to be constant at the mean value of $E_A(k_p) = 17.6$ kJ·mol^{-1}.

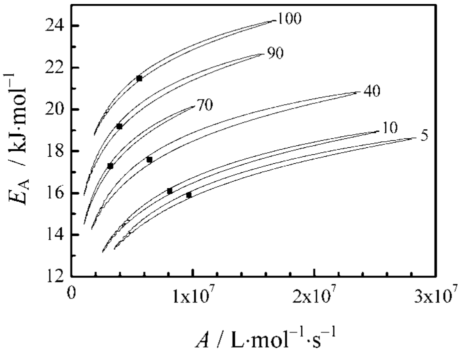


Figure 6. 95% joint confidence intervals (JCIs) for propagation rate coefficient, k_p, of *N*-vinyl pyrrolidone (NVP) at different NVP weight concentrations in water (indicated by the numbers at the JCIs) and of NVP in bulk. The black squares represent the Arrhenius parameters from nonlinear least-squares fitting of the k_p data collated in Tables 1 and 2.

Preceding investigations into MAA k_p revealed that case (a) applies for this monomer.[7] The analysis has been carried out such that the situation of higher conversion was simulated by the addition of either polyMAA or of the saturated analogue of MAA, isobutyric acid, which may be looked upon as the limiting case of low-molecular-weight “polymer”. At these “virtual” conversions to high and to low molecular weight polymer, PLP−SEC experiments were carried out, each of them covering only a small conversion interval as is characteristic of PLP−SEC studies. The results indicate that the effect on k_p is brought upon by low-molecular-weight components containing carboxylic acid moieties. MAA and the saturated analogue are part of the intracoil environment and thus may interact with the radical site embedded in such a coil. Carboxylic groups on polyMAA molecules, on the other hand, do not or not significantly contribute to these interactions unless macroradical and polymeric coils are strongly interpenetrating each other. In essence, the MAA study revealed that k_p in aqueous solution varies with the actual ratio of monomer to water concentrations in the system as far as high-molecular-weight polymer is produced. This ratio depends on both the initial monomer concentration and the monomer-to-polymer conversion.

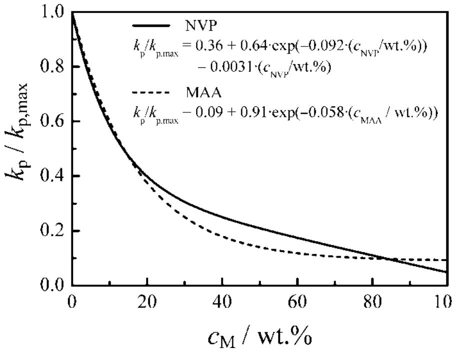
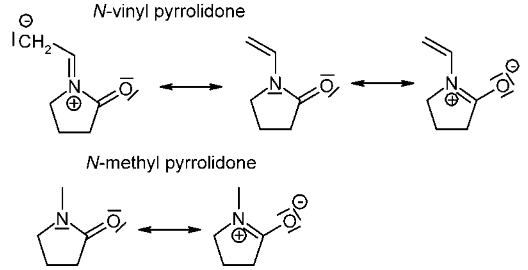


Figure 7. Exponential fits of the variation with (initial) monomer concentration of reduced propagation rate coefficient, $k_p/k_{p,max}$, for polymerization in aqueous solution of NVP and of nonionized MAA.[5] The underlying k_p values are deduced from PLP−SEC experiments and thus hold for low degrees of monomer conversion referring to the widely differing initial monomer concentrations plotted on the abscissa.

Scheme 1. Resonance Structures of *N*-Vinyl Pyrrolidone and *N*-Methyl Pyrrolidone, Respectively



A corresponding study was carried out for NVP polymerization at 25 °C with *N*-ethyl pyrrolidone, NEP, being the saturated analogue, and with two commercial polyNVP samples of the weight average molecular weights of 24 000 and 360 000 g·mol^{-1}, as reported by the supplier, that are used for simulating NVP conversion to high-molecular-weight material. It should be noted that the molecular weights measured on these polyNVP samples with our setup differ from the reported values. M_w = 47 000 g·mol^{-1} and M_n = 12 000 g·mol^{-1} were determined for the lower molecular weight polyNVP sample and M_w = 872 000 g·mol^{-1} and M_n = 157 000 g·mol^{-1} for the higher molecular weight polyNVP sample. Listed in Table 4 are the type of additive, NEP or polyNVP; the virtual conversion, $X_{virtual}$, which will be described further below; c_{NVP}, the initial NVP concentration; N_P, the number of applied laser pulses; X_{PLP}, the NVP conversion induced by PLP; M_1, the molecular weight at the first point of inflection (POI) of the MWD; and M_1/M_2, the ratio of molecular weights at the first and second POIs.

Table 4. Experimental Results for Pulsed-Laser Induced Polymerizations of *N*-Vinyl Pyrrolidone (NVP) in *N*-Ethyl Pyrrolidone (NEP) and Water at Different NVP to NEP Ratios but Constant Overall Acid Concentration of 20 wt %, and Polymerizations of NVP in Aqueous Phase with Added PolyNVP of Molecular Weight of 24 000 or 360 000 g·mol^{-1}[a]

NVP grade	additive	X_{virtual}	c_{NVP}		N_{P}	X_{PLP}	M_1[b] × 10^{-3} (g·mol^{-1})	M_1/M_2	k_{p} (L·mol^{-1}·s^{-1})
			wt %	mol·L^{-1}					
>97%		0.015	20.0	1.81	300	0.031	65.0	0.49	9839
		0.025	20.0	1.81	600	0.050	66.4	0.50	10 144
>97%	polyNVP 360 000	0.265	15.0	1.36	300	0.031	62.0	0.49	12 528
		0.275	15.0	1.36	600	0.050	62.1	0.50	12 679
		0.515	10.0	0.90	300	0.031	40.7	0.44	12 385
		0.525	10.0	0.90	600	0.050	41.0	0.48	12 593
>97%	polyNVP 24 000	0.265	15.0	1.36	300	0.031	54.9	0.48	11 114
		0.275	15.0	1.36	600	0.050	57.4	0.51	11 724
		0.515	10.0	0.90	300	0.031	44.8	0.48	13 643
		0.525	10.0	0.90	600	0.050	42.4	0.46	13 007
		0.765	5.0	0.45	300	0.031	33.2	0.49	20 273
		0.775	5.0	0.45	600	0.050	30.0	0.48	18 499
>97%	NEP	0.275	15.0	1.36	300	0.051	52.5	0.49	10 722
		0.300	15.0	1.36	600	0.100	48.3	0.49	10 121
		0.517	10.0	0.90	300	0.033	35.8	0.49	10 926
		0.535	10.0	0.90	600	0.070	35.6	0.49	11 056
		0.757	5.0	0.45	300	0.014	17.6	0.48	10 646
		0.768	5.0	0.45	600	0.035	17.1	0.45	10 467

[a] Polymerizations were performed at 25 °C and an initiator concentration, c_{D1173}, of 2 mmol·L^{-1} and a laser repetition rate of 30 Hz. The table collates the virtual conversion, X_{virtual}, the initial monomer concentration, c_{NVP}, the number of applied laser pulses, the PLP-induced monomer conversion, X_{PLP}, the molecular weight (MW) at the first point of inflection (POI) of the MWD distribution, M_1, the ratio of the MWs at the first and second POI of the MWD distribution, and the resulting propagation rate coefficient, k_{p}. [b] M_1 values obtained by effective calibration against narrow polystyrene standards and multiplication of the so-obtained molecular weights by a factor of 1.53 (see Experimental Section).

The quantity X_{virtual} has been selected for easier comparison of k_{p} data determined in aqueous solution without any additive to k_{p} values measured in aqueous solution in the presence of either NEP or polyNVP. The reference system for the entire data set in Table 4 is the one in which 20 wt % NVP is dissolved in water without any additive. Different amounts of NEP and polyNVP are added to aqueous NVP solutions such that the overall content of pyrrolidone moieties is 20 wt %. The "virtual" conversion is determined by taking the NEP and polyNVP contents, respectively, into account in such a way as if they were produced by preceding polymerization of NVP; i.e., NVP has reacted either to low-molecular-weight NEP or to high-molecular-weight polyNVP. The numbers in Table 4 reveal that replacing NVP by NEP at constant overall pyrrolidone content does not significantly affect k_{p}, at least not up to a ratio of 3:1 ($X_{\text{virtual}} \sim 75\%$). A closer look at the NVP k_{p} data measured in the presence of NEP indicates that the so-obtained values are slightly above the ones measured at the same overall pyrrolidone content, but with only NVP being present. This observation might be explained by a smaller dipole moment of NEP as compared to NVP (see the above discussion related to Scheme 1), which goes with weaker intermolecular interactions, thus with a lower friction and a slightly higher k_{p}.

Replacing NVP by polyNVP, on the other hand, significantly enhances k_{p}. The polymer appears to be not available at the site of the growing radical, an observation which is in full agreement with what has been found for MAA.[7] The data from Table 4 are plotted in Figure 8. Also contained in this figure are a few data points for aqueous solution of NVP at concentrations below 20 wt % (without any additive). Within the concept of "virtual" conversion, these data are treated as if the lower NVP concentration results from reaction to polyNVP with the polymer however being removed from the solution as, e.g., in a precipitation polymerization, i.e. throughout all data sets plotted in Figure 8 the mass-ratio of monomer to water is the same at a certain virtual conversion. Interestingly, the so-obtained k_{p} vs "virtual" conversion data points are close to the ones obtained for NVP/polyNVP systems thus supporting the view that only the pyrrolidone species which may access the interior of macroradical coils are affecting k_{p}. With respect to polymerization of NVP in aqueous solution up to high degrees of monomer conversion, the information may be summarized that k_{p} is determined by the actual ratio of NVP to water and thus increases with the degree of NVP conversion.

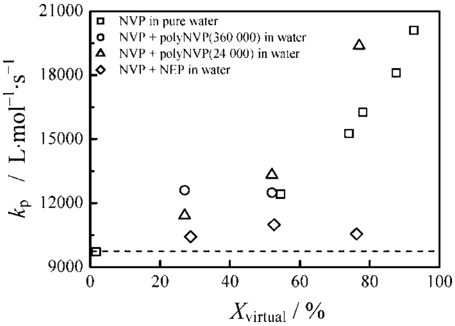


Figure 8. Dependence of k_{p} on virtual conversion, X_{virtual}, for polymerizations of *N*-vinyl pyrrolidone (NVP) in water at 25 °C, c_{D1173} = 2 mmol·L^{-1} and 30 Hz. The squares represent polymerizations of NVP in water (Table 1) at different $c_{\text{NVP}} \leq 20$ wt %. The k_{p} values indicated by the circles and triangles refer to polymerizations of NVP in the presence of polyNVP of different molecular weight, while the diamonds refer to polymerizations of NVP in the presence of *N*-ethyl pyrrolidone. X_{virtual} was calculated based on the conversion-dependent change in the ratio of NVP to water in polymerizations of an initial monomer concentration (or overall pyrrolidone concentration) of 20 wt % (see text). The dotted line indicates the mean value of low conversion k_{p} from Table 1 and Table 5 in this work.

With MAA, the k_{p} values turned out to be strongly dependent on the p*H* with this effect being particularly pronounced at low monomer concentrations, where k_{p} is decreased by about 1 order of magnitude in passing from nonionized to fully ionized MAA.[6] This effect becomes very weak at intermediate MAA concentrations and is even reversed at monomer concentrations above 40 wt %.[6] Although no significant effect of p*H* is expected to occur with NVP, as the molecule cannot dissociate, a series of experiments for several NVP concentrations has been carried out to investigate whether k_{p} of NVP exhibits some sensitivity to p*H*. The early kinetic studies into NVP polymerization rate within the p*H* interval 7 to 10 provided no indication of any p*H* effect.[21] In the present study, p*H* was varied from 3 to 11. This extended range encompasses p*H* situations as are met in

Table 5. Propagation Rate Coefficients, k_p, of *N*-Vinyl Pyrrolidone in Aqueous Solution Measured at 25 °C As a Function of p*H* [a]

NVP grade	p*H*	c_{NVP} wt %	c_{NVP} mol·L^{-1}	ν_{rep} (Hz)	N_P	fract convn	$M_1 \times 10^{-3}$ (g·mol^{-1})	M_1/M_2	k_p (L·mol^{-1}·s^{-1})[b]
>97%	3.3	5.0	0.45	10	300	0.08	64.3	0.53	13 371
	3.3			10	600	0.19	63.4	0.49	14 015
	3.3			20	600	0.11	35.9	0.50	15 226
	3.3			20	300	0.05	36.5	0.53	15 001
	6.2			10	300	0.07	66.4	0.53	13 801
	6.2			10	600	0.18	66.7	0.51	14 641
	6.2			20	300	0.05	38.0	0.56	15 621
	6.2			20	600	0.14	39.8	0.56	17 120
	10.9			10	300	0.07	79.8	0.59	16 575
	10.9			10	600	0.12	57.8	0.53	12 340
	10.9			20	300	0.05	42.2	0.43	17 294
	10.9			20	600	0.10	29.2	0.56	12 313
>97%	3.8	40	3.65	10	600	0.14	193.6	0.50	5124
	3.8			20	300	0.04	102.8	0.51	5171
	3.8			20	600	0.14	107.2	0.52	5693
	6.2			10	600	0.15	206.1	0.47	5502
	6.2			20	300	0.05	110.2	0.55	5578
	6.2			20	600	0.11	114.6	0.54	5967
	10.9			10	300	0.09	216.8	0.50	5582
	10.9			10	600	0.20	253.5	0.55	*6924*
	10.9			20	300	0.09	98.9	0.50	5094
	10.9			20	600	0.18	102.3	0.46	5527
>97%	3.9	60	5.52	10	600	0.15	273.5	0.63	4818
	3.9			20	300	0.07	103.5	0.46	3490
	3.9			20	600	0.12	122.2	0.57	4227
	6.1			20	300	0.05	106.9	0.40	3573
	6.1			20	600	0.08	117.5	0.47	3980
	10.9			10	300	0.13	185.8	0.40	*3230*
	10.9			10	600	0.18	218.8	0.45	3908
	10.9			20	300	0.08	117.2	0.51	3987
	10.9			20	600	0.14	125.0	0.50	4389
>97%	6.7	100	9.39	20	300	0.02	60.7	0.51	1177
	6.7			20	600	0.04	79.3	0.45	1548
	10.9			10	300	0.02	132.7	0.48	1285
	10.9			10	600	0.04	119.7		1173
	10.9			20	300	0.01	47.4	0.55	*916*
	10.9			20	600	0.04	92.3	0.62	*1803*

[a] Given in Table 5 are the experimental conditions and the measured k_p values: c_{NVP}, initial NVP concentration; N_P, number of applied laser pulses; fract convn, fractional NVP conversion induced by laser pulsing; M_1, molecular weight (MW) at the first point of inflection (POI) of the MWD; M_1/M_2, ratio of the MWs at the first and second POI of the MWD. [b] k_p values written in *italics* were not considered in the subsequent data evaluation. Those k_p values were observed to be departing from the arithmetic mean k_p value at the selected monomer concentration and temperature by more than 20%.

copolymerization reactions of NVP with comonomers exhibiting acid or base properties.

Presented in Table 5 are the k_p values for NVP concentrations of 5, 40, 60 and 100 wt % obtained at 25 °C for different p*H*. It appears justified to state that there is no systematic effect of p*H* on k_p. Plotted in Figure 9 are the arithmetic mean values of k_p data measured at identical NVP concentration and polymerization temperature including the entire data set in Table 5. The open symbols refer to aqueous NVP solutions with the p*H* being adjusted by using either sodium hydroxide or acetic acid. The filled symbols represent data taken on solutions without adjusted p*H*. The p*H* of these aqueous NVP solutions increases, between 5 to 100 wt % from 6 up to 11, because NVP "as supplied" was used which contained *N,N′*-di-*sec*-butyl-*p*-phenylenediamine as the stabilizer. Higher NVP content thus is correlated with a higher amine content which in turn results in a higher p*H*. Figure 9 and Table 5 demonstrate that k_p for the aqueous solution polymerizations of NVP is not affected by p*H* in the interval from 3 to 11 over the entire c_{NVP} range examined experimentally. NVP decomposes at acidic p*H* and higher temperature.[17] The experimental k_p data for low p*H* in Table 5 and Figure 9 may nevertheless be considered reliable, because of the short time interval required for the experiment and the low polymerization temperature of 25 °C.

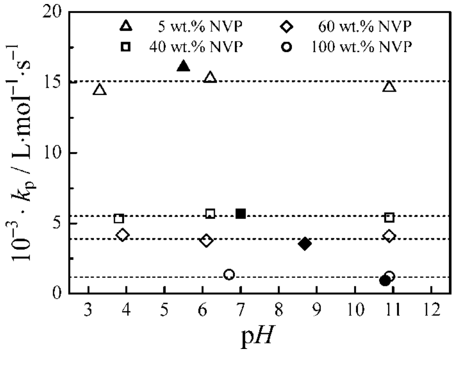


Figure 9. Dependence on p*H* of the propagation rate coefficient, k_p, for polymerizations of *N*-vinyl pyrrolidone at 25 °C in aqueous phase at NVP concentrations of 5, 40, 60 and 100 wt % (plotted here are the arithmetic mean values deduced from polymerization experiments at identical NVP concentration and temperature). The open symbols refer to polymerizations with the p*H* adjusted either by NaOH or acetic acid. The filled symbols refer to solutions prepared by using NVP as received (from Fluka stabilized with *N,N′*-di-*sec*-butyl-*p*-phenylenediamine) without additionally adjusted p*H*. The dashed lines indicate the arithmetic mean k_p values for each initial NVP concentration.

Conclusions

The pronounced increase of NVP propagation rate coefficient, k_p, upon passing from bulk NVP polymerization to reaction in dilute aqueous solution has been measured. The large variation of k_p with solvent environment is assigned to a genuine entropic effect. Intermolecular interactions which lower the internal rotational mobility in the transition state structure for propagation are becoming weaker upon gradually replacing NVP by water molecules. Basically the same effect has been observed for aqueous solutions of nonionized methacrylic acid. Other than with methacrylic acid, it can however not be ruled out that changes in activation energy, $E_A(k_p)$, may contribute to the large effects seen with NVP. As k_p increases toward lower NVP concentrations in water, k_p is enhanced during polymerization to higher monomer conversion of a given aqueous solution of NVP. At constant NVP concentration, the pH value has been varied from 3 to 11 without giving rise to any significant effect on k_p.

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