Monomers for Adhesive Polymers, 8[a] Crosslinking Polymerization of Selected *N*-Substituted bis(Acrylamide)s for Dental Filling Materials

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ABSTRACT: The free-radical polymerization of bis-(*N*-ethylacrylamido)-ethylenglycol (**I**), *N,N′*-dimethyl-1,6-bis(acrylamido)-hexan (**II**), and *N,N′*-diethyl-1,3-bis(acrylamido)-propan (**III**) were investigated. The cross-linking polymerization was followed in bulk by using the ampoules technique and gravimetry. Polymerizations exhibited an abnormal kinetic behavior. For the monomer **II**, for example, the reaction order to 2,2′- azobisisobutyronitril (AIBN) initiator of 1.28, and the polymerization overall activation energy of 151 kJ/mol between 50 and 75°C were determined. The increasing temperature and decreasing initiator concentration resulted in an increase of double bonds consumption in the formed polymer network. At 75°C the residual unsaturation was under 2%, compared with 9.9% at 50°C. The monomer conversion-time dependences were complemented also with differential scanning calorimetry (DSC) recording the heat released during polymerization. The extension of peak time with decreasing the instant heat flow rate at this point sort the studied bis(acrylamide)s according the reactivity in the following sequence: monomer **III** > **I** > **II**. The polymer samples sol–gel analyses in ethanol allowed the determination of the molecular weight M_c between the network crosslinks. The presence of microgel particles at the very beginning of polymerization and the changes in chain conformation with temperature we consider as the way in which was affected the polymerization kinetics of these monomers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3137–3145, 2009

**Key words:** crosslinking; dental polymers; kinetics (polym)

INTRODUCTION

In the presently applied commercial resin-based enamel-dentin adhesives and composite restoratives, mixtures of dimethacrylates are used as organic matrix[1,2] because dimethacrylates give rise to the formation of a polymer network, which results in a number of favorable effects. First, the fast polymerization as a consequence of the increasing polymer crosslinking from an early stages of polymerization that results to the decreasing radical termination–gel effect. Second, the mechanical properties of polymer networks are superior to those of linear polymers. Third, the resulting crosslinked polymer matrix is not water soluble. The dimethacrylates are used together with strongly acidic adhesive monomers, such as phosphonic acids or dihydrogen phosphates in self-adhesive cements or enamel-dentin adhesives.[3] For self-etching enamel-dentin adhesives water is primarily used as solvent. Thus, especially in the case of one-bottle adhesives, the methacrylates undergo hydrolysis of the methacrylate ester bond which changes the chemical composition of the adhesive and also deteriorates its performance. Therefore, new monomers with improved hydrolytic stability under acidic conditions were necessary. In this respect, new bis(acrylamide)s,[4] can be used to substitute commonly used methacrylates in self-etching enamel-dentin adhesives. The properties of polymer matrix have been varied by changing the spacer group between both amides nitrogens and by alteration the nitrogen substituents. The results demonstrated that bis(acrylamide)s prevail over dimethacrylates in hydrolytic stability, solubility in water and organic solvents. It should be mentioned that many bis(acrylamide)s showed a significantly lower cytotoxicity than frequently used dimethacrylates.[4]

The crosslinking of the multifunctional monomers however exhibits an abnormal kinetic behavior during the polymerization. The rapid mobility decrease of the reacting species with increasing conversion caused at first autoacceleration, in later stages autodeceleration, reaction diffusion controlled termination and limiting double bonds conversion.[5] Because the manner in which the monomer double bonds react and form the network will affect the physical properties of cured materials an understanding of the crosslinking polymerization kinetics is essential.

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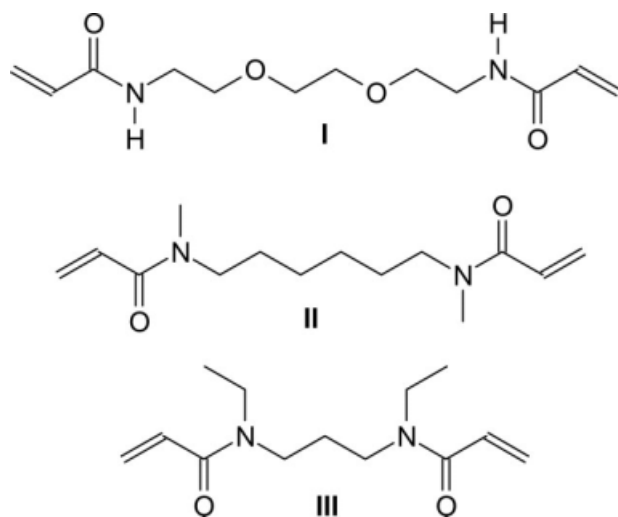
Scheme 1 Formulas of bis (acrylamide)s used in the polymerization studies.

In preliminary studies,[4] the same or slightly higher reactivity of the bis(acrylamide)s in crosslinking polymerization was observed in comparison with dimethacrylates.

In this article, the free-radical polymerization of selected bis(acrylamide)s was studied in more details. We investigated the monomer, 1,8-bis-(acrylamido)-3,6-dioxaoctane (**I**), N,N′-dimethyl-1,6-bis (acrylamido)-hexane (**II**), and N,N′-diethyl-1,3-bis (acrylamido)-propane (**III**) (Scheme 1) that did not show any mutagenic effect.[4]

EXPERIMENTAL

Polymerization

The nondiluted monomers **I-II-III** were polymerized in glass ampoules and in aluminium pans assigned for DSC measurements. Polymerization batches were prepared at room temperature by dissolving 2,2′-azobisisobutyronitril (AIBN) initiator in liquid monomer **I** and **II,** or by mechanical homogenization with crystalline monomer **III**. The sets of 7 ampoules in 0.5 g were prepared from the each batch. Ampoules were flushed with the nitrogen and sealed before starting the polymerization in a tempered water bath at a desirable temperature and time. Cooling the ampoules in an ice water the reaction was stopped. The formed polymer networks were swelled in ethanol containing 0.1 wt % of hydroquinone straight after polymerization. The residual monomer was separated from crosslinked polymer by migration into the solvent. The twice exchange of the fresh solvent provided the complete extraction of a soluble portion that was proved to be the monomer. The open aluminum pans of 5 mm in diameter and coated in an inner surface with a gold

layer were used for polymerization experiments in DSC apparatus (Mettler–Toledo DSC 821 thermal analyzer). Of about 10 mg of the monomer–initiator batch was filled in and an inert atmosphere was maintained by flushing the DSC measuring cell with nitrogen.

Analyses

The residual double bonds were determined from Fourier transform infrared spectra recorded with Nicolet Impact 400 spectrometer. The KBr technique and standard baseline evaluation of absorbance peaks in the region 796 cm^{-1} was used. This sharp peak we hold for out-of-plane deformation of acrylamide double bonds, usually situated for acrylates at wave number 816 cm^{-1}.

The equilibrium swelling extraction in ethanol after 5 days immersion of the polymer sample in solvent at 20–22 °C was used for sol–gel analysis. The average molecular weight M_c between polymer network crosslinks, which is directly related to the network degree of swelling, was estimated according to the Flory–Rehner equation[6] from results of sol–gel analysis in ethanol.

For a perfect tetra-functional network valid formula:

$$1/M_c = [\ln(1 - v_p) + v_p + \chi v_p{}^2]/[\rho V_s(v_p{}^{1/3} - v_p/2)]$$

V_s is the molar volume of solvent, ρ is the density of the crosslinked polymer and v_p is the volume of polymer in the swollen gel. Flory-Huggins interaction parameter χ was calculated from solubility parameters of the polymer and solvent. The group contribution method data from the Polymer Handbook[7] were used. The following χ values for polymer networks **I**, **II**, and **III** were calculated: 0.387, 0.488, and 0.350 respectively.

It is worth to mention that values of Mc include in densely crosslinked networks not only chains between chemical crosslinks, but include also chains between the physical crosslinks due to chains entanglement (the mechanically effective average molecular weight between crosslinks).

Materials

The free radical polymerization initiator AIBN was recrystalized from methanol (m.p. 103°C). All solvents used for swelling, extractions, and analytical procedures were of analytical grade purity, purchased from Merck, Germany. The bis(acrylamide)s were prepared as previously described.[4]
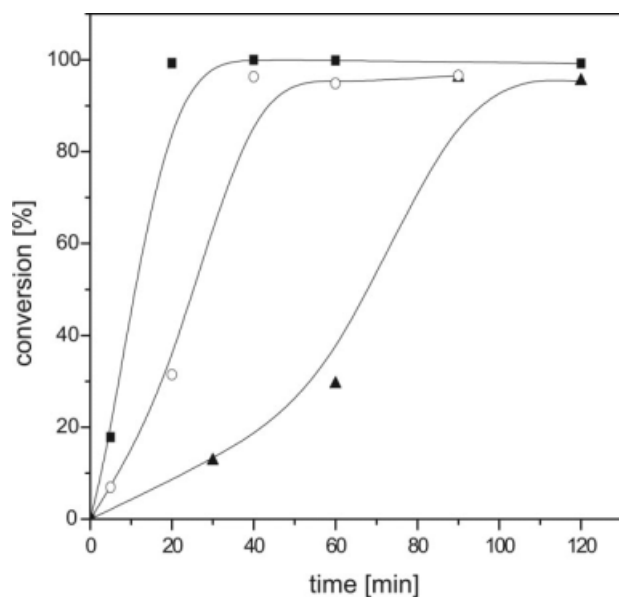
Figure 1 The monomer **I** bulk polymerization at 65°C. Conversion-time dependences for the variety of AIBN initiator concentrations (22.5 ■; 11.2 ○; 5.6 ▲ [mmol/L].

RESULTS AND DISCUSSION

As a part of our continuing research on polymer matrices with application in dental materials we have been interested in the polymerization activity of bis(acrylamide)s with various substituents on amide nitrogen.[4,8,9] In this study, the desirable properties of polymer matrix used in dental composites, the excellent hydrolytic stability, very good mechanical properties and the lowest cytotoxicity were the decisive aspects in selection monomers for detail tests. The investigated monomers **I**, **II**, and **III** (Scheme 1) differ in the length of spacer that linked through the amide nitrogen two acryl amide groups in the monomer molecule. The second hydrogen on amide nitrogen was substituted by methyl in monomer **II** and by ethyl in monomer **III**. Because informations on the polymerization reactivity of substituted (meth)acrylamides are not very extensive it is very difficult predict only on analogy the polymerization behavior of new acrylamide derivates. Like other hydrophilic monomers the acrylamides polymerize extremely fast.[10–12] Their propagation rate coefficients are very sensitive to changes of polymerization environment,[13] e.g. monomer concentration in water solutions. Acrylamides generally polymerize more rapidly than methacrylamides.[14] Information on the polymerization of s. Roughly the bulky substituents on nitrogen reduce the easy of homopolymerization.[15,16] N-alkyl groups exert predominantly steric suppression of propagation and termination rate constants. The N-tert-butylacrylamide polymerization rate dropped approximately to one tenth of that one of the acrylamide. It has been

shown that N,N-disubstituted methacrylamides do not homopolymerize under conditions of radical polymerization.[16,17]

Glass ampoule polymerizations

The monomer **I** was a crystalline substance with melting point 70.5°C, determined by DSC. However, the melting range between 63.5 and 67 °C was observed by the hot-plate microscope. Below the melting point the polymerization rate was very slow. The rate of monomer conversion to polymer at 50°C and 0.4 wt % AIBN initiator reached only 1.2 wt % /h. The isolated polymer formed fine grains. The reaction rate at 65°C, just in the monomer melting temperature range increased considerably. According to the Arrhenius relation can be predicted roughly 3.2 times polymerization rate acceleration, if usually observed for acrylamides the polymerization overall activation energy 70 kJ/mol was considered.[14] Nevertheless, in reality the polymerization rate increased nearly 200 times.

The conversion-time dependences at 65°C and for various initiator AIBN concentrations are plotted on Figure 1. The characteristic conversion curves for autoaccelerated reaction points out two polymerization stages. In the first one chain grow predominates over crosslinking, in the second one crosslinking prevails over the polymer chains extension (Table I). We have checked that soluble portions in polymerized samples were the nonreacted monomer and consequently the gel content equals to monomer conversion. In the batches with the highest AIBN concentration only insoluble polymer was formed already from the early stages of polymerization.

TABLE I
Molecular Weight Between Crosslinks M_c and Residual Unsaturation Found Out in the Polymer Network Formed During the Monomer I Bulk Polymerization at 65°C and Various AIBN Concentrations. Glass Ampoule Experiments

AIBN (mmol/L)	Time (min)	Conversion (%)	$M_c \times 10^{-2}$ (g/mol)	Residual double bonds (%)
22.5	20	99.3	3.94	–
	60	99.9	4.83	5.7
	120	99.2	6.65	5.4
	180	99.5	6.96	5.9
11.2	5	6.9	19 200	9.9
	20	31.4	1 550	–
	60	94.9	8.6	7.0
	90	96.6	7.2	4.4
	180	96.6	4.7	3.2
5.6	30	12.7	12 300	13.7
	60	29.4	2 210	–
	120	96.1	11.63	–
	180	95.2	5.20	7.8
	300	96.4	13.32	5.7
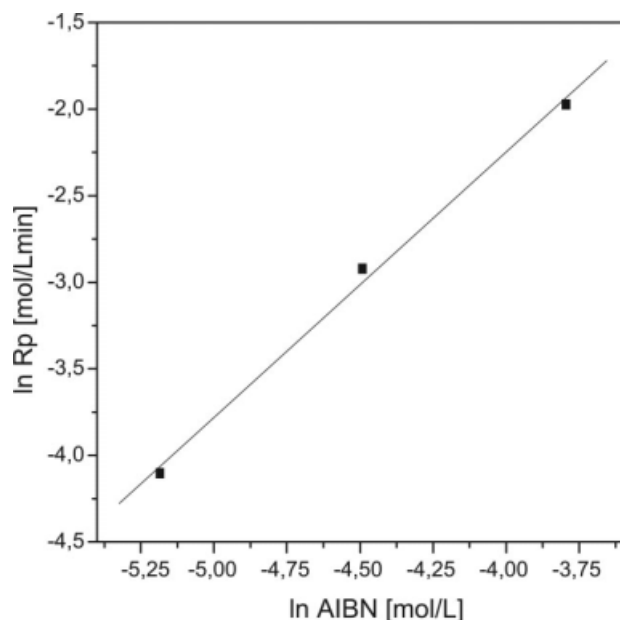
Figure 2 Instantaneous polymerization rates in the first stages of monomer **I** polymerization at 65°C in dependence on AIBN concentration. The logarithmic plot.

The rate of polymerization and intensity of acceleration were very sensitive to changes of the rate of initiation (initiator concentration and temperature). By increasing AIBN concentration to 22.5 mmol/L, the linear first stage polymerization nearly split with the accelerated polymerization phase. The plot of initial polymerization rates in dependence on initiator concentration in a double logarithmic scale is lin-
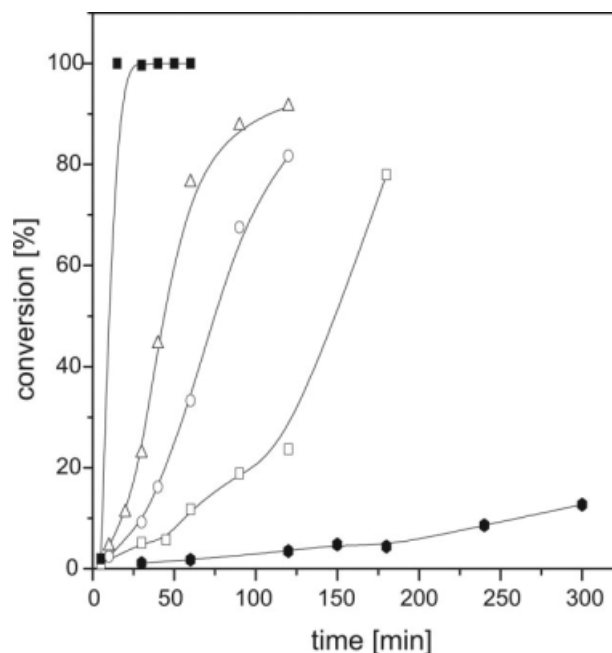
ear (Fig. 2). The slope 1.53, which represents the rate intensity exponent to AIBN concentration, showed unusually high value. This is far from the half-order dependence, ordinary observed during conventional free radical polymerization. An atypical initiator concentration effect on the crosslinking polymerization rate we explain by the specific features of the reaction kinetic.[5] An early appearance of the gel-point caused growing chains trapping already in the formed network seeds. This phenomenon accentuates the chain length dependent termination[18] and accumulation of long living free radicals. Moreover, at this stage of reaction predominates the reaction diffusion in moving the free radicals to recombination distance that also contributed to nonstationary reaction conditions.

The slightly lower, but still exceptionally high rate intensity exponent 1.28 to AIBN concentration (Fig. 3) we have seen also in the monomer **II** initial phase of a crosslinking polymerization. It is evident from the conversion-time dependences shown on Figure 4 that the monomer **II** compared with the monomer **I** was less active in the first polymerization stages. The reaction rates determined from this very beginning polymerization period showed round about one decimal order lower values for the monomer **II** polymerization (Table II).

Not only an unexpected high reaction order to the initiator, but also the overall activation energy $E_a =$

Figure 3 Instantaneous polymerization rates in the first stages of monomer **II** polymerization at 60°C in dependence on AIBN concentrations. The logarithmic plot.

Figure 4 Conversion-time dependences of the monomer **II** bulk polymerization; i) for the variety of temperatures (50 ⬣, 60 □, and 75°C ■) and 22.5 mmol/L AIBN concentration; ii) for the variety of AIBN initiator concentrations (22.5 □, 45 ○, and 67.5 △, mmol/L) and 60°C.

TABLE II
Instantaneous Polymerization Rates R_p Taken from the Initial Polymerization Stages of the I and II Bulk Monomer Polymerization in Glass Ampoules

Monomer	AIBN (mmol/L)	T (°C)	$Rp \times 10^2$ (mol L min)	Remark
	22.5	65	13.90	Reaction order to
I	11.2	65	5.38	initiator = 1.53
	6.5	65	1.65	
	22.5	60	0.77	Reaction order to
II	45.0	60	1.78	initiator = 1.28
	67.5	60	3.17	
	22.5	50	0.17	Activation energy
II	22.5	60	0.77	E_a = 151 kJ/mol
	22.5	75	4.95	

151 kJ/mol determined for the monomer **II** polymerization rate dependence on temperature is difficult to explain (Fig. 5). The monomers of this type are capable to associate molecules and formed polymers with an ability of temperature-dependent changes in chain conformation. Further, now universally accepted phenomenon of the microgel particles formed from the very beginning of cross-linking polymerization caused the system inhomogeneous in micro scale. This might be the way in which the temperature affects the polymerization of the monomer **II**. The network II effective Mc and residual double bonds in dependence on monomer conversion presents Table III.

The shape of conversion curves was similar to that one observed for the ordinary autoaccelerated free radical polymerization course. Because a gel molecule approximates to an infinitely large molecule the network chain segments movement and limitations of reactants translation was intensified with a progress of the polymerization. The steep acceleration of the reaction in the crosslinking polymerization according to a convention is considered as the gel point. Thus, the large increase of polymerization rate in a later stage can be explained by a continuous increase of crosslinks density. The active free radicals concentration dramatically increased, but still free monomer translation diffusion made possible their recombination by means of reaction diffusion. Nevertheless, the monomer **II** in relation to the monomer **I** polymerization turned to the fast network forming phase after a longer reaction time. The delayed gel-point conversion in polymerization of monomer **II** is an evidence of the existence of significant primary cyclization reactions[19] that strongly affect the network structure and its resulting properties. The primary cyclization during the chains grow decreases network crosslinks density, increases swelling, heterogeneity, and share of microgels.[20–23]

In comparing the monomers **I** and **II** polymerization rates, the first one was substantially more active in the early monomer conversion phase before the

fast network forming stage. The monomer **II** polymerization rate was slowed down probably because of the methyl substituent effect on amide nitrogen rather than due to an influence of spacer chain length decrease.[24] Generally, the acrylamide N-substitution tend to suppress the rapid acrylamide propagation,[25,26] however the quantitative comparison of monomers with various molecular structures is very complex. It was concluded that N-substituents exert predominantly a steric effects on the chain grow. The chemical structure of the inner spacer sequences was considered with a lesser effect on vinyl group reactivity. Nevertheless the monomer **I**, **II**, and **III** reactivity comparison on this basis failed. The monomer **III** showed the highest polymerization activity in spite of short, only three methylene units connection of acrylamide groups. Moreover, the acrylamide nitrogen second substituent is the bulky ethyl group. Even at the mildest polymerization conditions conversion was closed to 90% during the initial 15 min (Table IV). This points out on a difficulty in forecasting the bis-acrylamide monomers **I**, **II**, and **III** polymerization reactivity by means of the other acrylamide molecular structure analogy.

Polymerization in calorimeter

The bulk polymerization investigation of monomers **I**, **II**, and **III** in calorimeter is an useful complement to gravimetry experiments. Heat flow data versus time were recorded isothermally during the polymerization. The temperature of 75°C was selected
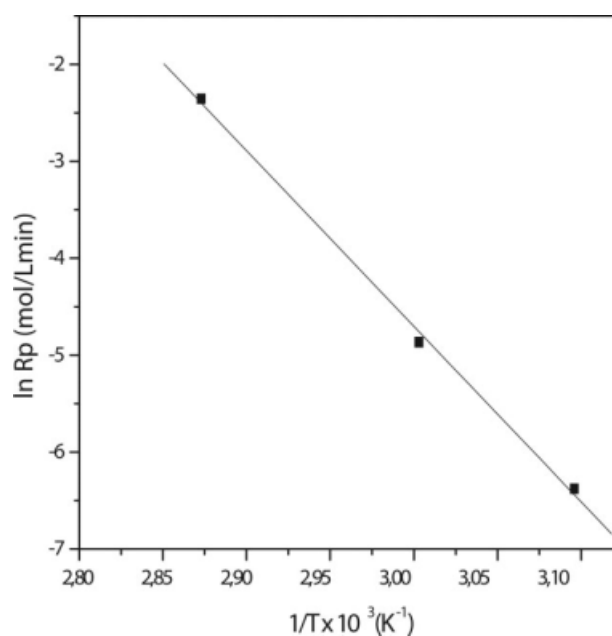
Figure 5 Instantaneous, early stage polymerization rate of monomer **II** as a functional of temperature at 22.5 mmol/L AIBN. An Arrhenius plot.

TABLE III
Molecular Weight Between Crosslinks M_c and Residual Unsaturation Found Out
in the Polymer Network Formed During the Monomer II Bulk Polymerization
in Glass Ampoules at Variety of Initiator AIBN Concentrations and Temperatures

AIBN (mmol/L)	Time (min)	Conversion (%)	$M_c \times 10^{-2}$ (g/mol)	Residual double bonds (%)	Remark
22.5	30	5.1	–	–	60°C
	45	5.7	3 640	–	
	60	11.8	1 310	17.6	
	120	23.7	143	14.1	
	180	78.0	8.57	12.9	
45.0	10	2.4	–	–	60°C
	30	9.2	2 770	–	
	40	16.2	367	23.0	
	90	67.6	21	16.9	
	120	81.7	9.52	13.3	
67.5	10	4.5	–	–	60°C
	30	22.9	1 790	21.6	
	40	44.5	51.1	18.8	
	90	87.7	8.49	–	
	120	91.5	8.54	13.2	
22.5	120	3.5	–	–	50°C
	180	4.4	10 100	11.8	
	240	8.6	2 300	–	
	300	12.7	615	9.9	
22.5	15	a	0.66	–	75°C
	30	a	0.75	1.6	
	60	a	0.47	–	
	75	a	0.42	1.7	
45.0	5	a	0.73	–	75°C
	10	a	0.77	4.9	
	25	a	0.53	5.6	
	35	a	0.38	–	

[a] Conversion closed to 100%.

because of all the monomers are in the molten state. The main parameters of released heat-time dependences are summarized in Table V. The time to attain the maximum of heat flow (peak time) and the heat flow peak read from DSC recorded curves were used to the polymerization rate estimation.

The shortest peak time with the highest heat flow rate at this point were evidenced throughout the monomer **III** polymerization. A gradual extension of the polymerization period before gel-point (time before the accelerated heat flow appeared) and the decreased instant heat flow rates sorts the studied bis(acrylamide)s according to reactivity in the following order: monomer **II** < monomer **I** < monomer **III**.

The determination of conversions based on integrated heat release, in present calorimetric experiments yielded very low values (Table VI). The increasing concentration of AIBN in polymerization batch caused in the monomer **III** polymerization a mild conversion increase from 51% to 63%. Weighting the polymer in the end of polymerization provides evidence that during polymerization the loss of monomer was insignificant. The analogical results were obtained for monomers **I** and **II**.

Because of the uncertainty about the present monomers heats of polymerization, the value for acrylamide polymerization in benzene, 13.8 ± 0.3 kcal/mol, was used in calculations. If the association of the monomer molecules through N—H⋯O type

TABLE IV
Molecular Weight Between Crosslinks M_c and Residual
Unsaturation Found Out in the Polymer Network
Formed During the Monomer III Bulk Polymerization
at Various Temperatures and at 22.5 mmol/L AIBN.
Glass Ampoule Experiments

T_p (°C)	Time (min)	Dry gel (wt %)	M_c (g/mol)	Residual double (bonds %)
50	30	100	300	9.0
	60	99.6	246	8.7
	90	98.0	243	6.0
60	15	94.6	184	12.3
	30	99.8	193	9.0
	60	89.2	162	8.2
75	15	86.6	289	11.3
	45	84.4	277	9.5
	90	92.3	221	9.2

TABLE V
Isothermal Bulk Polymerization of Monomers I, II, and III Followed by Calorimetry. The Main Parameters of the Released Heat Flow DSC Records and the Sol-Gel Analyses of Formed Polymers. Polymer Samples Were Swelled in Ethanol at 20–22°C. The Presented Data Were the Average of at Least Two Measurements

Monomer	T_p (°C)	AIBN (mmol/L)	Released heat (J/g)	Peak height (W/g)	Peak time (min)	Sol content (wt %)	M_c (g/mol)
I	75	5.6	207	0.55	1.27	17.0	30,300
		11.2	199	0.51	1.35	14.5	28,400
		22.5	266	1.10	0.91	7.0	19,500
		45.0	280	1.17	0.63	3.0	7450
		67.5	296	3.73	0.41	1.3	9800
II	75	22.5	364	0.42	22.04	11.5	244
		45.0	361	0.93	7.22	10.1	184
		67.5	393	1.61	4.28	6.3	208
III	75	22.5	249	7.85	0.23	–	–
		45.0	279	18.53	0.20	–	–
		67.5	307	20.40	0.13	4	235
III	60	22.5	253	0.36	8.10	20.4	62
		45.0	259	0..93	3.14	14.3	130
		67.5	258	1.54	2.65	9.4	325
I[a]	10°/min	0	350	1.43	19	22.7	1260
		22.5	266	1.10	0.91	0	1370

[a] Temperature ramping experiment, heating rate 10°C/min.

hydrogen bonding occurs, the appreciable increase in enthalpy can be anticipated. In that case, the calculated conversions should be even lower.[27]

The most problematic in the evaluation calorimetric records remains the requirement to specify the exact out set of reaction. This is basic to determine exact integral of heat evolved in polymerization. However, this uncertainty does not explain the discrepancy between calorimetry and gravimetry determined conversions, not even if the residual unsaturation observed in samples from ampoule experiments was considered. Several authors have pointed out that DSC technique monitors the polymerization rate rather than conversion and this method fail for conversion measurements in the case of very slow processes.[24,28] On the other hand, the DSC measurements with recording the dynamic of a polymerization are valuable in conversion curves determination. This is a very useful factor in the monomer polymerization behavior evaluation despite an uncertainty in the exact heat release determination. Bearing in the mind this fact, the results from calorimetry conform that of ampoule samples analyses only in trends.

The two last rows in Table V shows the DSC data recorded in the monomer **I** polymerization in dynamic mode. The heating rate of the batch was 10°C/min and a course of pure monomer **I** polymerization without initiator was compared with monomer containing 22.5 mmol/L AIBN. In the first case on the heat flow curve appeared endotherm (monomer melting point) with the minimum at 70.5°C. The exothermic process started at 135°C with the sharp increase from 180°C to the peak at 212°C and to the

zero heat flow at 260°C. The surprisingly great portion, 22.7 wt %, of the sample migrated to ethanol and the integrated released heat 350 J/g corresponds to 77.8% conversion (Table VI). The second in dynamic mode polymerized and with AIBN initiated batch transformed much more faster in completely insoluble product. Time to the heat release peak was 21 times shorter compared with the system without AIBN. Nearly, the same crosslinking degree as was

TABLE VI
Calculated Conversions, Based on Integrated Heat Released During the Monomer I, II, and III Polymerization in Calorimeter

Monomer	T_p (°C)	AIBN (mmol/L)	Released heat (J/g)	Conversion (%)
I	75	5.6	207	46.0
		11.2	199	44.2
		22.5	266	59.1
		45.0	280	62.2
		67.5	296	65.8
II	75	22.5	364	79.6
		45.0	361	79.0
		67.5	393	86.0
III	75	22.5	249	51.4
		45.0	279	57.6
		67.5	307	63.4
III	60	22.5	253	49.3
		45.0	259	53.53
		67.5	258	53.3
I[a]	10°/min	0	350	77.8
		22.5	266	59.1

[a] Temperature ramping experiment, heating rate 10°C/min.

formed in the previous polymer sample prepared without AIBN initiator was determined. This is quite understandable if we anticipate in the system with thermal initiator a substantially higher rate of initiation at lower temperature and higher concentration of immobilized free radicals attached to the network branches. These, primary hindered, later released by the gradual increase of the temperature become capable of grafting the nonreacted residual monomer trapped in the network. This is a nice example how the rate of initiation and polymerization temperature in the first stages of crosslinking polymerization influence the monomer conversion in the final polymer network.

Sol-gel analyses

The prepared polymer samples were analyzed on the average mechanically effective molecular weights M_c between crosslinks and residual double bonds in dependence on reaction time, respective monomer conversion (Tables I, III, and IV). It is worth to mention that the network crosslinks density $1/M_c$ is dependent only on monomer conversion (Fig. 6) independently on the initiator concentration and temperature.

The completely soluble polymer was formed below of about 5% monomer conversion. The detectable macroscopic weakly crosslinked (Mc of around 10^6 g/mol) network was observed already passing this conversion, independently on the reaction conditions. Despite this fact the steep acceleration of the polymerization was noted not earlier than following the 20% monomer conversion and the Mc decrease of about to 10^3 g/mol. Before speeding up the network formation the polymerization proceeded more or less at constant rate. As the formed polymer existed in the 3D network and soluble polymer was not observed, we concluded that all propagating chains were connected to the network. A high concentration of the monomer imbibed in the moderately crosslinked gel facilitated to maintain the steady state polymerization conditions at a relative low concentration of the propagating free radicals. This nicely correlates with reaction diffusion termination mechanism that operates if the macromolecules translation diffusion was suppressed.

The sol-gel analyses results of the monomer **III** polymerization products are collected in Table IV together with residual double bonds find out in polymer network. Specific to this monomer polymerization in comparison with monomers **I** and **II** is the highest polymerization rate. This fact make impossible to differentiate the early polymerization stages before reaching the gel-point. The M_c values indicate that formed polymers were densely cross-linked networks already right from the polymerization begin-
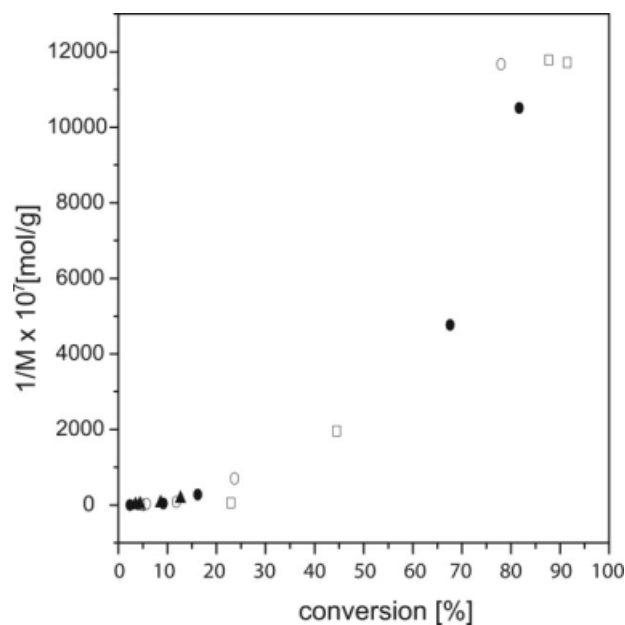
Figure 6 The polymer network **II** crosslinks density $1/M_c$ (mol/g) increase in dependence on conversion and for variable reaction conditions; 60°C and AIBN 22.5 ○, 45 □, 67.5 ● mmol/L; 50°C, AIBN 22.5 mmol/L ▲.

ning. The reaction time prolongation had no substantial effect on crosslinks density. Further, we did not observe significant differences in the course of reaction and the network density for all the used polymerization systems. Nevertheless, with increasing the polymerization temperature a slight tendency to decrease the extent of double bonds conversion exists. The fast network forming process proceeds, but only to limited conversion (86.6%), which was followed by period of slow monomer incorporation into the network structure. These facts indicated that at higher temperature the higher initiation rate promoted forming the network seeds and shorter the time to setting the gel point. The rigid network was formed more rapidly and mobility restrictions led to less effective consumption of the monomer and double bonds, especially at higher polymerization temperature.

The sol-gel analyses of networks removed from calorimeter pans show clearly that soluble portion in final products decreased with increasing the concentration of initiator, a frequent observation in the free radical crosslinking polymerization.

On the contrary, the molecular weight M_c between crosslinks in the network of monomer **III** exhibited the opposite tendency from compact to less crosslinked networks. This is connected likely to lasting polymerization period before setting the gel point and to fixing by crosslinking a temporary appeared free volume. Nevertheless, for network of monomers **I** and **II** exists an optimal initiator concentration in

the batch to form the most densely cross-linked network.

CONCLUSIONS

The deficiency of systematic studies of *N*-substituents effect on the (meth)acrylamide derivates free radical polymerization limited the monomers polymerization course prediction. The most of published data come from solution polymerization studies of the single vinyl group containing monomers. Nevertheless, similar studies for bi-functional acrylamides crosslinking polymerization in bulk lacking, as far as we know.

This work demonstrates a wide range of effects on kinetic, degree of crosslinking and extent of double bonds consumption during studied monomers polymerization. Polymerization kinetic dependences exhibited unusually large deviations from the course predicted by theory. For monomer **II**, with six-methylene chain spacer in the molecule structure, the reaction order to AIBN initiator is 1.28 and activation energy E_a was calculated 151 kJ/mol for early stages of polymerization (Figure 4, Table II). An analogous dependence for monomer **I** (the eight carbon–oxygen atoms spacer chain) showed even higher value 1.53, far from 0.5 mostly found in standard polymerization.

The reaction ran in the three subsequent stages. At first, the steady reaction rate was maintained up to 20% conversion. The soluble polymer was formed below 5% conversion. After that came the fast gel forming process that decelerate at roughly 80% monomer conversion. that followed by slow polymerization period to the nearly complete monomer consumption.

The monomer **II** compared with **I** was less active, round about one decimal order. The reaction rate was slowed down probably due to the methyl substituting effect on amid nitrogen rather than by an influence of the spacer chain length decrease. The increasing reaction temperature and decreasing initiator concentration favored an extent double bonds consumption and crosslinks density.

The monomer **III** showed the highest polymerization activity regardless of only short three methylene units chain connection of acrylamide groups and nitrogen the bulky ethyl group second substitute.

The increased polymerization activity according the reaction rate in the early polymerization stages ranks the studied monomers in the order: monomer **II** < monomer **I** < monomer **III**, based both on ampoules or calorimeter polymerizations.

The concentration and structure of microgel particles formed at the very beginning of polymerization were considered as the decisive way in which the polymerization kinetic was affected in later reaction stages. The acryl amide nitrogen substituents and spacer length between acrylamide groups seemed less important. So the rate of initiation, temperature, and initiator concentration, that govern microgel formation play an important role in the course and extent of crosslinking polymerization of the investigated monomers.

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