

POLYMERIZATION KINETICS OF N,N-DIETHYLACRYLAMIDE

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The kinetics of polymerization of N,N-diethylacrylamide in dimethyl sulphoxide and dimethylformamide was investigated as part of the investigation of the relationship between the monomer structure and kinetics of radical polymerization of N-substituted acrylamides and methacrylamides. The polymerization rate in dimethyl sulphoxide at 60°C is described by the equation $R_p = 6.85 \cdot 10^{-3} [M] \cdot [I]^{0.5}$. For the polymerization in dimethylformamide it holds $R_p = 9.5 \cdot 10^{-3} [M]^{1.18} \cdot [I]^{0.6}$. The activation energy of polymerization in dimethyl sulphoxide is 74.3 kJ · mol⁻¹. The polymerization course of N,N-diethylacrylamide is compared with the polymerization course of other N-substituted acrylamides or methacrylamides.

Polymers of N-substituted acrylamides and methacrylamides are interesting from the standpoint of biomedical applications^{1,2}. Kinetics of the radical solution polymerization of these monomers have been studied by a number of authors. Owing to the different reaction conditions used by the respective authors, no complex conclusions could be made as to the relationship between monomer structure and the kinetic course of polymerization. Kinetics of the radical polymerization of N-(2-hydroxypropyl)methacrylamide in water and in dimethylformamide³, of N-phenylmethacrylamide in acetonitrile⁴, and of 2-methacrylamido-2-(hydroxymethyl)-1,3-propanediol in dimethylformamide⁵ were determined. The effect of viscosity of the reaction medium on the polymerization of N-(hydroxymethyl)methacrylamide was also investigated⁶. The polymerization rates of a number of N-substituted acrylamides and methacrylamides were compared^{7,8}. The polymerization kinetics of N-tert-butylacrylamide⁹ and N,N-dimethylacrylamide¹⁰ were investigated in detail. Kinetics of the polymerization of N-ethylmethacrylamide¹¹, N-butylmethacrylamide¹¹, N-phenylmethacrylamide¹², N-ethylacrylamide¹² and N-butylacrylamide¹² were measured under comparable conditions. An investigation of the polymerization kinetics of N,N-diethylacrylamide reported in this paper supplements the papers referred to above^{11,12}.

EXPERIMENTAL

Chemicals. N,N-Diethylacrylamide was prepared by reacting diethylamine (2.2 mol) with acryloyl chloride (1 mol) in diethyl ether at -5°C; the monomer was purified by rectification

in vacuo (pressure $2.5 \cdot 10^2$ Pa, b.p. 64°C , Cu_2Cl_2 as inhibitor). Purity of the monomer determined by gas chromatography (gas chromatograph Perkin-Elmer F-11, columns 10% Apiezon (Chromosorb W) and Octoil S) was $>99.9\%$. 2,2'-Azobis(isobutyronitrile) (Lachema, Brno) was crystallized five times from ethanol. Dimethylsulphoxide (DMSO), Fluka A. G., reagent grade, was purified by rectification at reduced pressure ($4 \cdot 10^2$ Pa) and dried over a molecular sieve Nalsit 4; it was freshly distilled before use. N,N-Dimethylformamide (DMF) was purified by employing a standard procedure¹³. The other solvents were distilled.

Polymerization. The polymerization was carried out in lens-shaped dilatometers at $60 \pm 0.1^\circ\text{C}$. Oxygen was removed from the polymerization mixture by repeated evacuation (pressure $6 \cdot 10^{-3}$ Pa, liquid nitrogen temperature). The change in volume corresponding to 1% conversion in the polymerization of 1 g of monomer is 0.00159 ml. The polymerization was stopped at 5–7% conversion by immersing the dilatometer into liquid nitrogen. The polymer was precipitated into water at 40°C and dried by lyophilization. The weight average molecular weights were determined by the light-scattering method in dimethylformamide with a Wippler-Scheibling apparatus.

RESULTS AND DISCUSSION

In measuring the polymerization kinetics we determined, for the polymerization rate, the constants of the basic equation:

$$R_p = K \cdot [M]^m \cdot [I]^n \quad (1)$$

(R_p is the polymerization rate, K is the overall rate constant of polymerization, $[M]$ is the monomer concentration, $[I]$ is the initiator concentration, m and n respectively are the reaction orders with respect to monomer and to initiator). The polymerization rates were determined as slopes of the linear dependences of losses in the monomer concentrations in the polymerization mixture on time; the initial compositions of the polymerization mixtures and the corresponding polymerization rates are given in Table I. The reaction order with respect to monomer was determined from the dependence $\log R_p$ vs $\log [M]$ at $[I] = \text{const.}$; the reaction order with respect to initiator was assessed from the dependence $\log R_p$ vs $\log [I]$ on the condition $[M] = \text{const.}$ (degree of reaction 7% at utmost). The overall rate constant of polymerization was ascertained from the dependence R_p vs $[M]^m \cdot [I]^n$. The activation energy was calculated assuming that the reaction order (m, n) did not change with temperature. The activation energy of polymerization was determined from the polymerization rates at 40, 50, 60 and 70°C .

The effect of the reaction medium on the polymerization kinetics was estimated by means of comparison between the polymerization kinetics in dimethyl sulphoxide and in dimethylformamide (Table II).

The polymerization kinetics measured in DMSO is controlled by the basic theoretical relationship ($m = 1.0, n = 0.5$) valid for the kinetics of radical polymerization¹⁴. However, in the polymerization in DMF deviations from the basic theoretical

equation ($m = 1.18$, $n = 0.60$) appear in the reaction orders with respect to monomer and to initiator. These deviations may be due to a number of factors^{1,5}. We believe that the polymerization kinetics in DMF is influenced by the high transfer to solvent (mol.weight of the polymer prepared in DMF is lower by an order of magnitude than that of the polymer in DMSO, Table I). Some effect on the polymerization course should also be assigned to the initial viscosity of the polymerization mixture (dependence of the viscosity of the polymerization mixture on the monomer con-

TABLE I

Polymerization Kinetics of N,N-Diethylacrylamide

$[M]_0$ and $[I]_0$ are the starting concentrations of monomer and initiator respectively, R_p is the polymerization rate, \bar{M}_w is the weight average molecular weight.

$[M]_0$ mol l ⁻¹	$[I]_0 \cdot 10^4$ mol l ⁻¹	$R_p \cdot 10^4$ mol l ⁻¹ s ⁻¹	$\bar{M}_w \cdot 10^{-6}$
Solvent: DMSO			
2.238	12.618	5.40	2.17
2.251	6.917	4.17	—
2.244	6.852	4.13	2.30
2.241	3.866	2.96	2.17
2.252	3.043	3.02	—
2.250	2.411	2.51	2.50
2.255	1.460	1.75	—
3.896	5.102	6.02	2.86
2.555	4.969	3.71	2.50
2.473	5.178	3.64	2.27
1.056	5.028	1.48	—
1.034	5.075	1.62	2.00
0.707	5.190	1.02	2.08
Solvent: DMF			
2.251	11.431	4.61	0.36
2.261	6.774	3.13	—
2.260	3.586	2.17	—
2.261	1.999	1.46	0.38
3.162	4.972	3.69	0.54
2.237	5.182	3.35	0.42
1.400	4.996	1.23	0.20
1.331	5.188	1.30	—
0.773	5.178	0.70	—

TABLE II

Comparison of Measured Kinetic Data of N,N-Diethylacrylamide with the Other Acrylamides and Methacrylamides under Investigation

Conditions of comparison of the polymerization rate: $[M] = 2.56 \text{ mol l}^{-1}$, $[I] = 6.15 \cdot 10^{-4} \text{ mol l}^{-1}$, 60°C .

Amide	Solvent	m	n	$K \cdot 10^4$ $\text{l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$	$R_p \cdot 10^4$ $\text{mol}^{-1} \text{ l}^{-1} \text{ s}^{-1}$	E_a kJ mol^{-1}	Reference
N-Ethylacryl	DMSO	1.15	0.50	84.9	6.25	—	12
N-Butylacryl	DMSO	—	—	—	3.71	—	12
N,N-Diethyl- acryl	DMSO	1.00	0.50	68.5	4.35	74.3	this paper
	DMF	1.18	0.60	95.0	3.41	—	
N-Phenyl- methacryl	DMSO	1.15	0.50	8.06	0.589	71.4	11
N-Ethyl- methacryl	DMSO	1.15	0.50	3.62	0.264	68.3	11
N-Butyl- methacryl	methanol	1.50	0.50	1.54	0.156	81.6	
N-Butyl- methacryl	DMSO	1.15	0.50	2.42	0.177	77.3	11
	methanol	1.50	0.50	1.32	0.134	68.0	

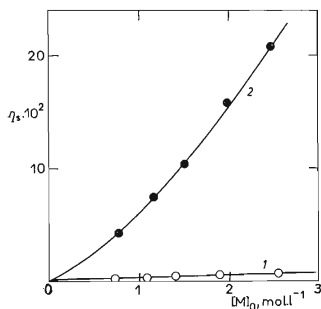


FIG. 1

Dependence of Specific Viscosity of the Polymerization Mixture on the Starting Monomer Concentration

Solvent: 1 DMSO, 2 DMF.

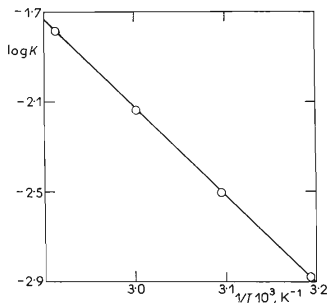


FIG. 2

Determination of the Activation Energy of Polymerization of N,N-Diethylacrylamide in Dimethyl Sulphoxide

centration, Fig. 1), because the relationship¹⁶ between R_p and the product $\eta^{0.5} [M]$ is a linear one. The effect of other factors on the magnitude of the reaction orders with respect to monomer and to initiator cannot be ruled out either, however, such as *e.g.* the cage effect or a degradative transfer to solvent, which is also indicated by a slightly increasing reaction order with respect to initiator in the polymerization in DMF.

The dependence of the molecular weight of the polymer on the monomer or initiator concentration in the starting mixture in the case of DMSO as solvent is not too pronounced (Table I). This phenomenon may be related with the high rate constant of the propagation reaction. If we use dimethylformamide as solvent the changes of molecular weights are strongly dependent on the amount of DMF in the starting mixture (Table I). In this case the influence of the relatively high transfer to solvent is the decisive one.

The activation energy of the polymerization of N,N-diethylacrylamide in DMSO calculated from the Arrhenius equation (Fig. 2) is 74.3 kJ mol^{-1} . This value is comparable with those obtained for the polymerizations of other N-substituted acryl- and methacrylamides^{11,12}. The results obtained by measurements of the polymerization kinetics of a series of N-substituted acrylamides and methacrylamides under comparable conditions are summarized in Table II.

The overall rate constant of the solution polymerization of N,N-diethylacrylamide agrees as to its order of magnitude with the polymerization constant of N-ethylacrylamide and is considerably higher than that of N-substituted methacrylamides. By comparing the polymerization rates (under similar conditions) of the above monomers, one may infer that the conclusive influence on the polymerization rate should be assigned to the substitution of hydrogen on α -C of acrylamide with the methyl group. Compared with acrylamides, the polymerization rate of methacrylamides (both substituted and unsubstituted) is lower by an order of magnitude.

The polymerization rate in the individual groups of monomers (acrylamides or methacrylamides) is probably influenced not only by the steric effect, but also by the polar and resonance effects. The steric hindrance effect appears in monomers the substituents of which exhibit the electron donor effect (N-butylsubstituted amides polymerize slower than N-ethylsubstituted amides). On the other hand, however, a change in the polarity of the reaction medium leads to a change in the ratio of the polymerization rates (*cf.* polymerization in DMSO and in methanol, Table II). N-Phenylmethacrylamide, a monomer exhibiting an opposite electron effect, polymerizes faster than the other N-substituted methacrylamides under investigation.

The following can be postulated as a conclusion from the series of three papers dealing with the kinetics of radical polymerization of selected N-substituted acrylamides or methacrylamides in solution^{11,12}:

The reaction order with respect to initiator in the polymerization of N-substituted acrylamides and methacrylamides is 0.5 with the exception of the polymerization

of N,N-diethylacrylamide in DMF (Table II). The reaction order with respect to monomer is not affected by the type of the substituent, but varies depending on the type of the solvent used. N-substituted acrylamides polymerize faster by an order of magnitude than the respective methacrylamides (N,N-disubstituted methacrylamides under the usual conditions of radical polymerization do not polymerize at all or form only oligomers¹⁷). The polymerization rate of N-substituted acrylamides and N-substituted methacrylamides is controlled by the size of the aliphatic substituent on the nitrogen atom of the amide group. An aromatic substituent increases the polymerization rate. N-substituted acrylamides have higher molecular weights than the respective methacrylamides with the exception of N-phenyl methacrylamide. The activation energies of polymerization of the monomers discussed above lie within 60–90 kJ mol⁻¹, which is usual for radical polymerizations.

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