

POLYMERIZATION KINETICS OF N-ETHYLACRYLAMIDE

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The kinetics of the radical polymerization of N-ethylacrylamide in dimethyl sulphoxide at 60°C was studied. The overall rate constant was found to be $8.49 \pm 0.30 \cdot 10^{-3} \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$; $k_p/k_t^{1/2} = 0.815 \pm 0.120 \text{ l mol}^{-1/2} \text{ s}^{-1/2}$; $k_i = 1.09 \pm 0.40 \cdot 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$. The comparison of the above values with results obtained earlier for N-ethylmethacrylamide allowed a conclusion to be drawn about the effect of the $-\text{CH}_3$ group bonded in the α -position on the course of kinetics of radical polymerization.

It follows from results published earlier^{1,2} that $k_p/k_t^{1/2}$ at 25°C for acrylamide is $4.7 \text{ l}^{1/2} \cdot \text{mol}^{-1/2} \text{ s}^{-1/2}$, while for methacrylamide it is $0.2 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$. The difference of one order of magnitude between these constants can be assigned to a difference between the rate constants of propagation of these monomers. This is confirmed by data on the polymerization rate and on molecular weights; both these quantities are considerably higher for acrylamide³. Although the controversial data appearing in the literature allow to assume that conclusions for acrylamide and methacrylamide may give a clue for the characterization of the polymerization behaviour of N-substituted methacrylamides and N-substituted acrylamides⁴, the problem has not yet been studied in sufficient detail and the results obtained so far are not unequivocal. The $k_p/k_t^{1/2}$ value for the polymerization of N-tert-butylacrylamide⁵ is $0.63 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$, which is very close to the value obtained for methacrylamide². Also a comparison of the polymerization behaviour of N-cyclohexyl-, N-tert-butyl- and N-tert-heptylacrylamides and methacrylamides has shown that the differences observed for acrylamide and methacrylamide are considerably reduced by substitution at the nitrogen atom.

In order to contribute to the elucidation of the effect of the substitution at the α -carbon atom of N-substituted acrylamides with the methyl group on the course of polymerization, we investigated the kinetics of the radical polymerization of N-ethylacrylamide in dimethyl sulphoxide and confronted the conclusions thus obtained with the results obtained by studying the polymerization of N-ethylmethacrylamide⁶, N-butylmethacrylamide⁶, N-phenylmethacrylamide⁶ and N-(2-hydroxypropyl)methacrylamide⁷.

EXPERIMENTAL

Materials and Methods

N-ethylacrylamide was prepared by a reaction of ethyl amine with acryloyl chloride in benzene solution at -5°C (procedure similar to the preparation of N-ethylmethacrylamide⁶). The mono-

mer used for the polymerization experiments was rectified five times on a 0.5 m column packed with Helli-pack coils (Cu_2Cl_2 as inhibitor), b.p. $69^\circ\text{C}/93.3\text{ Pa}$, $d_{25} 0.947\text{ g/cm}^3$. The purity of the monomer was checked by gas chromatography¹; the monomer did not contain any detectable admixtures. 2,2'-Azobis(isobutyronitrile), Lachema, Brno, crystallized five times from ethanol, was used as initiator. Dimethyl sulphoxide, reagent grade, Lachema Brno, was dried by distillation with 10% benzene, repeatedly rectified on a 1 m column packed with stainless steel coils at 1.33 kPa, stored over a molecular sieve Potasit 3 and freshly distilled immediately before use.

The polymerization was carried out in lens-shaped dilatometers at $60 \pm 0.02^\circ\text{C}$. On filling, the dissolved oxygen was removed from the dilatometers by evacuating them five times (pressure $6.67 \cdot 10^{-3}\text{ Pa}$, liquid nitrogen temperature); catalytically purified nitrogen was used for balancing the pressure. After that the dilatometers were sealed. On reaching a 5–7% conversion the polymerization was stopped by immersing the dilatometers into liquid nitrogen. On defreezing the polymer was precipitated from the dimethyl sulphoxide solution into a twentyfold excess of dry ether, dried *in vacuo* after separation to constant weight and weighed. A contraction of 0.00135 cm^3 corresponds to a 1% conversion of 1 g of the monomer.

Linear dependences were calculated by the least squares method and the experimental error was determined as standard deviation.

Weight average molecular weights were determined by the light-scattering method on a Wippler-Scheibling apparatus. Number average molecular weights were determined osmotically in methanol (or methylcellosolve) solution with an automatic Knauer osmometer.

RESULTS AND DISCUSSION

The dependence of polymer concentrations on time during the polymerization of N-ethylacrylamide in dimethyl sulphoxide at various monomer concentrations (Fig. 1a) and various initiator concentrations (Fig. 1b) are reproducible; rate in the region of conversions $>1.5\%$ corresponds to the stationary region. Therefore, the polymerization rates of the individual experiments were read from the linear part of the $-(d[M]/dt)$ vs t dependence within the conversion range 1.5–8%. Fig. 1b shows clearly that in the first minutes of polymerization (approx. to 1.5% conversion) the polymerization rate is lower than in the conversion region 1.5–20%. An explanation of this phenomenon should be sought either in the impurities of the polymerization mixture, in not observing constant temperature, or in a diffusion-controlled termination reaction in the region above 1.5% conversion. Even though the time during which the polymerization proceeds at a lower rate is relatively short (8–10 min), we concentrated our efforts on explaining this phenomenon, which in the case of a gravimetric investigation of the course of polymerization⁵ may lead to errors.

During the rectification of the monomer (*cf.* Experimental) spontaneous purification by prepolymerization took place, because each time some 10% of the batch polymerized; with the monomer obtained after the third and fifth rectification, identical and completely reproducible dependences of the monomer loss on time were obtained. The solvent used was carefully purified, and the polymerization mixture was thoroughly degassed.

By using a thermocouple immersed in the polymerization mixture it was verified that the temperature of the mixtures was always constant. The possibility of the diffusion control of termination starting already at a 1.5% conversion was verified by mea-

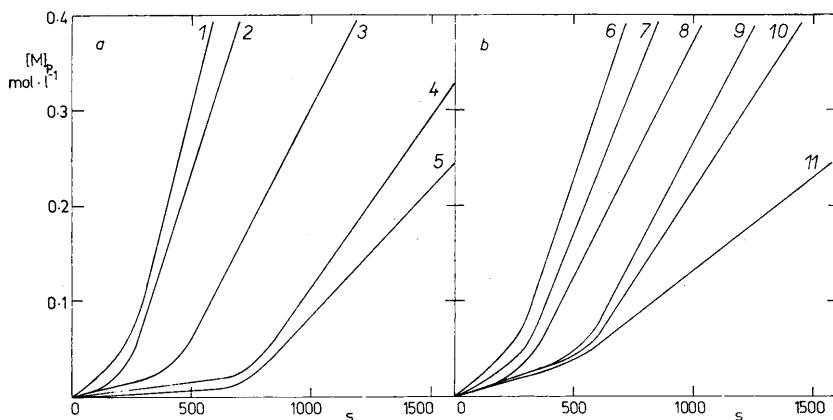


FIG. 1

Time Dependence of the Concentration of Monomer Repeat Units Incorporated in the Polymer in the Polymerization of N-Ethylacrylamide in Dimethyl Sulphoxide at 60°C

a $[I] = 4.1 \cdot 10^{-4}$ mol/l; $[M]$, mol/l: 1 5.06, 2 3.80, 3 2.59, 4 2.04, 5 1.50; *b* $[M] = 2.7$ mol/l; $[I] \cdot 10^4$, mol/l: 6 8.06, 7 6.24, 8 4.24, 9 3.57, 10 2.43, 11 0.631.

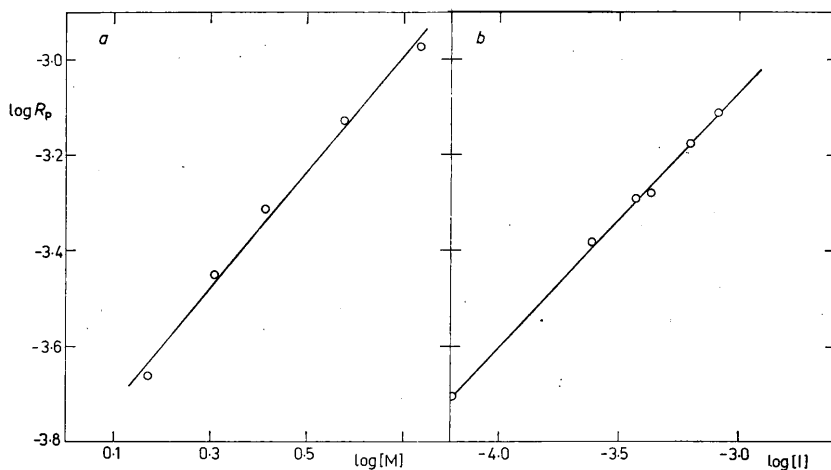


FIG. 2

Overall Rate of Polymerization (R_p) of N-Ethylacrylamide in Dimethyl Sulphoxide at 60°C

a $[I] = 4.1 \cdot 10^{-4}$ mol/l; *b* $[M] = 2.7$ mol/l.

asuring the molecular weights of polymers prepared by the polymerization of the same mixture to various conversions. For a polymerization mixture containing 2.32 mol/l of monomer and $4.0 \cdot 10^{-4}$ mol/l of initiator the molecular weights (\bar{M}_w) at conversions of 2,8 and 14% lay within the range $4.35 - 4.4 \cdot 10^5$. The result suggests that within such range of conversions the concentration of radicals is constant. The experiments described above do not still allow an unambiguous decision as to the source of the decrease in the polymerization rate within the conversion range <1.5 . The presence of undetectable admixtures in the monomer, the effect of the monomer structure (amide-iminol tautomerism) and the polymerization by route of micellar mechanism can each one be regarded as responsible.

The reaction rate with respect to initiator (I) for the polymerization of N-ethylacrylamide is 0.5 (Fig. 2a), the reaction rate with respect to monomer (M) is 1.15 (Fig. 2b); this value corresponds both to the values for N-substituted methacrylamides⁶ and to that obtained for the polymerization of acrylamide⁸. The overall rate constant of polymerization, K_c , in the relationship

$$R_p = K_c [M]^m [I]^n \quad (I)$$

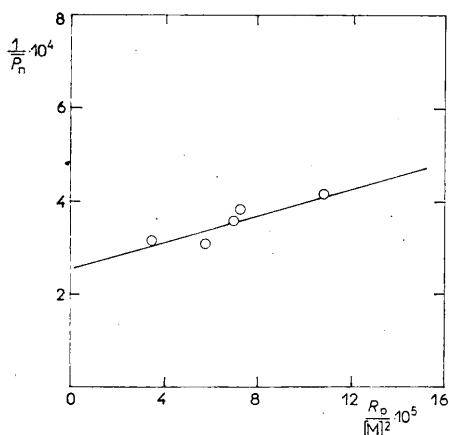


FIG. 3

Determination of the Ratio of the Rate Constants, $k_p/k_t^{1/2}$, during the Polymerization of N-Ethylacrylamide in Dimethyl Sulphoxide at 60°C

$[M] = 2.7$ mol/l; P_n is the number average degree of polymerization, R_p is the overall rate of polymerization.

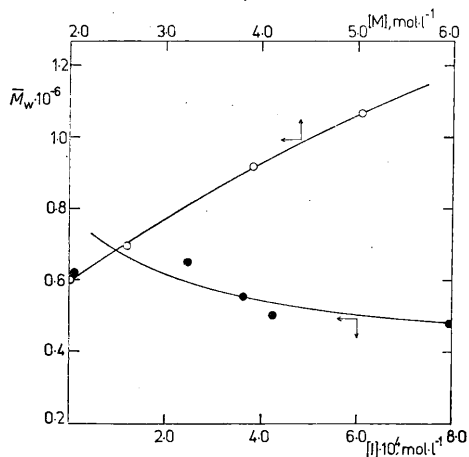


FIG. 4

Polymerization of N-Ethylacrylamide in Dimethyl Sulphoxide at 60°C

Dependence of molecular weight (\bar{M}_w) on the initiator concentration $[I]$ in the starting mixture (\bullet , $[M] = 2.7$ mol/l) and on the monomer concentration in the starting mixture (\circ , $[I] = 4.1 \cdot 10^{-4}$ mol/l).

and calculated from data given in Figs 1 and 2 is $8.49 \pm 0.30 \cdot 10^{-3} \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$. This value is higher approximately by one order of magnitude than that for N-ethylmethacrylamide. Owing to the comparable termination constants (k_t) for the polymerization of acrylamide and methacrylamide³ one can — assuming that the same is true for N-substituted derivatives — draw a conclusion that the increase in K_c is above all due to an increase in the rate constant of propagation (k_p) of N-ethylacrylamide. The contribution of a different rate constant of initiation (k_i) cannot however be ruled out.

We have ascertained experimentally that the polydispersity of poly(N-ethylacrylamide) samples is approximately 2. From papers of other authors^{9,10} we assumed termination by disproportionation, which allowed us to calculate $k_p/k_t^{1/2}$ $0.815 \pm \pm 0.120 \text{ l mol}^{-1/2} \text{ s}^{-1/2}$ (Fig. 3). The same value for N-ethylmethacrylamide¹ under comparable conditions (60°C, DMSO) is $0.108 \pm 0.008 \text{ l mol}^{-1/2} \text{ s}^{-1/2}$. The higher value of the above ratio obtained for N-ethylacrylamide can be assigned to the higher propagation constant. k_i calculated from K_c and $k_p/k_t^{1/2}$ was $1.09 \pm 0.40 \cdot 10^{-4} \text{ s}^{-1}$, which is higher than that for N-ethylmethacrylamide ($1.17 \pm 0.24 \cdot 10^{-5} \text{ s}^{-1}$); this confirms the above assumption that both k_p and k_i participate in increasing the overall rate constant of polymerization (k_p). The rate constants for N-ethylacrylamide and N-ethylmethacrylamide can be compared in Table I.

TABLE I
Rate Constants of the Polymerization of Acrylamides in Dimethyl Sulphoxide (60°C)

Monomer	$K_c \cdot 10^4$ $\text{l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$	$k_p/k_t^{1/2}$ $\text{l}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$	$k_i \cdot 10^4$ s^{-1}
N-Ethylmethacrylamide ^a	3.61 ± 0.10	0.108 ± 0.010	0.117 ± 0.025
N-Ethylacrylamide	84.9 ± 3.0	0.815 ± 0.120	1.09 ± 0.40

^a Ref.⁶.

Dependences of the molecular weights of poly(N-ethylacrylamide) on the monomer and initiator concentrations are given in Fig. 4. The molecular weights of poly(N-ethylacrylamide) are only a little higher than those of poly(N-ethylmethacrylamide)⁶. This phenomenon can undoubtedly be explained by the participation of transfer reactions in the former case. The substitution of the methyl group at the α -carbon atom of N-substituted methacrylamides with a hydrogen atom considerably increases the rate constant of propagation while influencing also the rate constant of initiation. The reaction rates with respect to monomer are the same for both N-ethylacrylamide and N-ethylmethacrylamide. Under comparable conditions the rate of polymerization

of N-ethylacrylamide is approximately twenty times higher than that of N-ethylmethacrylamide. Owing to the transfer reactions in the former case there is only a small difference between \bar{M}_w of both polymers. Also in the series of alkylacrylamides a bulkier substituent reduces the rate of polymerization. Under comparable conditions the rate of polymerization of N-ethylacrylamide is twice as high as that of N-butylacrylamide¹¹.

REFERENCES

1. Dainton F. S., Tordorff M.: *Trans. Faraday Soc.* 53, 499 (1957).
2. Dainton F. S., Sisley W. D.: *Trans. Faraday Soc.* 59, 1377 (1963).
3. Yocum R. M., Nyquist E. B. (Eds): *Functional Monomers*, Vol. 1. Marcel Dekker, New York 1973.
4. Zurakovska-Orszagh J.: *International Symposium Macromolecular Chemistry*, Budapest 1964, Preprints 4, 61.
5. Cavell E. A., Gilson I. T.: *Makromol. Chem.* 119, 153 (1968).
6. Ulbrich K., Kopeček J.: *Eur. Polym. J.*, in press.
7. Kopeček J., Bažilová H.: *Eur. Polym. J.* 9, 7 (1973).
8. Riggs J. P., Rodriguez F.: *J. Polym. Sci. Part A-1*, 5, 3151 (1967).
9. Cavell E. A. S.: *Makromol. Chem.* 54, 70 (1962).
10. Rossler D. F., Suen T. J.: *J. Appl. Polym. Sci.* 3, 126 (1960).
11. Ulbrich K., Kopeček J.: Unpublished results.

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