

Polymerization of vinyl monomers initiated by the system of *N*-bromosuccinimide (*N*-bromocaprolactam) and hydroperoxides

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Received 7 November 1975

Dedicated to Professor RNDr. J. Gašperík on his 70th birthday

It has been ascertained that *N*-bromosuccinimide accelerates the polymerization of vinyl monomers initiated by hydroperoxides, the maximum rate of polymerization being at the ratio of about one to two moles of *N*-bromosuccinimide for one mole of α -cumyl hydroperoxide. The same range of molar ratios for both initiating compounds corresponds also to the maximum rate of decomposition of α -cumyl hydroperoxide. The synergistic effect in the action of both initiators has been explained by the formation of an active and thermally labile initiator in a fast chemical reaction of both components of an initiator system. As a consequence, the species retarding the polymerization originate in subsequent reactions of some by-product with surplus component of the initiator system at the initial concentrations of α -cumyl hydroperoxide and *N*-bromosuccinimide above and below the given ratio.

Установился синергизм воздействия *N*-бромсукцинимида (или *N*-бромкапролактама) и гидроперекисей на скорость полимеризации виниловых мономеров. Максимальная скорость полимеризации достигается при молярном отношении инициаторов: один наиболее два моля *N*-бромсукцинимида на один моль кумилгидроперекиси. В подобной области молярных отношений смеси инициаторов наблюдалось наиболее быстрое разложение кумилгидроперекиси. Синергическое воздействие объясняется активным и термически нестабильным инициатором, который образуется ускоренной химической реакцией обоих компонентов иницированной системы. При высшем молярном отношении кумилгидроперекиси или *N*-бромсукцинимида возникают последовательными реакциями промежуточного продукта с избыточным компонентом замедлители полимеризации.

As early as in 1960 *Dannley and Esayian* [1] found that *N*-bromosuccinimide (NBS) initiated the radical polymerization of methyl methacrylate still inhibiting the polymerization of styrene. This observation was interpreted in terms of both the different stability and the reactivity of succinimidyl radicals produced in homolysis of N—Br bond with respect to corresponding monomer. Alternatively, the initiation effect of NBS in polymerization of methyl methacrylate may be explained also by a radical decomposition of an electron donor acceptor complex of NBS with monomer [2].

The rate of formation of active radicals from NBS may be considerably increased by its interaction with some co-agent as it was observed *e.g.* in the case of reduced nickel which efficiently transformed bromine atoms into corresponding anions and eliminated thus a competitive brominating process [3].

The present work was stimulated by the above-mentioned idea of an increased production of radicals in bimolecular reaction of NBS with a suitable compound. As a co-agent to *N*-bromosuccinimide or *N*-bromocaprolactam, hydroperoxides have been chosen because of a fairly good understanding of their initiating action in the polymerization of vinyl monomers.

Experimental

N-Bromosuccinimide was prepared by bromination of succinimide [4]. Recrystallization of the product yielded a compound with m.p. 171–173°C. The content of active substance determined iodometrically was 92.6%.

The preparation of *N*-bromocaprolactam was described in [5].

α -Cumyl hydroperoxide was purified *via* its sodium salt and distilled *in vacuo*. The purity of product was 95.4%.

The rate of α -cumyl hydroperoxide decomposition was followed by a iodometrical determination of peroxides, *i.e.* by the titration of iodine liberated. The procedure was adapted in such a way that hydroperoxide in benzene solution reacted with an excess of crystalline potassium iodide in glacial acetic acid. In the course of determination the solutions were bubbled through by a mild stream of nitrogen. Iodine is liberated from KI quantitatively also by *N*-bromosuccinimide [6] and in mixtures with hydroperoxides the total concentration of both compounds has been determined.

After removing of inhibitors and drying, monomers as methyl methacrylate, *n*-butyl methacrylate, ethyl and butyl acrylates were distilled twice under reduced pressure in a nitrogen atmosphere. The medium fraction from the second distillation was used for polymerization.

Vinyl acetate was purified twice under nitrogen on a rectification column with 50 theoretical plates at the reflux 2. The fraction used had b.p. 71.8–72.0°C at a pressure of 99 kPa.

Monomers were polymerized in glass ampules sealed under nitrogen. Polymerization was performed in a thermostated bath. At the dosing as well as during the polymerization the content of ampules was protected against the light effect. After precipitation of polymer by isooctane the conversion of monomer was determined gravimetrically.

The e.s.r. measurements were carried out at room temperature using a spectrometer Varian E-4.

Results

Polymerization experiments

The polymerization of methyl methacrylate is initiated either by α -cumyl hydroperoxide or *N*-bromosuccinimide itself. The synergistic effect consisting in a considerable increase of the polymerization rate surpassing the sum of polymerization rates due to individual initiators was observed when mixing these two initiators with monomer (Fig. 1). Maximum effect has been observed at molar ratios ranging from 1 to 2 moles of *N*-bromosuccinimide for 1 mole of α -cumyl hydroperoxide at a concentration of 10 mmol dm⁻³ at 60°C the rate of polymerization of methyl methacrylate is more than 5 times higher as compared to the sum of the individual rates of polymerization. Qualitatively the

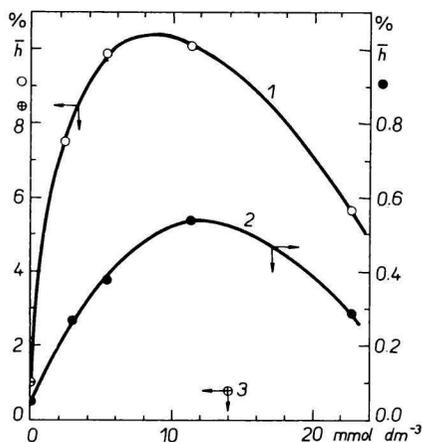


Fig. 1. Dependence of initial rate of polymerization of methyl methacrylate initiated by α -cumyl hydroperoxide ($5.36 \text{ mmol dm}^{-3}$) on concentration of *N*-bromosuccinimide. Temperature 60°C (1) and 20°C (2); point 3 corresponds to the rate of polymerization initiated by *N*-bromosuccinimide alone at 60°C .

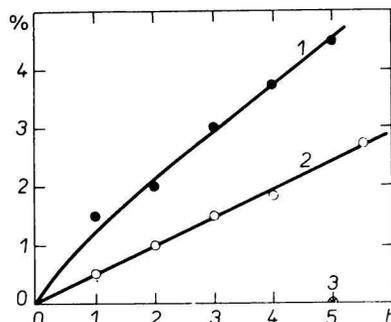


Fig. 2. Conversion curves of polymerization of methyl methacrylate. Initiator: *N*-bromosuccinimide (33 mmol dm^{-3}) and α -cumyl hydroperoxide (57 mmol dm^{-3}) (curve 1) or *tert*-butyl hydroperoxide (38 mmol dm^{-3}) (curve 2). Temperature 40°C ; point 3 corresponds to conversion due to *tert*-butyl hydroperoxide alone.

same dependence was observed also at 80°C (Table 1) and at 20°C (Fig. 1). Provided that succinimide was used instead of *N*-bromosuccinimide no increase of the polymerization rate was observed.

Similar synergism as the one displayed by *N*-bromosuccinimide in the presence of hydroperoxides was observed also with *N*-bromocaprolactam (Table 2). The effect of the latter is, however, quantitatively less expressed. Likewise as for succinimide, caprolactam itself has no perceivable influence on the rate of polymerization catalyzed by α -cumyl hydroperoxide. A 10-fold increase in initial concentrations of both initiators (*N*-bromocaprolactam, α -cumyl hydroperoxide) or their equimolar mixtures leads to about 3-fold increase in the polymerization rate. This corresponds to the frequently observed square root dependence of the polymerization rate on the initiator concentration.

Synergism of *N*-bromosuccinimide is not specific only for polymerization of methyl methacrylate initiated by α -cumyl hydroperoxide, but becomes evident also in systems containing *tert*-butyl hydroperoxide (Fig. 2) or benzoyl peroxide (Table 3) and the acceleration of initiation may be observed

Table 1

Conversion of methyl methacrylate in dependence on concentration of *N*-bromosuccinimide (NBS) in the presence of $5.36 \text{ mmol dm}^{-3}$ α -cumyl hydroperoxide after 1 hr of polymerization at 80°C

NBS mmol dm^{-3}	Conversion %
—	5.1
2.81	19.1
5.62	27.6
11.24	14.9
22.48	10.4

Table 2

Conversion of methyl methacrylate (MMA) at 60°C after 6 hrs of polymerization in dependence on different concentrations of *N*-bromocaprolactam (BrC) and α -cumyl hydroperoxide (CHP)

Initiator mmol dm ⁻³		Conversion %	
BrC	CHP	calculated ^a	found
—	—	—	0.05 ^b
—	5.36	—	3.6
—	53.6	—	10.2
5.73	—	—	3.2
	5.36	6.8	8.6
	53.6	13.4	18.3
57.3	—	—	9.3
	5.36	12.9	20.0
	53.6	19.5	35.3

a) Sum of conversions at the separate action of individual initiators.

b) Thermal polymerization.

Table 3

Dependence of the conversion of methyl methacrylate on concentration of *N*-bromosuccinimide (NBS) at 60°C and concentration of benzoyl peroxide 4.13 mmol dm⁻³ MMA

NBS mmol dm ⁻³	Conversion, %		
	1 hr	2 hrs	4 hrs
—	3.32	9.1	21.2
1.4	6.14	10.3	23.2
2.8	7.59	12.0	23.4
28.0	9.47	13.5	25.9

Table 4

Conversion of monomers at 60°C after 6 hrs of polymerization ; initiation system : α -cumyl hydroperoxide (4.8 mmol dm⁻³) and *N*-bromosuccinimide (5.0 mmol dm⁻³)

Monomer	Conversion, % ^a
Vinyl acetate	3.0
Butyl methacrylate	5.5
Butyl acrylate	32.5
Ethyl acrylate	37.5

a) In the presence of only α -cumyl hydroperoxide conversion was below 0.1%.

Table 5

Rate of polymerization of methyl methacrylate and activation energies E at initiation with 5.62 mmol dm⁻³ *N*-bromosuccinimide and α -cumyl hydroperoxide (CHP)

CHP mmol dm ⁻³	% h			E kJ mol ⁻¹
	20°C	60°C	80°C	
5.29	0.66	10.5	27.6	53 ± 4
52.9	0.31	2.1	7.0	48 ± 4

*) Rate of polymerization at a conversion of about 10%.

Table 6

Effect of amines (triethylamine — TEA and piperidine — PIP) and acetic anhydride (AcA) on the rate of polymerization of methyl methacrylate initiated by α -cumyl hydroperoxide (11 mmol dm⁻³) and *N*-bromosuccinimide (5.62 mmol dm⁻³); E — activation energy of polymerization

Amine		AcA mmol dm ⁻³	% h ⁻¹			E kJ mol ⁻¹
TEA	PIP		20°C	40°C	60°C	
mmol dm ⁻³						
—	—	—	0.62	2.8	10.7	58
2.90	—	—	0.31	1.1	4.7	56
2.90	—	5.3	0.47	2.3	7.1	55
—	3.79	—	0.22	0.88	3.0	53
—	3.79	5.3	0.47	2.8	8.1	57

also with other monomers (Table 4). The synergistic system initiates *e.g.* even the polymerization of styrene (Fig. 3) which is inhibited by *N*-bromosuccinimide alone.

The increase of the initial concentration of one initiator component above an optimum molar ratio is indicated by a gradual decrease of the polymerization rate.

It should be mentioned that a decrease in polymerization rate of methyl methacrylate is effected not only by an increase of the initial concentration of *N*-bromosuccinimide above certain molar ratio with respect to α -cumyl hydroperoxide (Fig. 4, Table 5) but also in the case when the initial concentration of α -cumyl hydroperoxide exceeds considerably that of *N*-bromosuccinimide.

If some other compounds capable to form complexes with either hydroperoxides or *N*-bromosuccinimide are added to the initiator system of α -cumyl hydroperoxide and *N*-bromosuccinimide, the polymerization is not more accelerated but, on the contrary, it is retarded (Table 6).

Provided that 2,2'-azobisisobutyronitrile was used as initiator (0.05 g/100 cm³) of methyl methacrylate polymerization, the addition of *N*-bromosuccinimide contributes to the increase in polymerization rate only slightly, the resulting rate of polymerization being within the range of the additive values. At 60°C, *e.g.* conversion of monomer without *N*-bromosuccinimide was 17.9%, with 1 g NBS/l it was 18.5%, with 2 g NBS/l it was 20.8%, and with 5 g NBS/l it was 19.5%.

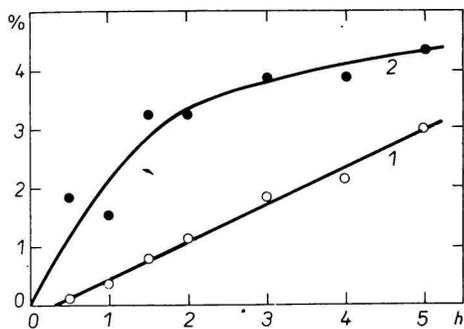


Fig. 3. Polymerization of styrene by 5.29 mmol dm⁻³ α-cumyl hydroperoxide and 5.62 mmol dm⁻³ N-bromosuccinimide (curve 2). Temperature 60°C; curve 1 shows polymerization initiated only by α-cumyl hydroperoxide alone.

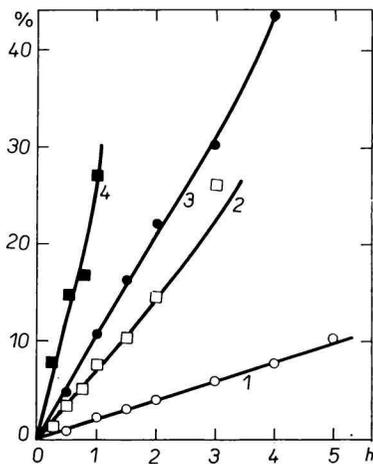


Fig. 4. Conversion curves of polymerization of methyl methacrylate in the presence of NBS (5.62 mmol dm⁻³) and α-cumyl hydroperoxide (52.9 mmol dm⁻³ — curves 1 and 2; 5.29 mmol dm⁻³ — curves 3 and 4) at 60°C (curves 1 and 3) and 80°C (curves 2 and 4).

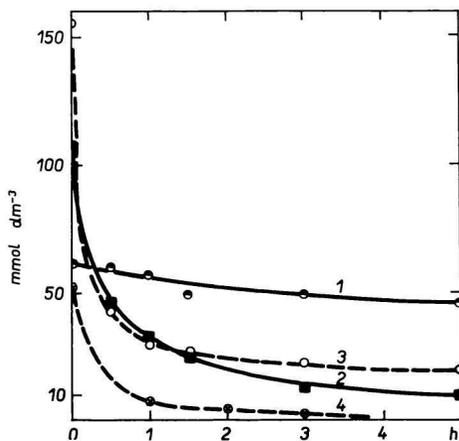


Fig. 5. Decrease of concentration of α-cumyl hydroperoxide (CHP) and N-bromosuccinimide (NBS) in methanol at 60°C.

Initial concentration of CHP:
62 mmol dm⁻³

Initial concentration of NBS (in mmol dm⁻³):
1. 11; 2. 52; 3. 104; 4. 52 (without CHP).

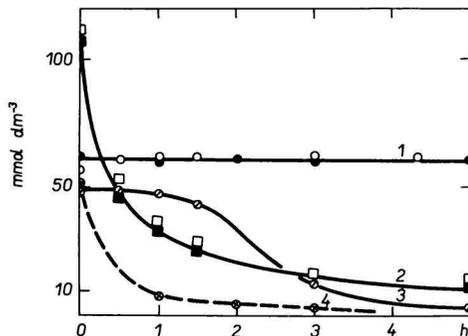


Fig. 6. Decomposition of α-cumyl hydroperoxide (CHP) and N-bromosuccinimide (NBS) in methanol at 60°C in the presence of succinimide (SI). Initial concentrations are in mmol dm⁻³
1. ● CHP (62); ○ CHP (62) + SI (110); 2. ■ CHP (62) + NBS (52) + SI (61); □ CHP (62) + NBS (52); 3. NBS (52) + SI (61); 4. NBS (52).

Catalyzed decomposition of peroxides

The presence of *N*-bromosuccinimide in solution in the absence of monomer brings about a considerable acceleration of hydroperoxide decomposition. From the course of both the α -cumyl hydroperoxide and *N*-bromosuccinimide concentration decrease it follows (Fig. 5) that the highest degree of hydroperoxide decomposition is attained at the same molar ratio of *N*-bromosuccinimide and hydroperoxide as it was in the case of maximum synergistic effect of both components in the polymerization of methyl methacrylate. Succinimide itself does not induce any significant decomposition of α -cumyl hydroperoxide (Fig. 6). On the other hand, the decomposition of *N*-bromosuccinimide is markedly slowed down in the presence of succinimide (as much as 50 times in our case). Since after an induction period the rate of decomposition of NBS increases to the value comparable with that in the absence of succinimide the decomposition reaction of *N*-bromosuccinimide is assumed to be of a chain character. If the induction period corresponds to the consumption of succinimide then the rate of succinimide concentration decrease is by 10 times higher than that of *N*-bromosuccinimide. This fact indicates that *N*-bromosuccinimide originates from succinimide in the course of reaction as an intermediate product.

On the other hand, the decomposition of hydroperoxide catalyzed by *N*-bromosuccinimide is not affected by the presence of succinimide. *N*-Bromosuccinimide even increases the rate of decomposition of benzoyl peroxide (Fig. 7), however, the acceleration is not so high as it was in the case of α -cumyl hydroperoxide.

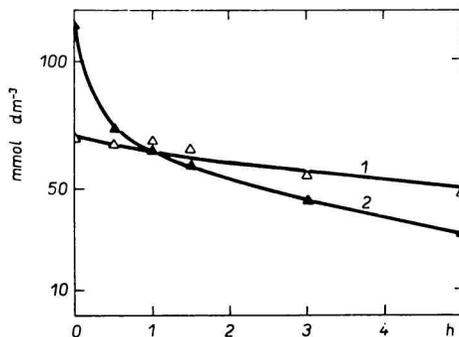


Fig. 7. Decomposition of benzoyl peroxide without (1) and in the presence (2) of *N*-bromosuccinimide (NBS) at 60°C in a mixture of methanol—benzene (4 : 1).

The initial concentration of benzoyl peroxide 70 mmol dm⁻³ and NBS 43 mmol dm⁻³

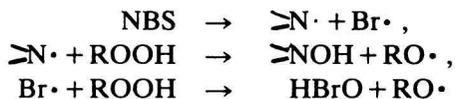
When mixing the solutions of *N*-bromosuccinimide and α -cumyl hydroperoxide (*tert*-butyl hydroperoxide) in methanol and benzene (the initial concentration of hydroperoxide was 10 mmol dm⁻³, that of *N*-bromosuccinimide 50–100 mmol dm⁻³) at room temperature one may observe relatively intense e.s.r spectrum of α -cumylperoxy radicals. The spectrum is a singlet with $g \approx 2.016$ and $\Delta H = 1.2$ mT (2.8 mT for *tert*-butylperoxy radicals). The e.s.r. signal is especially intense provided that non-dissolved *N*-bromosuccinimide is present in the system. The initial signal intensity corresponds to the rate of radical production about 0.1 mmol dm⁻³ s⁻¹; the intensity of signal decreases with increasing amount of methanol in its mixture with benzene.

Discussion

The evident synergistic effect of the initiation of polymerization of methyl methacrylate in the presence of both α -cumyl hydroperoxide and *N*-bromosuccinimide suggests that there exists a mutual interaction of these two initiators. This may also be deduced from the rate of α -cumyl hydroperoxide decomposition in solution in the presence of *N*-bromosuccinimide. The character of the interaction as well as the mechanism of the acceleration of polymerization are the subjects of discussion.

Taking into account the reaction of *N*-bromosuccinimide with hydroperoxides as an analogue of the redox reaction of hydroperoxides with amines we may assume that the donor of electrons should be the nitrogen atom in NBS whereas hydroperoxide should be the acceptor. As for α -cumyl hydroperoxide, according to the above conception α -cumyloxy radicals, bromine atoms and *N*-hydroxysuccinimide should be formed. However, under given conditions hydroperoxides do not react with succinimide. Considering the two carbonyl groups in the vicinity of the N atom in NBS, the electron donating effect of *N*-bromosuccinimide in its reaction with hydroperoxides should, however, be less significant in comparison with that of *N*-bromocaprolactam and, consequently, the rate of its interaction with hydroperoxides should be lower. In spite of this fact the rate of polymerization of methyl methacrylate and, therefore, also the rate of interaction of NBS with α -cumyl hydroperoxide was higher than that with *N*-bromocaprolactam. Similar difficulty is, however, encountered even when we assume that either nitrogen or bromine atoms in NBS are electron acceptors.

The kinetic curves describing the decrease of concentration of both components as well as the curve of decomposition of *N*-bromosuccinimide in methanol indicate that synergistic effect of both initiators might consist in decomposition of hydroperoxides induced by radicals resulting from the thermal decomposition of NBS



However, considering these reactions as main processes in the initiation of polymerization of methyl methacrylate makes it difficult to explain why the polymerization rate decreases with concentration of one reaction component increasing above a certain molar ratio (Fig. 1).

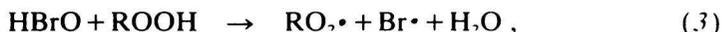
This decrease indicates that the polymerization inhibitor is formed by an interaction of some reaction intermediate with the excessive component of the initiation system. Therefore, we assume, that the observed maximum in the rate of polymerization as well as the synergistic initiation effect itself could be well explained by a bimolecular interaction of hydroperoxide and NBS according to the scheme



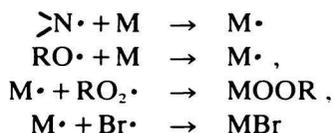
in which the afore-mentioned intermediate product is hypobromous acid (HBrO). At the same time, the reaction (1) cannot be considered as a redox process but only as a simple ionic reaction producing *N*-alkoxysuccinimide (NOR) which is the initiator of radical reaction *in situ*. In the subsequent reaction step, NOR is split into reactive radicals



Hypobromous acid may react with excessive ROOH [7] as follows



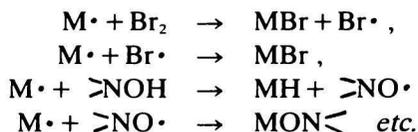
where radicals $\text{RO}_2\cdot$ and $\text{Br}\cdot$ may end the polymerization chain and effect the inhibition of the process



On the other hand, hypobromous acid may also react with excessive NBS under the formation of bromine and *N*-hydroxysuccinimide

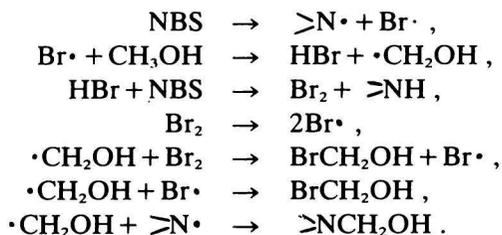


which both retard the polymerization reaction by taking part in reactions with macroradicals

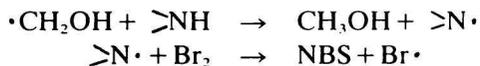


The lesser synergistic effect of *N*-bromocaprolactam in comparison with that of *N*-bromosuccinimide then follows obviously from the slower dissociation of N—Br bond during the interaction with hydroperoxide.

On the basis of the results obtained one may suggest the following scheme for the decomposition of NBS alone in methanol



In the presence of succinimide the transfer reaction of $\cdot\text{CH}_2\text{OH}$ radicals on bromine competes with the reactions



by which NBS is partly regenerated and the rate of its decomposition is thus retarded. As a consequence, by these reactions one may also explain the induction period in decomposition of NBS in the presence of succinimide.

When the monomer is present in the system, the chain radical reaction of NBS decomposition is inhibited by a systematic removal of bromine atoms due to both monomer and the propagating polymerization radicals, and the predominating process will thus be the bimolecular interaction.

The e.s.r. measurements showed that there were no peroxy radicals in the system in the range of initiators concentration where the maximum rate of polymerization has been achieved. An appreciable level of peroxy radicals may be observed only at a significant deviation from an approximately equimolar ratio of both components of the initiation system. This again supports the conclusion that peroxy radicals are formed in the reaction of some reaction by-product with hydroperoxide and that they are not responsible for the initiation of polymerization.

The decrease in rates of production of active radicals in the presence of amines depends very likely upon the formation of complexes between the reaction components (NBS, hydroperoxide) and amine. This fact is manifested by a lower rate of the primary reaction (reaction (1)) in which initiator >NOR is formed and consequently in a higher probability of side reactions (3) and (4).

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Translated by J. Rychlý