

Radical polymerization of methyl methacrylate initiated by thermal and catalyzed decomposition of 1,2,4,5-tetraoxane

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

The radical polymerization of methyl methacrylate initiated at elevated temperature by 6,6-bis(methoxycarbonylbutyl)-1,2,4,5-tetraoxane (TET) either alone or in the presence of nitrogen compounds (dimethylaniline, triethylamine, pyridine, *N*-bromosuccinimide), and Fe(III) or Co(II) acetylacetonate was studied. TET itself showed a very small initiation efficiency in polymerization, but its activity increased provided the decomposition of initiator was catalyzed by substances containing nitrogen. The overall energy of the methyl methacrylate polymerization initiated by the catalyzed decomposition of TET with dimethylaniline was determined to be $E_p = 67 \text{ kJ mol}^{-1}$. The transfer constant to TET in the polymerization of methyl methacrylate initiated by azobisisobutyronitrile (AIBN) depended on the concentration of TET.

Изучалась радикальная полимеризация метилметакрилата инициированная отчасти самим 6,6-бис(4-метоксикарбонилбутил)-1,2,4,5-тетраоксаном (ТЕТ) за повышенной температуры, отчасти за одновременного присутствия азотных веществ (диметиланилина, триэтиламина, пиридина, *N*-бромсукцинимид) и ацетилацетоната железа и кобальта. Сам ТЕТ имеет очень небольшую инициационную эффективность полимеризации. Когда катализируется разложение инициатора азотными веществами, инициационная эффективность повышается. Определилась суммарная энергия полимеризации метилметакрилата, инициированной катализируемым разложением ТЕТ, с диметиланилином $E_n = 67 \text{ кДж моль}^{-1}$. Постоянная переноса для ТЕТ при АИБН инициированной полимеризации метилметакрилата зависит от концентрации ТЕТ.

Thus far, fair attention has been paid to the polymerization of vinyl monomers initiated by simple peroxide compounds. However, this statement does not apply to more complicated peroxidic compounds, *e.g.* cyclic peroxides.

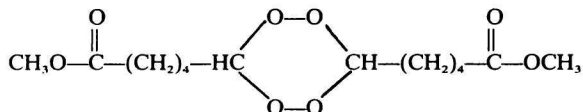
As for cyclic peroxides, phthalic peroxide was studied as initiator of the radical polymerization of methyl methacrylate, but its efficiency was very low [1]. It was reported in 1969 that the cyclic peroxide of 6,6-bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane was applicable as an initiator of polymerization [2]. Since the accessible literature did not give any detailed information on the possibility of using tetraoxane as an initiator of radical polymerization, we

tried to obtain such information by studying the radical polymerization of methyl methacrylate initiated by this substance. In handling tetraoxane peroxide is preferred to other peroxides for safety because it does not explode even during its thermal decomposition.

Experimental

Chemicals

6,6-Bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane



was prepared according to [2] by catalytic oxidation of ϵ -caprolactam and by rearrangement of the hydroperoxide formed in 80% sulfuric acid. The purification of tetraoxane was carried out by a twofold recrystallization from methanol; m.p. 84.5°C ([2]: m.p. 85°C).

Methyl methacrylate was deprived of stabilizer by washing with an aqueous sodium hydroxide solution and a twofold distillation in a nitrogen atmosphere under reduced pressure [3].

N,N'-Dimethylaniline was purified by distillation with water vapour and after the separation from the water, it was dried over KOH. Subsequently, dimethylaniline crystallized on cooling. After the separation of mother liquor the crystalline *N,N'*-dimethylaniline was allowed to melt at room temperature and then it was twofold distilled in an inert atmosphere under reduced pressure [4]. The refractive index of dimethylaniline thus purified was 1.6424 at 20°C.

Pyridine of anal. grade and triethylamine were products of Lachema, Brno. Co(II) and Fe(III) acetates were supplied by the Research Laboratory of the J. Dimitrov Chemical Works in Bratislava.

Procedures

The polymerization of methyl methacrylate was investigated in sealed glass ampules thermostatted at a specified temperature in nitrogen atmosphere. For the determination of the rate of polymerization 7 ampules were always used, and only those samples in which the conversion did not exceed 10% were taken for evaluation.

The molecular weight of polymethyl methacrylate was determined viscosimetrically in benzene at 25°C according to the formula [5]

$$[\eta] = 5.5 \times 10^{-5} \times M_w^{0.76}$$

The concentration of benzene solutions of polymethyl methacrylate was given in grams per 100 cm³ of solvent.

Results and discussion

Initiation of polymerization by tetraoxane in the absence of other substances

The initiation effect of tetraoxane on the polymerization of methyl methacrylate was insignificant within a wide range of temperatures (Table 1). It was interesting that tetraoxane even exerted a retardation effect on thermal (or initiated by trace peroxides) polymerization of methyl methacrylate at higher temperatures. The increase in the concentration of tetraoxane in monomer also had little effect on the

Table 1

Values of the initial rate of polymerization of methyl methacrylate expressed in weight % of the monomer polymerized in one hour at three temperatures

TET ^a mmol dm ⁻³	% h ⁻¹		
	60°C	100°C	140°C
0	0.08	2.56	28.7
8	0.12	3.23	13.3

a) Concentration of 6,6-bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane.

rate of polymerization. The initial rate of polymerization changed with increasing concentration of tetraoxane (mmol dm⁻³/% h⁻¹) as follows: 0/0.41, 2/0.59, 4/0.52, 8/0.66, 16/0.96. The order of the polymerization reaction with respect to the concentration of tetraoxane was approximately equal to 0.25 which indicated the participation of primary radicals in the termination of macroradicals. The low value of the order of the polymerization reaction with respect to the initiator may also have accounted for the lower activation energy of polymerization observed in the presence of tetraoxane (67 kJ mol⁻¹) in spite of the high activation energy of the decomposition of this initiator (151 kJ mol⁻¹) [6].

The observed low value of the order of the polymerization reaction could also be explained by the decreasing initiation efficiency in polymerization due to the side reactions of tetraoxane (or its radicals) which manifest themselves if the concentration of this substance increases in the polymerization system.

The thermal dissociation of the peroxidic bond in a molecule of tetraoxane did not seem to effect a direct initiation of the present monomer. As a matter of fact, the biradical formed caused a rapid intramolecular termination. Thus the effective initiation was evoked only by the bimolecular reactions between tetraoxane and monomers forming radicals which were able to diffuse from the place of generation and thus prevented the intramolecular termination reaction.

Influence of the concentration of tetraoxane and N,N'-dimethylaniline on the polymerization rate of methyl methacrylate

Similarly to nitrogen compounds, we studied the catalytic effect of dimethylaniline on the decomposition of tetraoxane during the polymerization of methyl methacrylate.

On the basis of the concentration change of both components of the initiation system, *i.e.* tetraoxane and *N,N'*-dimethylaniline, it was possible to calculate the exponents in the relationship between the rate of polymerization R_p and the concentrations of initiator and activator

$$R_p = k[\text{TET}]^m [\text{DMA}]^n \quad (1)$$

where [TET] and [DMA] are the concentrations of tetraoxane and dimethylaniline.

In the first case we used a constant concentration [DMA] = 1 mmol dm⁻³ in order to calculate the value of the exponent *m* (in eqn (1)).

By means of the experimental values of *R_p* found for different concentrations of TET the logarithmic form of eqn (1) was solved graphically (Fig. 1). The value of the exponent *m* = 0.2 was determined.

In the second case we used the constant concentration [TET] = 10 mmol dm⁻³ for the calculation of the value of the exponent *n*. By the procedure used in the

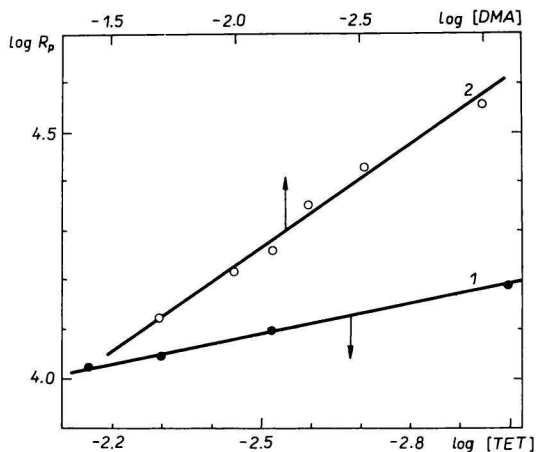


Fig. 1. Relationship between the logarithm of the polymerization rate of methyl methacrylate [mol dm⁻³ s⁻¹] and the concentration of tetraoxane [TET] [mol dm⁻³] at constant concentration of dimethylaniline ([DMA] = 1 mmol dm⁻³) (straight line 1) and the concentration of dimethylaniline [mol dm⁻³] at constant concentration of tetraoxane ([TET] = 10 mmol dm⁻³) (straight line 2) at 60°C.

Table 2

Rates of polymerization (*R_p*) of methyl methacrylate with catalyzed and non-catalyzed decomposition of 6,6-bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane at 60°C, with a concentration of initiator of 5 mmol dm⁻³

Initiator	DMA ^a Concentration mmol dm ⁻³	<i>R_p</i> mol dm ⁻³ s ⁻¹
Benzoyl peroxide	—	7.1 × 10 ^{-3b}
Tetraoxane	—	6.3 × 10 ⁻⁶
Tetraoxane	7	8.4 × 10 ⁻⁵
Tetraoxane	10	9.0 × 10 ⁻⁵

a) *N,N*-Dimethylaniline.

b) Ref. [7].

preceding case the value $n=0.4$ was calculated (Fig. 1). In both experimental series the temperature of polymerization was 60°C. The low value of the exponent n indicates again the important participation of the primary radicals from tetraoxane in the termination of macroradicals. Table 2 demonstrates the influence of dimethylaniline on the rate of polymerization. At the concentration of 5 mmol dm⁻³ of tetraoxane, the addition of 7 mmol dm⁻³ of DMA caused the rate of polymerization to increase approximately 10-fold at 60°C when compared with the polymerization with a non-catalyzed decomposition of tetraoxane. The rate of polymerization of MMA was about 20 times lower in the presence of the system tetraoxane—dimethylaniline than it is in the presence of benzoyl peroxide under equal conditions [7].

Overall activation energy of polymerization

We measured the polymerization rate of MMA for [TEF] = 1 mmol dm⁻³ and [DMA] = 1 mmol dm⁻³ at 60, 85, 90, and 100°C (Fig. 2). We used the experimental values of the polymerization rate for the calculation of the overall energy of activation according to the Arrhenius equation. The temperature dependence of the polymerization rate was linear in the investigated temperature interval. The overall activation energy calculated by the method of least squares was $E_p = 67$ kJ mol⁻¹. This value of the energy of activation was within the range of the values reported for the polymerizations of methyl methacrylate initiated by redox systems.

Molecular weights of the polymethyl methacrylate prepared by means of the redox system tetraoxane—N,N'-dimethylaniline

The molecular weights of the polymethyl methacrylate obtained by the polymerization with a conversion below 10% were in the range of the values achieved by the use of current radical initiators, *i.e.* of the decimal order of 10⁵ (Table 3).

Transfer to tetraoxane in the radical polymerization of MMA initiated by AIBN

Because of the presence of the two hydrogen atoms bonded to the tertiary carbon atoms in the structure of tetraoxane it was expected that tetraoxane should be an effective transferring agent especially at low temperatures. However, it was a very ineffective initiator of polymerization, as obvious from Table 1.

The transfer constant C_{TET} to tetraoxane was determined according to eqn (2) derived by authors [8] for the weight average degree of polymerization

$$\frac{1}{\bar{P}_w} + \frac{1}{\bar{P}_w} \sqrt{1 + \frac{\bar{P}_w k_t R_p}{k_p^2 [M]^2 (\delta + 1)}} - \frac{k_t R_p}{k_p^2 [M]^2} = C_M + C_{\text{TET}} \frac{[\text{TET}]}{[M]} + C_I \frac{[I]}{[M]}, \quad (2)$$

where k_p = rate constant of the growth of polymer chain,
 k_t = rate constant of termination,
 δ = ratio of the termination rates for the disproportionation
 and combination reactions,
 $[M]$ = concentration of monomer in mol dm^{-3} ,
 C_M = transfer constant to monomer,
 C_{TET} = transfer constant to tetraoxane,
 C_I = transfer constant to initiator [AIBN],
 $[I]$ = concentration of initiator in mol dm^{-3}

Because of the negligible value of the transfer constant to initiator [AIBN] the last term on the right hand of eqn (2) may be neglected.

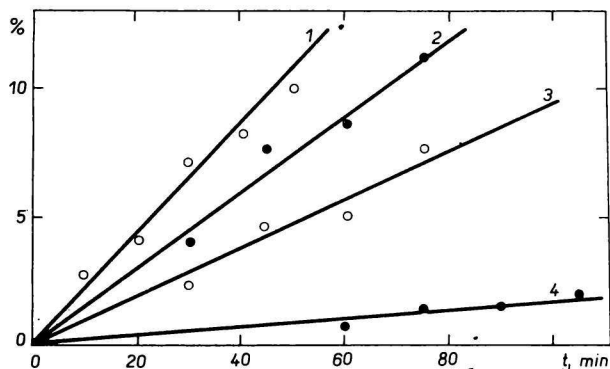


Fig. 2. Variation of conversion (%) with the time of polymerization for constant concentrations of TET and DMA ($[\text{TET}] = 1 \text{ mmol dm}^{-3}$ and $[\text{DMA}] = 1 \text{ mmol dm}^{-3}$) at different temperatures. 1. 100°C; 2. 90°C; 3. 85°C; 4. 60°C.

Table 3

Molecular weights of the polymethyl methacrylate prepared in the polymerization initiated by the redox system 6,6'-bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane (TET)—*N,N'*-dimethylaniline (DMA)

TET mmol dm^{-3}	DMA mmol dm^{-3}	Temperature of polymerization °C	$[\eta]^a$	Molecular weight $M_w \cdot 10^{-5}$
1	1	60	1.35	5.97
7	7	60	1.20	5.12
1	10	60	0.90	3.50
1	1	70	0.89	3.45
1	1	85	0.81	3.05

a) Limiting viscosity number in benzene ($100 \text{ cm}^3 \text{ g}^{-1}$).

The value of k_p^2/k_t was calculated according to the general formula valid for the radical polymerization of methyl methacrylate [8]

$$\log \frac{k_p^2}{k_t} = 3.45 - \frac{1810}{T}, \quad (3)$$

hence for 60°C

$$\frac{k_p^2}{k_t} = 1.05 \times 10^{-2}$$

The value of δ was calculated according to formula (4) [8]

$$\log \delta = 2.89 - \frac{1000}{T} \quad (4)$$

Thus it was found for 60°C $\delta = 1.28$ and $C_M = 2 \times 10^{-5}$

The experimental values of R_p and \bar{P}_w found for the polymerization of methyl methacrylate initiated by azobisisobutyronitrile at 60°C as well as the calculated values of the transfer constant to tetraoxane C_{TET} are given in Table 4. The transfer constant to tetraoxane was relatively high. The value of the transfer constant decreased with increasing concentration of TET which may have been due to similar factors as those which are responsible for the decrease in the efficiency of the initiation of polymerization at higher concentrations of tetraoxane. As a matter of fact, in both cases a competition of a bimolecular side reaction against the bimolecular initiation or the transfer pseudo-monomolecular reaction of tetraoxane took place.

Catalysis of the decomposition of tetraoxane by other nitrogen-containing substances or the cations of transition metals

Not only dimethylaniline, but also other substances containing nitrogen had a catalytic effect on tetraoxane. Among these substances *N*-bromosuccinimide was found to be the most efficacious compound. The rates of polymerization achieved

Table 4

Experimental values of the rate of polymerization of MMA initiated by azobisisobutyronitrile (concentration 5 mmol dm⁻³) at 60°C, values of \bar{P}_w of polymethyl methacrylate, and the transfer constant C_{TET} to 6,6'-bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane (TET)

Concentration of TET mmol dm ⁻³	[TET] [MMA]	10^3	$R_p \cdot 10^4$ mol dm ⁻³ s ⁻¹	$P_w \cdot 10^{-4}$	$C_{TET} \cdot 10^2$
2	0.212		1.436	1.222	8.2
4	0.425		1.446	1.190	4.9
16	1.704		1.497	1.133	1.5

Table 5

Polymerization of methyl methacrylate initiated by the decomposition of 6,6-bis(4-methoxycarbonylbutyl)-1,2,4,5-tetraoxane (1 mmol dm⁻³) catalyzed by nitrogen-containing substances or Co(II) acetylacetonate and Fe(III) acetylacetonate

Catalyst of the tetraoxane decomposition	Concentration of the substance added mmol dm ⁻³	Rate of polymerization mol dm ⁻³ s ⁻¹	Temperature of polymerization °C
<i>N</i> -Bromosucci imide	1	1.7×10^{-4}	85
<i>N</i> -Bromosuccinimide	1	2.0×10^{-4}	85
Pyridine	1	1.2×10^{-4}	85
Triethylami	1	1.1×10^{-4}	85
0	0	4.1×10^{-4}	85
Fe(III) Acetylacetonate	3.2×10^{-2}	2.9×10^{-4}	60
Fe(III) Acetylacetonate	3.2×10^{-2}	8.3×10^{-6a}	60
Co(II) Acetylacetonate	3.9×10^{-2}	3.7×10^{-5}	60
Co(II) Acetylacetonate	3.9×10^{-2}	1.4×10^{-5a}	60
0	0	6.8×10^{-6}	60

a) Rate of the thermal polymerization of MMA in the presence of catalyst and in the absence of tetraoxane.

in the presence of this substance were close to the results obtained with dimethylaniline as a catalyst (Table 5).

Pyridine and triethylamine, also accelerate the polymerization of methyl methacrylate initiated by tetraoxane.

Some complexes of transition metals, e.g. Co(II) and Fe(III) acetylacetonate significantly accelerated the polymerization reaction in the presence of tetraoxane. We assumed that the mechanism of the effect of these complexes resembles the mechanism operating in the known redox systems [9].

References

- Russel, K. E., *J. Amer. Chem. Soc.* **77**, 4814 (1955).
- Höft, E., Rieche, A., and Schön, W., *Justus Liebigs Ann. Chem.* **725**, 241 (1969).
- Braun, D., Cherdron, H., and Kern, E., *Praktikum der makromolekularen organischen Chemie*, p. 39. A. Hüthig Verlag, Heidelberg, 1966.
- Houben—Weyl, *Methoden der organischen Chemie* 1/2, p. 840. Thieme Verlag, Stuttgart, 1959.
- Brandrup, J. and Immergut, E. H. (Editors), *Polymer Handbook*, p. IV—26. Interscience, New York, 1966.
- Lazár, M., Ambrovič, P., and Borsig, E., *Thermochim. Acta* **10**, 55 (1974).
- Houwink, R. and Staverman, A. J., *Chemie und Technologie der Kunststoffe*, Band 1, p. 248. Akademische Verlagsgesellschaft Geest & Portig, Leipzig, 1962.
- Henrici-Olivé, G. and Olivé, S., *Fortschr. Hochpolym.-Forsch.* **2**, 525, 530, 532 (1961).
- Swern, D. (Editor), *Organic Peroxides*, Vol. 1, p. 561. Wiley—Interscience, New York, 1970.

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