Initiation of methyl methacrylate polymerization by 9,10-dioxyanthracene

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The initiation efficiency of 9,10-dioxyanthracene is very low in methyl methacrylate polymerization at temperatures between 100 and 140°C. This is explained by a high portion of induced decomposition of anthracene peroxide. Less than 1% of radicals participates in the initiation of polymerization.

Initiations by benzoyl peroxide and 9,10-dioxyanthracene proceeding simultaneously lead to a high polymerization rate and the possibility of limiting the gel effect.

Инициирующее действие 9,10-диоксиантрацена при полимеризации метилметакрилата в диапазоне температур 100—140°С весьма незначительно, что объясняется высокой долью индуцированного разложения перекиси антрацена. В инициации полимеризации принимает участие меньше, чем 1% радикалов.

При одновременной инициации бензоилперекисью и 9,10-диоксиантраценом достигается большая скорость полимеризации и одновременно подавляется гель-эффект.

9,10-Dioxyanthracene was employed as initiator for styrene polymerization [1]. A relatively low rate of polymerization and a high rate of decomposition of this cyclic peroxide initiator result in a low efficiency of the initiation of the polymerization reaction. This can be due to either intramolecular termination of the original or oligomeric biradicals [2] or a high portion of induced decomposition of this initiator [3]. The formation of a high-molecular polymer is enabled by side reactions of the initiator where free monoradicals able to initiate are created. Taking into account a relatively high level of little active radicals in the system, the use of this initiator for weakening the gel effect during the polymerization of methyl methacrylate might be interesting. In the initiation of the methyl methacrylate polymerization by common initiators, a rapid increase (100-fold) in the polymerization rate is observed at certain conversion after a critical rise of the viscosity of the system. The gel effect is explained by a decrease in the rate of termination of macroradicals by lowering their diffusion rate. In the presence of

little active radicals of the initiator, the gel effect should be smaller since the increase of the viscosity affects the mobility of the low-molecular radicals less than that of macroradicals, which helps to retain a steady state.

Experimental

9,10-Dioxyanthracene was prepared by photooxidation of anthracene in chloroform with methylene blue [4]. The photoperoxide prepared was purified by freezing out from carbon disulfide and the purity was checked by i.r. and u.v. spectrometry and by gel chromatography.

Methyl methacrylate was purified by washing with diluted sodium hydroxide, diluted sulfuric acid, and aqueous solution of sodium carbonate. After drying with calcium(II) chloride, methyl methacrylate was distilled twice under nitrogen.

The course of reaction was followed by weighting the precipitated poly(methyl methacrylate) on adding n-heptane and according to the amount of the heat released during polymerization. In the first case, the block polymerization of monomer was performed in sealed ampules containing 1 ml of monomer. Calorimetric measurements were carried out on a Perkin—Elmer DSC-1B differential calorimeter. The weighted samples (10—12 mg) of the polymerizing monomer were gastight closed in aluminium capsules.

Results and discussion

The polymerization of methyl methacrylate initiated by thermal decomposition of 9,10-dioxyanthracene was at first studied gravimetrically. For comparison, we polymerized methyl methacrylate without initiator and in the presence of anthracene (Table 1). About two-fold increase in the concentration of anthracene peroxide causes a 1.4-fold increase of the polymerization rate, indicating a common square-root relation between the rate of initiation and that of polymerization. Anthracene appears to be a slight retarder of the polymerization.

The measurement of the rate of the polymerization heat release (Fig. 1) and the data on the total heat released (Table 2) indicate fast but, in view of initiation, little effective decomposition of 9,10-dioxyanthracene in the polymerizing methyl methacrylate. On the other hand, in the presence of an effective initiator, such as e.g. benzoyl peroxide, the rate of the polymerization heat release slightly decreases at the beginning with decreasing concentration of the polymerizing monomer in the system. On achieving the critical conversion, the rate of the polymerization heat release rapidly increases in accordance with the course of polymerization under the conditions of the gel effect (Fig. 1). The value for the heat of polymerization of methyl methacrylate in the presence of benzoyl peroxide calculated from the area below the isothermal curve is 55 kJ mol^{-1}, which is in good agreement with the literature data [5].

Table 1

Comparison of the monomer conversion during methyl methacrylate polymerization initiated by 9,10-dioxyanthracene and polymerization in the presence of anthracene at 100°C

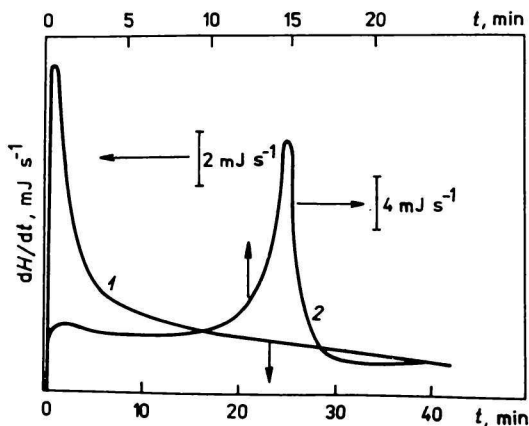| Polymerization in the presence of	% substance	Monomer conversion % in	
		30 min	60 min
—		0.95	2.12
Anthracene	0.128	0.93	
	0.270	0.62	
	0.144		1.86
	0.295		1.65
Anthracene peroxide	0.290	8.9	
	0.541	12.7	
	0.275		13.8
	0.532		19.5

Fig. 1. Two types of curves of the heat release during methyl methacrylate polymerization initiated by anthracene peroxide (125°C, 0.5 wt % of 9,10-dioxyanthracene at total sample weight 10 mg) (curve *1*) and by benzoyl peroxide (100°C, 0.3 wt % of initiator at total sample weight 12 mg) (curve *2*).

The conversion calculated from the reaction heat during initiation by 9,10-dioxyanthracene is only 25—40% (Table 2). For 100% conversion we reckoned with the reaction heat 55 kJ mol^{-1} A comparison of the initial rates of the polymerization heat release in the presence of benzoyl peroxide or 9,10-dioxyanthracene as a function of temperature (Table 3) shows that the initial rate of the methyl methacrylate polymerization is, by using benzoyl peroxide, about five times higher when compared with the use of the same molar concentration of 9,10-dioxyanthra-

Table 2

Values of the rate constants and reaction heats of methyl methacrylate polymerization initiated by 9,10-dioxyanthracene (0.7 wt %) as a function of temperature

T °C	k_1 $10^3\ s^{-1}$	$-\Delta H^a$ kJ mol^{-1}
105	1.84	23
110	3.41	22
115	3.71	21
120	5.69	21
125	10.60	18
130	17.50	16
135	22.50	16
140	32.10	14

a) Reaction heat released is expressed by the initial amount of monomer.

Table 3

Initial rates of the heat release during methyl methacrylate polymerization initiated by benzoyl peroxide (v_{BP}) and anthracene peroxide (v_{OA}) as a function of temperature at the concentration of i itiator 0.0033 mol/mol MMA
The initial rate (v) of the polymerization heat release is defined in Fig. 1

T °C	v_{BP}	J g^{-1} s^{-1}	$\dfrac{v_{BP}}{v_{OA}}$
105	0.93	0.21	4.4
110	1.32	0.24	5.5
115	1.65	0.34	4.9
120	2.14	0.41	5.2
125	2.61	0.52	5.0

cene. It is noteworthy that the rate of decomposition of 9,10-dioxyanthracene is three times higher than the rate of decomposition of benzoyl peroxide under the given conditions [3]. Since the rate of initiation is in the square-root relation to the rate of polymerization, we can assume that the initiation efficiency of anthracene peroxide is at least 75 times smaller than that of benzoyl peroxide. Because the initiation efficiency of benzoyl peroxide is about 0.5 (as has been many times experimentally proved), the efficiency of 9,10-dioxyanthracene in the initiation of polymerization is approximately 0.007. Thus, less than 1% of radicals being formed in the decomposition of the transannular anthracene peroxide reacts with methyl methacrylate and initiates polymerization. This result is in very good accord

with the fact that 9,10-dioxyanthracene decomposes by induced decomposition [3]. From the point of view of the initiation of the polymerization only the portion belonging to spontaneous decomposition represents efficiently decomposed peroxide. Radicals participating in propagation of induced decomposition are deactivated by transfer or addition reactions with decomposing peroxide.

The portion of the spontaneous decomposition of 9,10-dioxyanthracene under the conditions of the polymerization experiments is about 4% [3]. Agreement with the results of the initiation efficiency during polymerization seems to be good if, in addition, we consider that decomposition products of anthracene peroxide inhibit the polymerization process. The inhibition effect of the decomposition products was confirmed by additional increase in temperature after completion of the polymerization initiated by 9,10-dioxyanthracene, the expected thermal polymerization of methyl methacrylate not being observed.

With regard to a very low initiation efficiency of 9,10-dioxyanthracene, the indirect initiation by singlet oxygen, which can be liberated in a very small amount during thermal decomposition of 9,10-dioxyanthracene, can also be regarded as primary initiation. If this assumption were correct, the initiation by 9,10-diphenyl-9,10-dioxyanthracene should be considerably more efficient since this peroxide liberates singlet oxygen during thermal decomposition with almost 98% efficiency [6]. As we have proved experimentally, the polymerization is not initiated by this substance.

Apparent first-order rate constants k_1 were determined for various temperatures from a decrease in the rate of the heat release during polymerization initiated by 9,10-dioxyanthracene (Table 2). The constants k_1 obtained give in Arrhenius coordinates linear relation with a slope which yields the same value as the activation energy of the decomposition of 9,10-dioxyanthracene in solution (125 kJ mol^{-1}[1, 3]). The result indicates that the fast decomposition of anthracene

Table 4

Initial (v) and maximum rates (v_m) of the heat release and the total reaction heat ($-\Delta H$) during methyl methacrylate polymerization initiated by benzoyl peroxide (0.5 wt %) as a function of the amount of 9,10-dioxyanthracene added at 100°C

The rates v and v_m of the polymerization heat release are defined in Fig. 1

[OA] wt %	v	J g^{-1} s^{-1}	$-\Delta H$ kJ mol^{-1}
—	0.51	3.59	55
0.1	0.53	2.89	55
0.3	0.56	2.22	56
0.5	0.61	1.83	56
0.7	0.62	1.39	55

peroxide is the process controlling characteristic features of this polymerization.

Retardation of the polymerization initiated by 9,10-dioxyanthracene and the limiting of the gel effect includes a significant technological aspect. Combination of this initiator with benzoyl peroxide makes the course of the methyl methacrylate polymerization more fluent. This idea is described more concretely by values of the initial polymerization rates and reaction rates in the range of the gel effect as a function of concentration of 9,10-dioxyanthracene added during polymerization initiated by benzoyl peroxide (Table 4). Under the properly chosen conditions, in the initial phases of polymerization 9,10-dioxyanthracene added contributes to an increase of the polymerization rate by producing radicals; but later it retards the rapid course of polymerization.

References

1. Breitenbach, J. W. and Kastell, A., *Monatsh. Chem.* **85,** 676 (1954).
2. Borsig, E. and Lazár, M., *Chem. Zvesti* **22,** 627 (1968).
3. Lazár, M., Rychlý, J., and Markuš, S., *Chem. Zvesti* **33**, 81 (1979).
4. Foote, C. S., Wexler, S., Ando, W., and Higgins, R., *J. Amer. Chem. Soc.* **90,** 975 (1968).
5. Mortimer, C. T., *Reaction Heats and Bond Strengths*, p. 94. Pergamon Press, London, 1962.
6. Bowen, E. J., *Advan. Photochem.* **1,** 135 (1963).

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