Emulsion polymerization in the presence of inorganic material

D. MIKULÁŠOVÁ, V. CHRÁSTOVÁ, P. CITOVICKÝ, and I. HUDEC

*Department of Chemical Technology of Plastics and Fibres,
Slovak Technical University, CS-812 37 Bratislava*

Received 21 December 1981

Accepted for publication 28 January 1983

Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

The possibility of using synthetic inorganic materials Potasit, Calsit, γ-Alumina and metal oxides ZnO, MgO, NiO, CuO, Al_2O_3, TiO_2, PbO_2 as heterogeneous initiators for the homopolymerization of styrene or methyl methacrylate in an emulsion polymerization system, containing a nonionic type of emulsifier and triethylenetetramine as activator, was studied.

It was found that it is possible to use Potasit and Calsit, contrary to γ-Alumina, for the mentioned purpose, particularly after their contact with oxygen containing ozone, whereby the duration of the contact, as well as the concentration of the used activator, influence the yield of the polymer.

From the studied metal oxides as heterogeneous initiators of polymerization only aluminium oxide and titanic oxide were not suitable, and with these the polymerization at the given conditions did not take place with any monomer. The treatment of the metal oxides by preserving them in an oxygen atmosphere enriched with ozone did not influence the polymerization rate.

It was found that polymerization of methyl methacrylate does not proceed in the dark in the presence of zinc oxide and magnesium oxide, which indicates that zinc and magnesium oxide behave as photosensibilizers.

Была изучена возможность использования синтетических неорганических материалов Потасита, Кальсита, γ-Алумина и оксидов металлов ZnO, MgO, NiO, CuO, Al_2O_3, TiO_2, PbO_2 в качестве гетерогенных инициаторов гомогенной полимеризации стирола или метилметакрилата в эмульсионной полимеризационной системе, содержащей эмульгатор неионного типа и триэтилентетрамин в качестве активатора.

Было обнаружено, что Потасит и Кальсит в отличие от γ-Алумина можно использовать для данной цели, особенно после контакта с кислородом, содержащим озон, причем время контакта и концентрация активатора влияют на выход полимера.

Из исследованных оксидов металлов в качестве гетерогенного катализатора не пригоден только оксид алюминия и оксид титана, в случае которых полимеризация не протекала ни у одного мономера. Обработка оксидов металлов атмосферным кислородом, содержащим озон, не имела влияния на скорость полимеризации.

Было найдено, что полимеризация метилметакрилата в присутствии оксида цинка и оксида магния в темноте не протекает, что свидетельствует о действии оксида цинка и оксида магния как фотосенсибилизаторов.

The emulsion polymerization is generally initiated by an initiator soluble in aqueous phase. Hitherto mainly hydroperoxide of powdered isotactic polypropylene was used for the emulsion polymerization of styrene [1—3]. Inorganic materials, as far as they were used in a polymerization system (it was mostly a nonaqueous system), were combined with normal initiators or with radiation initiation. From the inorganic materials synthetic zeolites [4—6] and oxides of various metals [7—11] were mostly used. They act here either directly as initiators of polymerization, or it is a polymerization initiated in the usual manner, but in the presence of inorganic materials.

The polymerization of styrene on zeolite in a nonaqueous medium was studied by *Barson, Knight,* and *Robb* [5]. The authors considered cationic polymerization initiated by traces of adsorbed water.

The influence of inorganic materials on the polymerization of vinyl monomers was also studied in such polymerization systems, which contained an initiator, or radiation was used for the initiation. Among the authors, who published such papers are before all *Moustafa* and *Mansour* and coworkers [9—11]. They studied the polymerization of vinyl monomers and the grafting of cellulose by vinyl monomers in the presence of sodium-calcium glass and $NaHSO_3$ as polymerization initiator.

The possibility of polymerization of methyl methacrylate adsorbed on zeolite is quoted by *Le Bail* and *Zemb* [4], who used γ-radiation for the initiation of polymerization at -53 up to $+57$ °C.

Fukano and *Kageyama* [6, 12] studied the radiation initiated polymerization of styrene and methyl methacrylate, adsorbed on various inorganic materials and that on silica gel, white carbon blacks, anhydride of silicic acid, zeolite, and activated aluminium oxide. Gel permeation chromatography and electron microscopy used by the authors enabled to differ two different mechanisms, which take place simultaneously during the polymerization.

Unlike the published papers dealing with the polymerization in nonaqueous systems, in this paper was studied the initiation effect of inorganic material on the homopolymerization of styrene and methyl methacrylate, or in an emulsion polymerization system in the presence of a convenient activator of polymerization.

Experimental

Chemicals

Solid surfaces

a) Potasit and Calsit as synthetic zeolites and γ-Alumina were used in the form of little spheres with a specific surface (a/m^2 g^{-1}): 13.0, 17.8, 311.4. They were also modified by means of the fluid method in a stream of oxygen containing ozone (12 mg dm^{-3}) at laboratory temperature. b) Pulverized oxides of metals, anal. grade purity: ZnO, MgO, CuO, NiO, Fe_2O_3, Al_2O_3, PbO_2, TiO_2.

Activators

These were used in the form of aqueous solutions stored under inert atmosphere: a) triethylenetetramine (TETA); b) Chelaton III, anal. grade, disodium salt of ethylenediaminetetraacetic acid (EDTA); c) $FeSO_4 \cdot 7H_2O$, aqueous solution acidified by H_2SO_4 to pH = 5.

Emulsifier

Nonionic one — Slovasol 2430, a commercial product of CHZWP, Nováky, added as aqueous solution. It was boiled in an inert atmosphere under reflux for 1 h before using.

Monomers

Styrene — after removing the stabilizer and drying with $CaCl_2$ it was distilled twice in nitrogen atmosphere; methyl methacrylate after distillation and prepolymerization was once more distilled under inert atmosphere. The inert atmosphere was of the type of glow nitrogen, which was purified on a catalyst composed of 55 % MnO_2, 40 % MgO, and 5 % Cr_2O_3 at laboratory temperature.

Polymerization procedure

The polymerization was carried out in glass ampoules with volume of approximately 20 cm^3. Black ampoules were used for the polymerization without access of light. In the ampoules with the weighed inorganic material, the working inert atmosphere was reached by means of vacuum and nitrogen. The liquid components of the polymerization system were charged under inert atmosphere as follows: activator, emulsifier, water, and monomer. The polymerization system of one ampoule consisted of 0.4—0.8 g of solid phase of inorganic material, 3 cm^3 of organic phase (monomer), and 15 cm^3 of aqueous phase, in which the activator and emulsifier were dissolved. After sealing, the content of the ampoule was homogenized by shaking and the ampoule was inserted into a rotating frame (60 r.p.m.), placed in a bath temperated at 30 °C.

After completion of the polymerization the ampoule was opened and the content was treated by the following procedure:

— in the case when synthetic zeolites and γ-Alumina were used as initiators, the content of the ampoule was quantitatively poured through a sintered glass filter S_1, where the little spheres of the inorganic material were captured and the polymer was precipitated from the emulsion by methanol;

— when metal oxides in powdered form were used as initiators, the content of the ampoule was poured into a centrifuge cell. The metal oxides were separated from the emulsifier on the centrifuge Janetzki, type T 24, after centrifuging for 5 min at 83 r.p.s. To obtain the polymer quantitatively, the oxide, which remained in the cell, was rinsed with water, once again centrifuged and the separated residues of the emulsion were added to the first portion. The polymer was precipitated with methanol from the emulsion, obtained in this way;

— when metal oxides were used, their neutralization was tested in methanol acidified with hydrochloric acid (a 10-fold mole excess of HCl). This procedure could be used only in the case of ZnO, MgO, and CuO.

The precipitated polymer after 24 h staying was filtered off with a sintered glass filter S_2. The captured polymer was several times washed with water and finally with methanol. After drying to a constant mass, the conversion was expressed in mass percent according to the mass of the added monomer.

Results and discussion

Some synthetic inorganic materials as zeolites (Potasit, Calsit) and γ-Alumina were investigated for the emulsion polymerization of styrene at 30 °C. This effect was positively influenced in the case of zeolites by keeping them in oxygen atmosphere containing ozone (similarly as when using pulverized polypropylene as heterogeneous initiator [2]), as well as by the use of an activator in the polymerization system (for instance TETA). Without using the mentioned activator, which itself is not capable to act as initiator, the polymerization does not take place. The polymerization results are given in Table 1.

As can be seen from Table 1, neither the size of the specific surface nor the kind of the material used had a significant influence on the conversion of the monomer; the values of the conversion were relatively small.

With regard to the fact that with Potasit activated by oxygen, relatively the best results were achieved, it was investigated, if by using this kind of Potasit, the yield

Table 1

Rate of the emulsion polymerization of styrene v by using various types of inorganic materials at 30 °C[a]

Inorganic material (type)	Specific area $a/\mathrm{m^2\,g^{-1}}$	$v/(\mathrm{conv.}\ \%)\ \mathrm{h^{-1}}$	
		Inorganic material	
		activated by oxygen 30 min	nonactivated
Potasit	13.0	7.5	3.7
Calsit	17.8	6.3	3.7
γ-Alumina	311.4	—	2.4

[a] The system with 0.8 g of inorganic material contained a TETA concentration 3.3×10^{-3} mol $\mathrm{dm_{em}^{-3}}$ and an emulsifier concentration 2.3×10^{-2} mol $\mathrm{dm_{em}^{-3}}$.

of polymerization was not influenced by the concentration of the activator or by the time of its activation in oxygen atmosphere. The mentioned effects are characterized by dependences illustrated in Fig. 1. It is evident from Fig. 1 that over a certain concentration of TETA (3×10^{-3} mol $\mathrm{dm_{em}^{-3}}$) the polymerization rate does not change. It was shown that by increasing the retention time of Potasit in oxygen atmosphere the polymerization rate has, in the whole studied range, increased

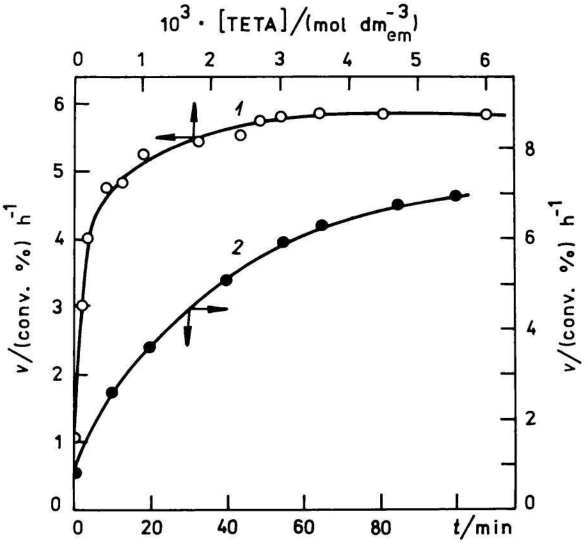

Fig. 1. Influence of the TETA concentration (curve *1*) and of the time of contact of Potasit with oxygen (curve *2*) on the polymerization rate of styrene v at 30 °C.

(curve *2*). In both cases the positive influence of the studied factors on the polymerization rate of styrene is evident. The stabilization of the influence of the change of the TETA concentration on the polymerization rate (curve *1*) can be in connection with the limiting factor, which is the number of the initiation centres on the solid phase. From the tendency of dependence characterized by curve *2*, it is possible to come to a similar conclusion, when the limiting factor is the TETA concentration.

Besides the investigation of the influence of synthetic zeolites and γ-Alumina on the polymerization rate, attention was also paid to pulverized metal oxides insoluble in water and suitable from the view-point of their chemical properties as heterogeneous initiators in the studied polymerization system. The influence of the following oxides was studied: CuO, NiO, ZnO, MgO, Fe_2O_3, Al_2O_3, PbO_2, TiO_2. The results obtained from the polymerization of styrene at 30 °C are summarized in Table 2.

Table 2

Rate of the emulsion polymerization of styrene in the presence of various metal oxides as heterogeneous initiators at 30 °C[a]

Activator type	v/(conv. %) h^{-1}							
	Oxide type							
	ZnO	CuO	MgO	NiO	Fe_2O_3	Al_2O_3	PbO_2	TiO_2
$FeSO_4$—EDTA	4.0	0.9	0	0	0	0	3.7	0
TETA	20.0	0	12.3	0	0	0	1.8	0

a) The system with 0.4 g of metal oxide contained a TETA concentration 1.6×10^{-3} mol dm_{em}^{-3}, or $FeSO_4$—EDTA concentration (1.1×10^{-3} mol dm_{em}^{-3}) and an emulsifier concentration (2.7×10^{-2} mol dm_{em}^{-3}).

All oxides were used without any treatment, because it has been found that storage of the metal oxides in oxygen atmosphere, enriched by ozone, has no influence on the polymerization rate.

Among the metal oxides zinc oxide in combination with TETA was chosen for the study of the course of styrene polymerization. The polymerization was carried out according to the procedure mentioned in Experimental. Four various ZnO concentrations were used in the polymerization system. The concentration of the other components of the polymerization system, as well as the phase ratio, was the same as in experiments with various types of metal oxides (Table 2). The determined dependences of conversion in percent as a function of the polymerization time are illustrated in Fig. 2. The conversion curve of the styrene polymerization initiated by Potasit at the same TETA concentration, is also given for comparison.

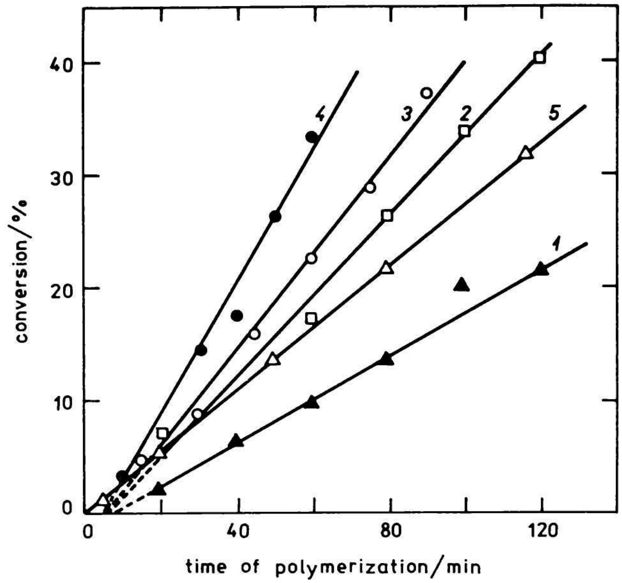

Fig. 2. Influence of the time on styrene polymerization in light at 30 °C, initiated with various types of heterogeneous initiators with mass concentration (ϱ/g dm^{-3}).
1. Zinc oxide 5.55; *2.* zinc oxide 11.1; *3.* zinc oxide 22.2; *4.* zinc oxide 44.4; *5.* Potasit contacted with oxygen 44.4.

Though the used ZnO had only a slightly smaller specific area (4 m^2 g^{-1}) than Potasit, the course of conversion is partly different, particularly in the presence of an induction period in the case of ZnO. While in the case of Potasit the conversion curve goes out from the origin of the coordinates, in the case of ZnO there appears an induction period on the conversion curve, which is the shorter, the higher the concentration of ZnO. This fact can be connected with the different initiation character, when this type of heterogeneous initiator is used.

It is well known from the literature [13, 14] that ZnO behaves as a photosensibilizer sensitive to u.v. and visible light. The authors of the mentioned papers assume that in consequence of the action of light on the surface of ZnO the ionic radical $\dot{O}_2^-$ is formed. In this way the crystal of ZnO loses electrons; the ionic radicals $\dot{O}_2^-$ or the oxygen molecule will be able on the site of the electron deficiency to pull off either the hydrogen

$$\dot{O}_2^- + H_2O \rightarrow HO_2^- + \dot{O}H \qquad (A)$$

or the electron from the organic molecule. In both cases the result is the initiation of the chain reaction.

For this reason the possibility of using ZnO and other chemically similar metal oxides as heterogeneous photosensibilizers was verified on the emulsion polymerization of methyl methacrylate at the same composition of the polymerization system as in the case of styrene polymerization. If the results were positive in daylight, the individual experiments were repeated in black ampoules. The obtained results are summarized in Table 3. From these it is evident that methyl methacrylate is also in this case a faster polymerizing monomer than styrene (Table 2), with the exception of the MgO—TETA combination, by the use of which the styrene polymerization was faster. Among the metal oxides used in the polymerization system only zinc oxide and magnesium oxide manifest themselves as photosensibilizers; without access of light polymerization does not take place at all, or a very low conversion, in comparison with the polymerization by the action of light, was reached.

Table 3

Polymerization rate of methyl methacrylate in the presence of various metal oxides as heterogeneous initiators at 30 °C[a]

Activator type	Oxide type	$v/(\text{conv. }\%)\ h^{-1}$	
		Daylight	Without access of light
$FeSO_4$—EDTA	CuO	48.5	53.2
	NiO	42.0	35.3
	ZnO	10.5	1.3
	Fe_2O_3	50.0	67.4
TETA	CuO	100.0	80.0
	ZnO	21.6	0
	MgO	4.3	0

a) The concentrations of the compounds are the same as in Table 2.

References

1. *Czech.* 159670 (1970).
2. Mikulášová, D., Chrástová, V., and Citovický, P., *Eur. Polym. J. 10*, 551 (1974).
3. Mikulášová, D., Chrástová, V., Citovický, P., and Fačková, T., *Chem. Zvesti 32*, 186 (1978).
4. Le Bail, H. and Zemb, T., *C. R. Acad. Sci., Ser. C 276,* 121 (1973).
5. Barson, C. A., Knight, J. R., and Robb, J. B., *Brit. Polym. J. 4,* 427 (1972).
6. Fukano, K. and Kageyama, E., *J. Polym. Sci., Polym. Chem. Ed. 13*, 1309, 1325, 2103 (1975).
7. Manley, T. R. and Murray, B., *Eur. Polym. J. 8,* 1145 (1972).
8. Taubman, A. B., Yanova, L. P., Blyskosh, G. S., and Ryabchikova, G. Ts., *J. Polym. Sci. 10*, 2085 (1972).
9. Moustafa, A. B., Ghanem, N. A., and Diab, M. A., *J. Polym. Sci. 13*, 1987 (1975).
10. Mansour, O. Y. and Nagaty, A., *J. Polym. Sci. 13*, 2785 (1975).
11. Mansour, O. Y. and Moustafa, A. B., *J. Polym. Sci. 13,* 2795 (1975).
12. Fukano, K. and Kageyama, E., *J. Polym. Sci., Polym. Chem. Ed. 14*, 23, 275, 1031, 1743, 2183, 2193 (1976); *15*, 65 (1977).
13. Markham, M. C. and Laidler, K. I., *J. Phys. Chem. 57*, 363 (1953).
14. Markham, M. C., Hannan, M. C., and Evans, S. W., *J. Amer. Chem. Soc. 76*, 820 (1954).

Translated by P. Rosner and Š. Bachratý