

## **Influence of triethylenetetramine on the emulsion polymerization of styrene**

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The influence of triethylenetetramine on the emulsion polymerization of styrene initiated by polypropylene polyhydroperoxide or AIBN at 30°C as well as its influence on the polymerization of styrene initiated thermally at 75°C was investigated.

The results obtained indicate that the investigated amine in addition to the activation of the decomposition of peroxides of oxidized polypropylene positively influences styrene polymerization also in another way. Because of its basic character it changes the pH and by that to some extent also the character of emulsion. Owing to its structure it can influence the polarization of the double bond of styrene and thus facilitate its bonding to a growing radical. These effects of triethylenetetramine considerably raise the rate of styrene polymerization in the investigated emulsion polymerization systems.

Изучалось влияние триэтиленetetрамина на эмульсионную полимеризацию стирола, инициированную полигидроперекисями полипропилена, или АИБН при 30°C и его влияние на термически инициированную полимеризацию стирола при 75°C.

Полученные результаты указывают, что изучаемый амин, наряду с активацией разложения перекисей окисленного полипропилена, положительно влияет на полимеризацию стирола и иным способом: своим щелочным характером изменяет pH среду и тем в определенной степени и характер эмульсии; своей структурой может влиять на поляризацию двойной связи стирола и тем облегчить его навязание на радикал ростовой. Приведенные влияния триэтиленetetрамина отчетливо повышают скорость полимеризации стирола в исследованных эмульсионных полимеризационных системах.

In preceding papers [1—3] it was stated that high-molecular polystyrene could be prepared by the emulsion polymerization initiated by a macromolecular initiator, that is by powdered oxidized polypropylene at low temperature. In these studies the influence of the components of polymerization system on the rate of polymerization and molecular weight of polystyrene prepared was investigated. It appeared that the activator used (triethylenetetramine) had significant influence on

the investigated parameters (although the polymerization proceeds also in its absence). It was revealed that triethylenetetramine accelerated the polymerization only up to a certain concentration over which it started to have a negative effect on the rate of polystyrene formation. The molecular weight of the polystyrene prepared decreased with increasing concentration of triethylenetetramine.

In connection with these results, the role of triethylenetetramine in the polymerization of styrene initiated by powdered oxidized polypropylene is investigated in more detail in this study. The obtained results are compared with the results of the polymerization initiated in other way.

## Experimental

### Chemicals

Isotactic powdered polypropylene (PP) was a product of Slovnaft, Bratislava. The residual atactic fractions and stereoblocks were removed by extraction with boiling *n*-heptane. Using the fluid fractionation a fraction with grain size of 0.15—0.1 mm was obtained. The fluid oxidation of polypropylene was carried out by oxygen enriched with ozone. The content of hydroperoxides was determined iodometrically with KI in glacial acetic acid at room temperature.

Styrene was purified by shaking with sodium hydroxide solution and distilled twice under reduced pressure in a nitrogen atmosphere.

Triethylenetetramine —  $\text{H}[\text{NH}(\text{CH}_2)_2]_3\text{NH}_2$  (TETA) was synthesized from ethylenediamine and ethylene dichloride [4]. The aqueous solution used was kept in an inert atmosphere.

$\alpha, \alpha'$ -Azobisisobutyronitrile (AIBN) was purified by recrystallization before use.

Slovasol 2430 — an aliphatic alcohol with 30 moles of ethylene oxide (a product of ChZWP, Nováky). It was used in the form of an aqueous solution which was kept in an inert atmosphere and boiled for one hour under nitrogen before polymerization.

Water was distilled in a glass apparatus, boiled under nitrogen, and held in an inert atmosphere.

Nitrogen (high purity) was before use further purified in a column the packing of which consisted of  $\text{MnO}_2$  (55%),  $\text{MgO}$  (40%), and  $\text{Cr}_2\text{O}_3$  (5%).

Other chemicals were anal. grade.

### Procedures

The emulsion polymerization was carried out either in glass ampules with the volume of emulsion of 18 cm<sup>3</sup> or in a two-neck vessel with the 5-fold volume of emulsion adapted for sampling in an inert atmosphere [1] and/or in a special apparatus [5] allowing to remove polypropylene by filtration in the course of polymerization.

The ampules containing a constant weighed amount of oxidized polypropylene were

evacuated to 65 Pa for 4 h and the vacuum was twice cancelled with nitrogen. Then other components of the polymerization system were dosed in an inert atmosphere. After filling the ampules were sealed and put into a revolving frame placed in a thermostat (30°C).

In the case of polymerization carried out in special arrangements (fully described in [1] or [5]) the weighed polypropylene was deprived of oxygen by two-fold evacuation and the particular components were added in an inert atmosphere in the same way as in the case of ampules. The filled vessel was put into a thermostat (30 or 75°C). The content was stirred with a magnetic stirrer. The samples were taken through a cap of elastic rubber by means of a syringe.

The aqueous phase of the polymerization system contained triethylenetetramine ( $3.6 \times 10^{-3}$  mol dm<sup>-3</sup> of emulsion) and Slovasol 2430 ( $1.2 \times 10^{-2}$  mol dm<sup>-3</sup> of emulsion) while the organic phase was represented by styrene (in the amount of 3 or 15 cm<sup>3</sup>).

When oxidized polypropylene was used as initiator, it contained  $4 \times 10^{-4}$  moles O<sub>2</sub> per 1 dm<sup>3</sup> of emulsion and if AIBN was used, its styrene solution of equal molar concentration was applied.

From the emulsion obtained by polymerization either in ampules or in both special arrangements polystyrene was precipitated by methanol. The conversion of styrene was expressed in weight % of initial monomer.

## Results and discussion

In examining the role of TETA in the emulsion polymerization of styrene initiated by oxidized polypropylene the previous results were used according to which TETA was able either to react with growing radicals and thus to cause the transfer reactions or to take part in the reaction with primary radicals. In order to eliminate the participation of TETA in transfer reactions, the macromolecular initiator — oxidized polypropylene — was replaced by a low-molecular initiator AIBN. It was observed that neither the rate of polymerization changed nor the molecular weights decreased with increasing concentration of TETA [1, 3] if this type of initiator was used for the initiation of the emulsion polymerization of styrene.

The investigation of the conversion curves of the emulsion polymerization of styrene initiated by AIBN in the absence and in the presence of amine (Fig. 1) revealed that TETA accelerated the polymerization even in the system containing an initiator the decomposition of which it should not have activated. Therefore in this case, the increase in the rate of polymerization should not be caused by a direct participation of TETA in initiation reactions but by another effect of TETA in the investigated polymerization system.

In order to eliminate the direct effect of TETA on initiator; the polymerization of styrene was initiated thermally in emulsion in the absence of amine at 75°C (Fig. 2, curve 2). The course of this polymerization was compared with the course of the polymerization which was also initiated thermally in a system into which

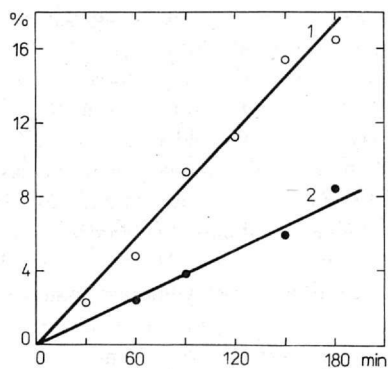


Fig. 1. Conversion curves of the emulsion polymerization of styrene initiated by AIBN at 30°C: 1. in the presence of TETA; 2. in the absence of TETA.

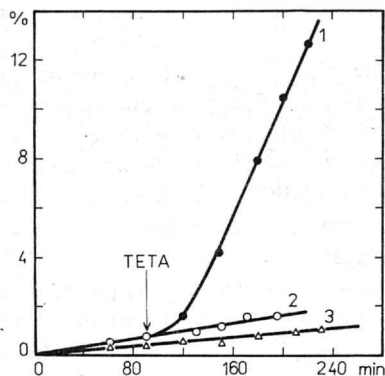


Fig. 2. Conversion curves of the polymerization of styrene initiated thermally at 75°C.

1. Emulsion polymerization, addition of TETA; 2. emulsion polymerization without TETA; 3. block polymerization, addition of TETA.

triethylenetetramine was added after 90 minutes' polymerization (Fig. 2, curve 1). It appeared that TETA raised the rate of thermally initiated polymerization again provided the process was carried out in emulsion. An addition of amine after 90 min in block polymerization of styrene had no accelerating effect (Fig. 2, curve 3). In the case of thermal initiation triethylenetetramine accelerates the polymerization of styrene in emulsion though it cannot activate the decomposition of initiator.

The effect of TETA which did not consist in a participation in initiation but in another role had also to be investigated for the emulsion polymerization of styrene initiated by peroxide of oxidized polypropylene. In this system the polymerization may be also carried out without simultaneous presence of initiator if the polymerization is started by the peroxide of oxidized polypropylene which can be after certain time separated from the system by filtration without interrupting the polymerization. The result presented in Fig. 3 (curve 3) gives evidence that the polymerization proceeds also after the separation of oxidized polypropylene without any addition of activator. If some amine is added into the polymerization system after the separation of macromolecular initiator, the rate of polymerization increases considerably (Fig. 3, curve 1). Since no initiator was present in the polymerization system in this case as well as in the case of thermal initiation, the effect of TETA must be due to influencing other components or characteristics of the polymerization system.

Owing to the basic character of TETA it was supposed that this substance could affect the pH of emulsion. The problem how the amine used affects the pH value

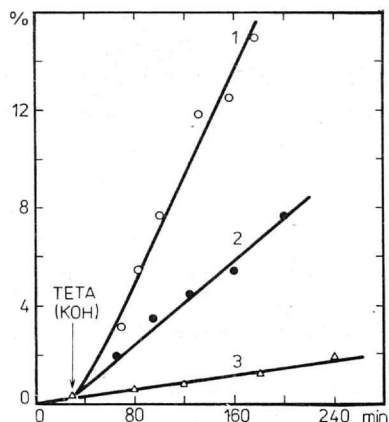


Fig. 3. Conversion curves of the emulsion polymerization of styrene initiated by oxidized polypropylene at 30°C.

1. Polypropylene filtrated after 30 min, addition of TETA; 2. polypropylene filtrated after 30 min, addition of KOH; 3. polypropylene filtrated after 30 min, no addition of TETA.

was solved by means of an experiment in which polypropylene was removed by filtration from the polymerization system and afterwards TETA was replaced by potassium hydroxide the concentration of which was so chosen that a comparable pH value could be obtained. The results of this polymerization are presented in Fig. 3 (curve 2). It appeared that the addition of KOH into the polymerization system, too, accelerates the polymerization but its influence is smaller than that of the addition of TETA.

It is obvious that the increase in the rate of polymerization in the presence of TETA in the system is due not only to its influence on the pH but also to a possible influence on other components of the polymerization system, which are styrene and emulsifier used. It is also possible that owing to its structure TETA is able to polarize the double bond of styrene and thus to facilitate its bonding to the growing radical (in the extreme case involving the use of acrylonitrile even the addition of polyamine to the double bond of monomer takes place [6]). As the polymerization proceeds in emulsion, it cannot be excluded that the effect of TETA on the rate of polymerization may be in connection with the character and concentration of the emulsifier used.

On the basis of the results obtained up to now it may be concluded that TETA influences the course of the emulsion polymerization of styrene initiated by oxidized isotactic polypropylene in various ways:

— In the complete polymerization system, that is in the presence of oxidized polypropylene and polyamine during the whole polymerization time, triethylenetetramine activates the decomposition of hydroperoxide [7]. Its reaction with primary radicals which could be responsible for the observed low efficiency of initiation [3] may be assumed.

— Owing to its basic character triethylenetetramine influences the pH and the

character of emulsion and because of its structure it may contribute to the polarization of the double bond of monomer. It was found that the effect of these two factors might significantly increase the rate of the emulsion polymerization of styrene in the investigated polymerization system.

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