

Asphalts as Inhibitors of Radical Polymerization

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Synopsis

The results of investigations concerning the effect of asphalts on radical polymerization of a monomer for model systems composed of styrene and two petroleum asphalts originated from two different crude oils: low sulphur nonparaffinic crude oil and medium sulphur paraffinic crude oil. Based on determination of styrene conversion in the radical polymerization process in the presence of asphalts, it was found that both asphalts act as inhibitors of this reaction. The inhibiting effect of asphalts is weakened by using higher temperatures and prolongation of polymerization time or application of greater initiator rates. On the basis of the analysis of group and elementary chemical composition of both asphalts as well as electron paramagnetic resonance, it was found that the inhibiting effect to radical polymerization is caused mainly by the presence of structures which are stable free radicals in character. The probability of inhibiting effect by sulphur compounds present in asphalts is also discussed.

INTRODUCTION

Polymerization inhibiting processes retard or stop polymerization. Typical inhibitors of radical polymerization react with free radicals and therefore produce nonreactive products or products of very low reactivity.

The group includes many various substances. The most popular radical polymerization inhibitors are quinones¹⁻³ and aromatic nitro compounds.⁴⁻⁶ For many monomers the inhibiting features are shown by aromatic amines⁷ and ions of variable valency metals such as copper, iron, chromium, lead, silver, and mercury in the form of sulphates, chlorides, acetates, and salicylates.^{8,9} In the radical polymerization of some monomers the inhibiting performance is shown by such chemical elements as oxygen and sulphur.

Very interesting inhibitors of radical polymerization are complex structures which stabilize free radicals^{10,11} in polymerization media, mainly by recombination and disproportionation. In experimental studies on the radical polymerization process, the free radical inhibitors show several practical advantages: They are usually colored substances which lose color on recombination, thus the possibility of analysis by colorimetric or spectrophotometric methods. The effective inhibitor should, even in low concentration, protect the monomer against polymerization during transportation and storage. Moreover, such an inhibitor should be easily removable.

Šhostakowskij and his collaborators suggest that all the above criteria of inhibitors for radical polymerization can be met by asphaltenes from crude oil.^{12,13} The mechanism of polymerization inhibiting by asphaltenes is explained by Šhostakowskij as a function of their structure based on conjugated bond systems. Free radicals existing in such systems are stabilized by the conjugation and, therefore, are not subjected to recombination but show inclination for reaction

with active radicals of the polymerization media. Asphaltenes have also been used as inhibitors for polymerization of products in pyrolysis processes.¹⁴

In the light of literature reports on the inhibiting influence of asphaltenes to radical polymerization, it was decided to start a more detailed investigation of this problem, for two main reasons: to determine the behavior of asphalts containing asphaltenes, in polymerization processes; to evaluate practical possibilities of conducting radical polymerization of some monomers "in situ" in the asphalt to modify its chemical properties. The present study shows the results of investigations on asphalt behavior in radical polymerization media.

EXPERIMENTAL

Model systems composed of styrene and naphthenic asphalts were used in this study. These systems were subjected to radical polymerization initiated by benzoyl peroxide.

Styrene monomer was selected since it is easily dilutable with asphalt and highly inclined to polymerization according to radical mechanism.

Among several grades of naphthenic asphalts, two grades of different chemical and physical properties were selected for this study: road asphalt D-35 of low melting point, originating from romashkino crude oil of medium sulphur content; asphalt Filex 110 used for painting purposes, originated from domestic crude oil.

Characteristics of the asphalts are given in (Table I). For this study, styrene-asphalt systems containing in their initial composition no more than 20 wt % of asphalt were investigated. Just before use in polymerization, the inhibitor was removed from styrene by means of washing with NaOH water solution and distillation under pressure of 20 mm Hg. Benzoyl peroxide was purified by dissolving in chloroform and then recrystallization with methyl alcohol.

Bulk polymerization of styrene in the presence of asphalts was conducted in nitrogen atmosphere. Polymerization initiator was dissolved in monomer, to which the weighted portion of asphalt was added and carefully stirred at ambient temperature until the asphalt completely dissolved in styrene.

Then the mixture was heated in a reactor equipped with mixer, at specified temperature and heating time. Since it was found that the reaction process can lead to a high degree of monomer reaction, the gravimetric method was used for quantitative evaluation of the polymerization process. After completing the experiment, the reaction product was precipitated in methanol, filtered, and dried at a temperature of 30°C and 0.1 kg/cm² pressure.

As a final result the arithmetic mean of at least two experiments (results of difference not exceeding 2%) was taken into account. Preliminary investigations showed that polymerization of the system containing 95 wt % styrene and 5 wt % asphalt, initiated with the addition of 0.5 wt % of benzoyl peroxide (to monomer) should be performed at the temperature not exceeding 115°C and within a time period not shorter than 180 min.

Investigations on the influence of asphalts on radical polymerization of styrene were conducted in aspects of quantity of this material in reaction medium content of initiator as well as temperature and time of the reaction.

The behavior, was also investigated in a polymerization medium of individual

TABLE I
Physicochemical Properties of Asphalts

| Properties of asphalts | Values | | Methods of measurement |
|------------------------------|--------|-----------|---------------------------|
| | D-35 | Filex 110 | |
| Softpoint (ring-and-ball) °C | 57.5 | 129.5 | PN/C-04021 |
| Penetration at 25°C | 32.0 | — | PN-62/C-04134 |
| Ductility (cm) | 26.1 | — | PN-62/C-04132 |
| Break point (°C) | -7.0 | — | PN/C-04130 |
| Flash point, (°C) | 240.5 | 253.5 | PN-65/C-04008 |
| Density (g/cm ³) | 1.007 | 1.094 | PN-66/C-04004 |

group components of asphalts separated with benzene and acetone applying the solvent-precipitation method according to Polish Standard BN-64/0538-02.

Spectroscopic investigations of electron paramagnetic resonance (EPR) of asphalts and styrene polymerization products in the presence of asphalts were conducted with EPR spectrometer operating in X band at modulation 100 kHz at room temperature, calibrated to 1,1-diphenyl-2-picryl-hydrazine. Elementary analyses of asphalts and their group components for carbon and hydrogen were performed in a Coleman Type M33 apparatus. Elementary sulphur content was determined in a Hermann-Moritz apparatus and nitrogen content in a Coleman type M29 apparatus. The molecular mass of polymerization products was determined by viscosity, using benzene as a solvent.

RESULTS AND DISCUSSION

In radical polymerization asphalts act as inhibitors, and the inhibiting efficiency strictly depends on the asphalt content in reaction medium (Fig. 1). A decreasing line of curves expressing the dependence of the styrene conversion rate from asphalt content in reaction medium shows a slowing down of styrene polymerization initiated by benzoyl peroxide. Simultaneously to the increase of D-35 asphalt quantity introduced to a polymerization medium, a continuous

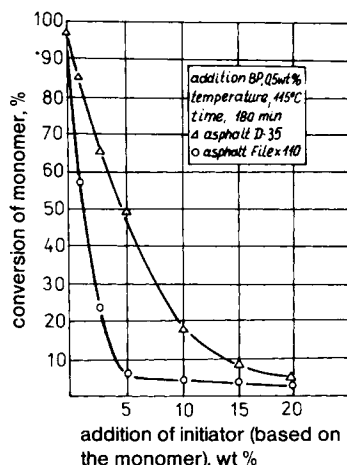


Fig. 1. Dependence of styrene conversion rate on asphalt content in the reaction medium.

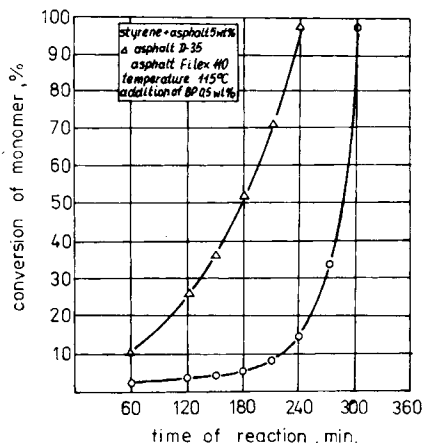


Fig. 2. Dependence of styrene conversion rate in the presence of asphalt on time of reaction.

decrease of styrene conversion range (till the value of 5%) can be seen. The presence of Filex 110 asphalt in quantity equivalent to 1–1.5 wt % monomer wt produces a rapid decrease in styrene conversion rate up to the value of a few percent, but a further increase in asphalt weight participation in reaction does not produce essential changes in monomer conversion. An effective decrease in styrene conversion for the determined quantity of D-85 asphalt in the range of 1–10 wt % is much smaller than the case of the same quantities of Filex 110 asphalt. Thus, a different inhibiting efficiency was observed for the two investigated asphalts. A further series of experiments performed to investigate the influence of time and temperature as well as initiator content on the range of monomer conversion were provided to determine whether it is possible to limit the inhibiting action of asphalts in polymerization processes. Results of these investigations (Fig. 2) illustrate dependence of the styrene reaction range in the presence of D-35 and Filex 110 asphalts on the time of reaction. The curves are much different in shape. The growth of monomer conversion rate in the presence of D-35 asphalt and within experimental time limits are rather proportional, while in the case of Filex 110 asphalts the remarkable rise of polymerization efficiency appears for a reaction time of 240–300 min.

A similar range of dependence was obtained for both asphalts as a result of temperature influence investigations (Fig. 3). The temperature 135°C is the maximum temperature at which the inhibiting action of both asphalts is eliminated. The styrene polymerization process is retarded by D-35 and Filex 110 asphalts. Investigations were conducted on the influence of quantity of benzoyl peroxide used as reaction initiator in order to determine the sensitivity of such activity for the increased initiation efficiency and what quantities of initiators in polymerization media would reduce the retarding effect of both the asphalts in given process conditions. Experiments conducted within this series of investigations indicate that the results (Fig. 4) comply with the theory and with experiments on inhibition in radical polymerization. An increase in initiator quantity gives an increase in the extent of monomer reaction.

Comparison of curves (Fig. 4) shows, however, that for analogical quantities of benzoyl peroxide much higher values of styrene conversion are noted, especially

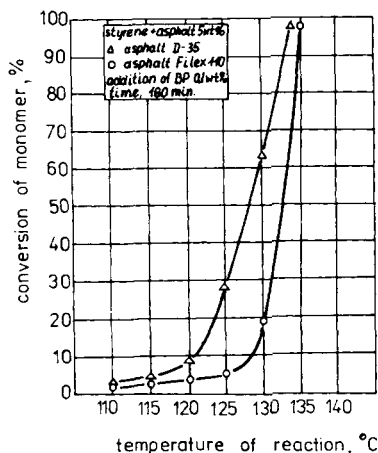


Fig. 3. Dependence of styrene conversion rate in the presence of asphalt on temperature of reaction.

in the area of 0.5–1.5 wt % of initiator content. The maximum extent of monomer reaction (ca. 100%) in presence of D-35 asphalt is obtained by initiating the polymerization process with 1.5 wt % benzoyl peroxide. To reach such polymerization efficiency in presence of Filex 110 asphalt requires nearly double the quantity of initiator amounting to 2.5–3.0 wt % monomer. The inhibiting effect of Filex 110 asphalt in styrene radical polymerization is stronger than that of D-35 asphalt. Reduction or total elimination of the polymerization inhibiting effect as a result of rise of temperature or prolongation of time of reaction, or by increasing initiator quantity, is more difficult to obtain in systems containing Filex 110 asphalt than with D-35 asphalt.

The inhibiting effect of asphalts in radical processes is related to the presence of asphaltenes containing particles of free radicals. The presence of free radicals

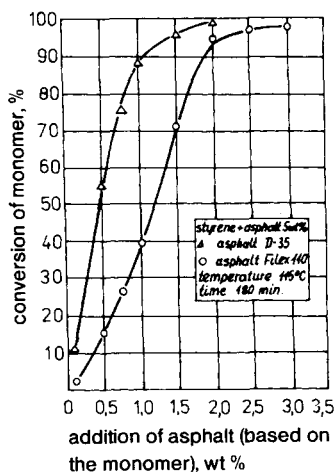


Fig. 4. Dependence of styrene conversion rate in the presence of asphalt on addition of initiator.

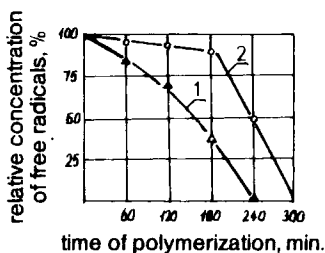


Fig. 5. Change of relative concentration of free radicals in styrene polymerization products on dependence of time of reaction: (1) for asphalt D-35; (2) for asphalt Filex 110.

was detected in both asphalts using EPR; for D-35 asphalt 1.5×10^{16} free radicals, for Filex 110 asphalt, 4.1×10^{16} free radicals.

Since it was experimentally proven that progressive elimination of the retarding effect of asphalts with a rise in temperature, prologation of polymerization time, and an increase in quantity of benzoyl peroxide, a supposition was that these factors cause a decrease in quantity of asphalt free radicals participating actively in the process.

By analysis of changes in free radicals concentration in polymerization products, obtained at progressively increased time and temperature of reaction, it was discovered that such phenomenon exists. Changes in relative concentration of free radicals complying with individual values of polymerization time and temperature are shown in Figures 5 and 6.

Relative concentration was obtained assuming the content of free radicals in initial asphalts as 100%. The higher the temperature and longer the time of polymerization, the lower the free radical content in the products, such content being ultimately eliminated. This can be explained by recombination of free radicals during the reaction process. A decrease in free radical concentration is faster in the case of products in styrene polymerization in the presence of D-35 asphalt.

EPR investigations indicate the active role of free radicals in the inhibiting effect of asphalts in radical polymerization of styrene. This is also confirmed by determination of molecular mass of styrene polymerization products in presence of D-35 and Filex 110 asphalts. Values of average masses were deter-

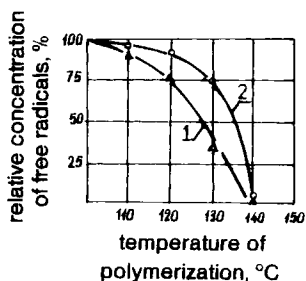


Fig. 6. Change of relative concentration of free radicals in styrene polymerization products on dependence of temperature of reaction: (1) for asphalt D-35; (2) for asphalt Filex 110.

TABLE II
Results of Determination of Average Molecular Weight of Styrene Polymerization Products in Presence of Asphalts

| Amount of asphalt in polymerization medium (wt % based on styrene) | Mean mol. weight of polymerization products of styrene in the presence of asphalts | |
|--|--|---------------------|
| | D-35 | Filex 110 |
| 0.0 | 9.55×10^4 | 9.55×10^4 |
| 5.0 | 10.10×10^4 | 13.24×10^4 |
| 10.0 | 12.31×10^4 | 14.10×10^4 |
| 15.0 | 12.95×10^4 | 14.05×10^4 |
| 20.0 | 13.42×10^4 | 15.05×10^4 |

mined for monomer polymerization product in presence of variable asphalt additives.

Results of determinations are given in Table II. Filex 110 asphalt has a higher deactivation effect.

Group composition of the investigated asphalts is shown in Table III. To investigate the styrene polymerization process in the presence of separated group components of D-35 and Filex 110 asphalts, a series of experiments was conducted introducing various quantities of oils, resins, and asphaltenes to the monomer. The polymerization process was conducted under conditions as provided in the first stage of the investigation. Surprising was the fact of polymerization inhibited by both types of asphalt oils, since EPR investigations did not detect the content of free radicals in oils in contrast to resins and asphaltenes. Free radicals are not the unique cause of the polymerization-inhibiting effect. When analyzing the cause for such a process by some other factors, consideration was given to the content of sulphur compounds which are present in both kinds of oils. The presence of comparable quantities of sulphur identified in compounds other than mercaptanic and sulphide were found. Probability of the above hypothesis is confirmed by similar character of inhibiting effect of both oils to polymerization efficiency (Fig. 7). In the discussion on the inhibiting effect of resins and asphaltenes to radical polymerization of styrene, it should therefore be taken into account the presence of both free radicals and some quantities of sulphur. When comparing the results, it should be underlined that free radicals are most important in the inhibiting process. Due to difficulties in the selection of a proper investigation method, it was not possible to determine the amount of inhibition caused by the presence of sulphur. Since resins of both

TABLE III
Group Composition of Asphalts

| Type of asphalt | D-35 | Filex 110 |
|-----------------|------|-----------|
| Oils | 43.4 | 48.4 |
| Resins | 27.3 | 15.7 |
| Asphaltenes | 29.4 | 35.9 |

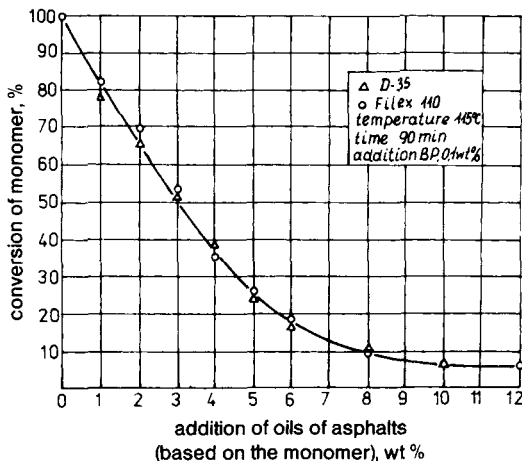


Fig. 7. Dependence of styrene conversion rate on asphalt oil content in reaction medium.

asphalt grades contain less sulphur than corresponding oils, its presence in inhibiting polymerization in the presence of resins is rather negligible.

However, in the case of asphaltenes of high concentration of stable free radicals, their action is so dominant that the eventual effect of sulphur is unrecordable.

Inhibiting of styrene polymerization is more intense than that of the two group components and, therefore, it should be assumed that action of unseparated asphalts in polymerization medium is dominated by asphaltenes.

CONCLUSIONS

1. In styrene radical polymerization initiated by benzoyl peroxide, the petroleum asphalts D-35 and Filex 110 act as inhibitors. The inhibiting effect of those asphalts is weakened by the rise in reaction temperature, prolongation of reaction time, or introduction to reaction medium of larger quantities of initiator.

2. The effect of polymerization inhibition is caused mainly by active participation in reaction of asphalt free radicals, but may also be due to sulphur compounds present in asphalts.

3. In the radical polymerization inhibiting process the most important role is played by asphalt free radicals; asphalt Filex 110 of low sulphur content and high content free radicals is a better inhibitor than asphalt D-35 medium sulphur crude oil with lower concentration of free radicals.

4. The inhibiting effect of asphalt Filex 110 is more difficult to eliminate than asphalt D-35. EPR investigations show that free radicals present in asphalt Filex 110 are of longer life.

5. Among three basic group components separated from the investigated asphalts, the most inhibiting in character are asphaltenes. Since asphaltenes contain free radicals and a large quantity of sulphur, it should be assumed that in radical polymerization inhibition caused by asphalts the main effect is due to asphaltenes.

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