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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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INTERACTION OF POLYCHLOROPRENE WITH THIOBENZOIC ACID

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In order to study the influence of a strongly electronegative chlorine atom on the reactivity of the double bond in diene polymers, the kinetics of the reaction of polychloroprene* with thiobenzoic acid (TBA) was investigated. The reaction was carried out in benzene, xylene, and chlorobenzene in an inert medium (argon) in the presence of an initiator (cumene hydroperoxide). Polychloroprene and TBA were taken in an equimolecular ratio; their concentration was varied from 0.5 to 2%. The extent of reaction was determined by conductometric titration of unreacted TBA with silver nitrate. The dependence of the reaction rate on temperature, the concentration of the reacting substances, the concentration of initiator, and the nature of the solvent was studied.

The influence of the initiator concentration on the reaction rate is shown in Fig. 1. When the reaction is carried out in benzene and xylene at temperatures of 75 and 125°, the introduction of up to 12 mole % of cumene hydroperoxide has practically no effect on the course of the reaction.

Fig. 1. Influence of the concentration of cumene hydroperoxide on the kinetics of addition of thiobenzoic acid to polychloroprene (A—solvent xylene, t 125°, concentration of reacting substances 1%; B—solvent benzene, t 75°, concentration of reacting substances 1%; a—0°, b—12, c—2.4, d—6 mole % cumene hydroperoxide)

The dependence of the reaction rate on temperature is shown in Fig. 2. In xylene the reaction at 75° proceeds faster and to a greater extent than at 125°. In chlorobenzene there is practically no difference.

Figure 3 presents the dependence of the reaction rate on the nature of the solvent. The reaction was carried out in benzene ($\varepsilon = 2.3$), xylene ($\varepsilon = 2.4$), and chlorobenzene ($\varepsilon = 10.3$) at a temperature of 75°. The reaction proceeds at the same rate and to the same extent in benzene and chlorobenzene, and to a considerably greater extent in xylene.

The absence of an influence of the initiator on the course of the reaction of TBA with polychloroprene indicates the nonradical character of this reaction. The reaction does not proceed by an ionic mechanism, since otherwise the dielectric constant of the solvent should play a significant role, which is not observed in our case. We assume that the addition of TBA to polychloroprene proceeds through the stage of formation of a π-complex due to interaction of the d-orbitals of the sulfur atom with the π-electrons of the double bond of polychloroprene. At higher temperatures the stability of the π-complex is lower, which leads to a negative temperature dependence of the reaction rate.

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* Polychloroprene rubber of low-temperature polymerization was used.

The role of the chlorine atom is as follows. The thiyl radical, when the reaction is carried out in the presence of an initiator, adds to the double bond contrary to Markovnikov' s rule:

$$\sim CH_2 - \underset{\cdot}{C} - \underset{|}{\underset{Cl}{CH}} - \underset{|}{\underset{SCOC_6H_5}{CH_2}} \sim$$

However, the macroradical formed, because of the stabilizing action of the chlorine atom, does not possess sufficient activity to continue the reaction. Therefore, the radical mechanism characteristic of the reaction of polyisoprenes with TBK[1–4] does not occur in the case of the reaction of TBK with polychloroprene.

Fig. 2. Effect of temperature on the kinetics of addition of thiobenzoic acid to polychloroprene (concentration of reacting substances 1%). 1, 1′—xylene, 2, 2′—chlorobenzene; 1, 2—at 75°, 1′, 2′—at 125° C.

Fig. 3. Effect of solvent on the kinetics of addition of thiobenzoic acid to polychloroprene (t 75°, concentration of reacting substances 1%). 1—xylene, 2—benzene, 3—chlorobenzene.

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Note: Figure translations are in progress. See original paper for figures.