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Abstract

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ON ANIONIC POLYMERIZATION IN THE PRESENCE OF AROMATIC COMPOUNDS

The generally accepted scheme of polymerization in the presence of metalloaromatic initiators ([1,2]) assumes the participation of the aromatic component only at the initiation stage (transfer of an electron from the aromatic ion-radical to the monomer). The possibility of participation of aromatic hydrocarbons in acts of anionic chain growth has not hitherto been considered.

We have established that anthracene causes a sharp decrease in the rate of anionic polymerization of styrene initiated by sodium-aromatic complexes in tetrahydrofuran, the magnitude of the decrease depending substantially on the anthracene : styrene ratio. If the rate constant for growth, or anionic polymerization, of styrene in THF at 25° is 285–570 l/mol · sec ([3]), then in the presence of anthracene the observed rate constant (the rate of polymerization divided by the concentrations of active centers and monomer) has, at 20°, a value of the order of 0.1 l/mol · sec at a molar ratio anthracene : styrene = 1 : 30, and $3 \cdot 10^{-3}$ l/mol · sec at a ratio anthracene : styrene = 1 : 6.

The inhibiting action of anthracene is observed both when it is introduced together with the initiator (sodium-naphthalene or sodium-anthracene) and when a styrene–anthracene mixture is added to "living" polystyrene obtained on sodium-naphthalene or sodium-diphenyl. The rate of polymerization is constant up to 30–40% conversion. The molecular weight of the polymers, except for those obtained on sodium-anthracene in the absence of free anthracene, agrees to within 10% with that calculated from the formula

$$\overline{M} = \frac{2M_0}{K}, \tag{1}$$

where M_0 is the amount of monomer in grams, and K is the amount of initiator in moles.

The facts cited indicate that the process proceeds with a constant number of active centers, equal to the amount of initiator taken, and in the absence of chain transfer. Consequently, the retardation is not connected with a decrease in the number of active centers as a result of a shift to the left of the initiation equilibrium:

Fig. 1. Electronic absorption spectra of the polystyrene—anthracene system in THF

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$$A^{\dot{-}} + C \rightleftarrows A + C^{\dot{-}} \quad \text{(II)}$$

(A and C are, respectively, anthracene and styrene; the asterisk marks ion-radicals, i.e., molecules having an excess electron)—and complete transfer of excess electrons from anthracene to styrene takes place. The absence of A^* in the system was also confirmed spectrophotometrically. This fact may seem strange, since the equilibrium constant of reaction (II) at 25° is 10^{-7} (difference of normal potentials −0.41 V (4)), and even at an anthracene : styrene ratio = 1 : 10 the equilibrium concentration of styryl ion-radicals C^* is 10^6 times less than the concentration of A^*. Apparently, complete depletion of A^* is promoted by the irreversible consumption of C^* as a result of reac-

···with the monomer and recombination (2), and a very small consumption of monomer at the initial stage owing to the sharp slowing of the rate of the growth reaction in the presence of anthracene. In polymerization on sodium-anthracene in the absence of free anthracene, an increase in molecular weight by a factor of 1.5–2 is observed in comparison with that calculated by formula (1); however, even in this case, despite the high rate of the process, ions A^* are not detected spectroscopically after completion of the polymerization.

Thus, the slowing effect is associated with the participation of anthracene in the acts of growth. In all probability, copolymerization of anthracene and styrene takes place. It is known that anthracene is very active in radical reactions (5); its radical copolymerization with butadiene has been described (6). The participation of anthracene in anionic copolymerization has not previously been reported. It may be expected that, on adding to the carbanions of styrene, it will form a rather stable and relatively inactive anion, owing to considerable delocalization of the charge; the observed kinetic effects agree well with such ideas.

Fig. 1. Electronic absorption spectra of the polystyrene—anthracene system in THF

To test the supposition that copolymerization of anthracene with styrene occurs, we carried out the following experiment. To a solution of "living" polystyrene obtained on sodium-naphthalene, anthracene was added in an amount three times greater than the number of active centers. In the electronic absorption spectrum of the system recorded after this, the peaks of free anthracene are clearly visible (341, 358, 378 mμ); at the same time, the absorption maximum of the "living" polymer shifts from 340 mμ to 445 mμ (see Fig. 1, curves 1, 2). After polymerization of additional amounts of styrene, free anthracene is practically not detected in the system (curve 3), which confirms its participation in copolymerization with styrene.

Curve 3 also shows that the shifted position of the absorption maximum in the spectrum of "living" polystyrene is retained even after polymerization of new portions of monomer; the polymer obtained on sodium-anthracene likewise has an absorption maximum at 445 mμ. Similar phenomena were observed long ago by Levy et al. ([7]). In contrast to ordinary "living" polystyrene, whose spectrum changes substantially as early as one day after its preparation ([8]), the spectrum of the polymer obtained in the presence of anthracene remains practically unchanged for 3 days. The observed shift in the spectra can be explained, as was done in ([7]), by complex formation between anthracene and the active centers of polymerization. It is possible, however, that the shifted maximum at 445 mμ corresponds to anthracene carbanions located at the ends of the polymer chains; this supposition is also consistent with the experimental data if the anthracene carbanion has an extinction coefficient at 445 mμ substantially greater than that of the styrene carbanion at 340 mμ.

It should be noted that the fact of the shift of the maximum in the spectrum of the polymer obtained on sodium-anthracene, whatever the nature of this phenomenon may be, indicates that initiation by addition of the aromatic component to the monomer, postulated for some cases ([2], [9]), is hardly represented here to any significant extent. With such an initiation mechanism, the polymer, owing to the absence of free anthracene in the system, would have the usual spectrum. Moreover, in light of the data presented, it is clear that the described in the work···

experiments ([2], [9]), the facts of detecting initiator fragments in polymers cannot in themselves serve as proof that initiation proceeds by this route, since aromatic components can enter the chain also during propagation events.

The presence of considerable amounts of naphthalene (up to 50% relative to styrene) has no noticeable effect on the rate of the process or on the molecular weight, but it substantially changes the spectrum of the "living" polymer: the maximum at 340 mμ disappears and maxima appear at 430 and 550 mμ. The polymer retains the ability to add new portions of monomer, but the altered spectrum is preserved. Similar changes in the spectrum of "living" polystyrene have been observed on standing ([8], [10]); it is possible that in that case too there was a slow interaction with the aromatic component of the initiator.

Fig. 2. Electron absorption spectra of the polybutadiene–anthracene system in THF.
1– "living" polymer obtained on sodium naphthalene; 2–the same with addition of anthracene; 3–the same after polymerization of a new portion of monomer.

It could be expected that the inhibiting action of anthracene on the polymerization of a less active monomer would be still greater, both because of the lower activity of the monomer and because of the higher rate of addition of anthracene

Figure 2. Electron absorption spectra of the polybutadiene-anthracene system in THF. 1— “living” polymer obtained on sodium naphthalene; 2—the same with addition of anthracene; 3—the same after polymerization of a new portion of monomer.

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to the active centers. In accordance with this it was shown that the polymerization of butadiene, which is less active in anionic polymerization than styrene ([11]), at 20° practically stops already at an anthracene:butadiene ratio of 1:30. When anthracene is added to “living” polybutadiene, as with styrene, a change in the spectrum is observed with the appearance of a maximum at 450-460 mμ (see Fig. 2, curves 1, 2); the same shifted spectrum is exhibited by the polymer obtained on sodium anthracene. This spectrum with a maximum at 450-460 mμ is retained after polymerization of new portions of monomer (curve 3; the free anthracene disappears in this case) and remains practically unchanged for 5 days. Apparently, “living” polybutadiene interacts with anthracene by the same type as “living” polystyrene.

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