Letters to the Editor

The synthesis of poly(styrenechromiumtricarbonyl) in the presence of triisobutylboron

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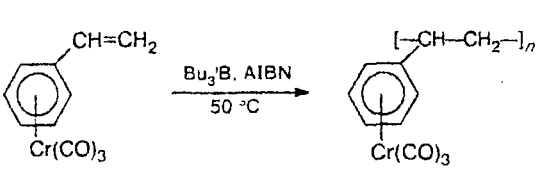
Poly(styrenechromiumtricarbonyl) was synthesized by radical homopolymerization of styrenechromiumtricarbonyl in AcOEt at 50 °C in the presence of AIBN and triisobutylboron.

Key words: styrenechromiumtricarbonyl, arene complexes, radical polymerization, triisobutylboron.

The first chromium-containing monomer, styrenechromiumtricarbonyl (SCT), was synthesized as long ago as 1970.[1] Copolymerization of SCT with its organic analog, styrene,[2] as well as with methyl acrylate and vinylcymantrene,[3] methyl methacrylate (MMA), and butyl acrylate[4] proceeds with ease. At the same time, it is believed[1,5,6] that the synthesis of SCT homopolymers is impossible.

In our recent physicochemical studies of elementary stages of the copolymerization of SCT with MMA and other acrylic monomers we found[4] that the arenechromiumtricarbonyl compound can form intermolecular complexes of the donor-acceptor type with acrylic monomers at their π-bonds in the chain propagation stage. In our opinion, that is the reason why attempts at obtaining homopolymers of SCT and its analogs have failed. In this connection, it can be suggested that poly(styrenechromiumtricarbonyl) can be synthesized by coordination radical homopolymerization in the presence of a strong electron acceptor which can react with both the metal-containing monomer and chain carrier radical.

In this work, we report the first synthesis of an SCT homopolymer by the polymerization of SCT in AcOEt at 50 °C in the presence of an equimolar amount of triisobutylboron as electron acceptor and AIBN as initiator. The yield of the polymer exceeded 20% after 6 h.



Triisobutylboron was chosen as electron acceptor not accidentally, but because of the ability of trialkylboranes to form complexes with monomers and radicals in coordination radical polymerization processes.[7,8]

Poly(styrenechromiumtricarbonyl) is a light-yellow powder. Spectrophotometric analysis showed that the content of chromium in the polymer (21.3 wt.%) is nearly equal to that in the monomer (the theoretical value is 21.7 wt.%). The weight-average molecular weight of the polymer was 3900 Da.

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The IR spectra of the polymer exhibit a characteristic absorption in the region near 1633 cm^{-1}, which is typical of the coordinated benzene ring, and two very strong signals at 1860 and 1930 cm^{-1} (a shoulder at 1890 cm^{-1}), corresponding to the $Cr(CO)_3$ group. Two singlets, at δ 2.04 and 2.97, from the methylene and methyne group protons, respectively, and a broad signal at δ 5.60 from the benzene ring protons were observed in the ^1H NMR spectrum (acetone-d_6). No signals of the vinyl group protons (a multiplet near δ 6.30 for SCT) were found for the polymer.

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