NOTES

Polymerization of Styrene by Ceric *n*-Dodecylbenzene Sulfonate in the Presence of Alcohol or a Carbonyl Compound

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(Received June 10, 1967)

The present investigation was undertaken to seek for a better co-catalyst for the polymerization of styrene by organoceric compounds. As an organoceric compound ceric *n*-dodecylbenzene sulfonate1) was used. From the results of the similar studies by Iwakura *et al.*2) and Ogiwara *et al.*,3) in the present paper alcohols and carbonyl compounds were selected as the co-catalysts.

To a solution of 22 g of ceric ammonium nitrate dissolved in 200 cc of 0.1 N aqueous nitric acid, a solution of 27.6 g of sodium *n*-dodecylbenzene sulfonate in 200 cc of water was added. The yellow precipitate was then separated by filtration and dried *in vacuo* at 40°C. This precipitate will hereafter be referred to as ceric *n*-dodecylbenzene sulfonate (CDBS) according to the reference.1) The yield was 41.9 g. When CDBS was burned in a crucible, 21.14% of the CDBS (in weight) remained as an ash. This ash was presumed to be ceric dioxide. In addition to the bands observed in the IR spectra of sodium *n*-dodecylbenzene sulfonate, the IR spectra of CDBS contain a band at 1380 cm^{-1}, assignable to the nitric ion, and a shoulder at 3150 cm^{-1}, assignable to the ammonium ion. These data show that 1.03 of the nitric ions in the original ceric diammonium hexanitrate were replaced by *n*-dodecylbenzene sulfonic ions. CDBS is soluble in ethyl acetate, methyl ethyl ketone, benzene, styrene, and diethyl ether, while it is insoluble in methyl, ethyl, amyl, *n*-octyl alcohol, and in acetone.

Polymerization was carried out *in vacuo* at 60°C for 48 hr. The concentration of CDBS in the polymerization mixture were expressed by the concentration of ceric ions. The results are shown in Table 1. Judging from the low conversions for such a long polymerization time, it can be said that the catalytic activity is low. It was an unexpected feature that ketone and aldehyde were better co-catalysts than alcohol. When ketones are used, radicals may be formed by the elimination of α-hydrogen atoms, because benzophenone, which has no α-hydrogen atoms, shows no catalytic activity. As for aldehyde, radicals may be formed, at least partly, by the elimination of aldehyde-hydrogen atoms, because benzaldehyde does show catalytic activity.

TABLE 1. POLYMERIZATION IN THE PRESENCE OF VARIOUS CO-CATALYSTS

Co-catalyst	mol/*l*	Conversion %
Methyl alcohol	1.0	1.81
Ethyl alcohol	0.50	1.8
Ethyl alcohol	1.0	2.2
Ethyl alcohol	1.5	1.6
Cyclohexanone	0.50	8.4
Cyclohexanone	1.0	11.3
Cyclohexanone	1.5	13.4
Cyclohexanone	2.0	12.7
Diethyl ketone	1.0	10.2
Caproic aldehyde	0.50	8.35
Caproic aldehyde	1.0	9.14
Benzaldehyde	1.0	3.46
Acetophenone	1.0	12.3
Acetone	1.0	5.4
Methyl ethyl ketone	1.0	10.8
Benzophenone	0.50	0
Ethyl acetate	1.0	0.31
Diethyl ether	1.0	0.33
—		0

CDBS: 4.43×10^{-3} mol/*l*
Styrene: 1.0 mol/*l*
Solvent: benzene

If the termination reaction is a combination of polymer radicals and if a steady state is assumed,

$$fk_i[\mathrm{Ce^{IV}\text{-}complex}] - 2k_t[\mathrm{M}n\cdot]^2 = 0$$

the rate of polymerization can be expressed as follows:

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1) S. Kaizerman, N. Plainfield and G. Mino, U. S. Pat. 2922801.

2) Y. Iwakura, T. Kurosaki and Y. Imai, *J. Polymer Sci.*, **A3**, 1185 (1965).

3) Y. Ogiwara, Y. Ogiwara and H. Kubota, Preprints for the 20th Annual Meeting of the Chemical Society of Japan (April, 1967), 4P213.

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{Mn}\cdot][\mathrm{M}]$$
$$= k_p(fk_i/2k_t)^{1/2}[\mathrm{Ce^{IV}\text{-}complex}]^{1/2}[\mathrm{M}]$$

The rate of polymerization is proportional to the square root of the concentration of the $\mathrm{Ce^{IV}}$-complex. If the termination reaction is the reaction of the polymer radical with the $\mathrm{Ce^{IV}}$-complex and if a steady state is assumed,

$$fk_i[\mathrm{Ce^{IV}\text{-}complex}] - k_t'[\mathrm{Mn}\cdot][\mathrm{Ce^{IV}\text{-}complex}] = 0$$

then

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = fk_ik_p/k'_t[\mathrm{M}]$$

Thus, the rate of polymerization is independent of the concentration of the $\mathrm{Ce^{IV}}$-complex.

As shown in Fig. 1, when diethyl ketone or cyclohexanone was used, the rate of polymerization was proportional to the square root of the concentration of CDBS; therefore the termination reaction was a combination of polymer radicals: when ethyl alcohol was used, the rate of polymerization was independent of the concentration of CDBS; therefore, the termination reaction was a reaction of the polymer radical with CDBS.[2,4,5] When caproic aldehyde was used, the rate of polymerization increased with a decrease in the concentration of CDBS. This phenomenon may be interpreted in terms of the change in the dissociation constant of the complex of $\mathrm{Ce^{IV}}$ and aldehyde.

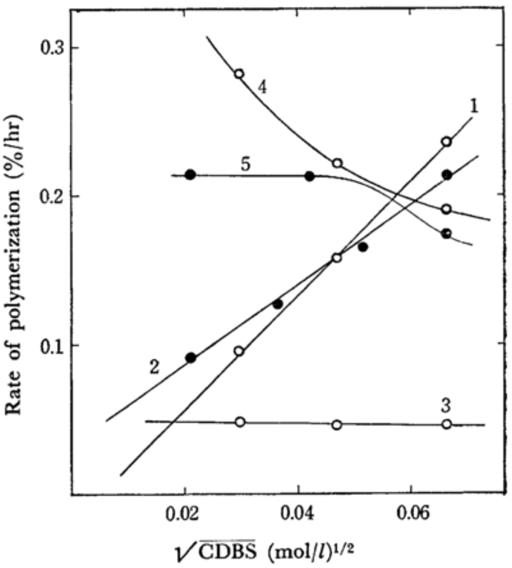

Fig. 1. Rate of polymerization *vs.* square root of the concentration of CDBS.

1 Cyclohexanone (1.0 mol/*l*)
2 Diethyl ketone (1.0 mol/*l*)
3 Ethyl alcohol (1.0 mol/*l*)
4 Caproic aldehyde (1.0 mol/*l*)
5 Caproic aldehyde (0.5 mol/*l*)

Further investigations are in progress on other organoceric compounds.

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[4] S. Kimura and M. Imoto, *Makromol. Chem.*, **42**, 140 (1960).

[5] V. S. Ananthanarayanan and M. Santappa, *J. Appl. Polymer Sci.*, **9**, 2437 (1965).