Tetrahedron Letters No.17, pp. 1145-1150, 1965. Pergamon Press Ltd.
Printed in Great Britain.

A CATION-RADICAL IN LIQUID SULFUR DIOXIDE. POLYMERIZATION OF STYRENE BY ANTHRACENE IN THE PRESENCE OF OXYGEN.

Niichiro Tokura, Toshikazu Nagai and Yuzo Sonoyama
Dept. of Applied Chemistry, Faculty of Engineering, Osaka
University
Higashinoda, Osaka, Japan

(Received 8 March 1965)

We wish to report that a cation-radical, $(C_6H_5CH{=}CH_2)^{\dot{+}}$, might be formed in liquid sulfur dioxide from styrene by anthracene and oxygen. When a mixture of styrene and anthracene was added with liquid sulfur dioxide in the presence of oxygen at 0°C, styrene polymerizes immediately. The conversion was neary quantitative and the product consisted of polystyrene exclusively, the elemental analysis, (Found, C, 91.88: H, 7.45; Calcd. for $(C_8H_8)_n$, C, 92.26: H, 7.74 %), indicating a cationic polymerization was undertaken during the experimental condition. The IR spectrum of the polymer was exactly superimposable with that of an authentic polystyrene. The product contained no sulfur atom as its constituent. The polymerization was inhibited by addition of dimethylsulfoxide, also indicating an additional evidence for the cationic nature of the polymerization[1].

The relationships among the yield, the molecular weight of the polymer and the anthracene used are listed in the TABLE 1.

TABLE 1 RESULTS OF THE POLYMERIZATION AT 0°C

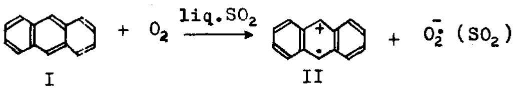
No.	Liq.SO_2 ml	Styrene Mole/l	Anthracene 10^3 x Mole/l	Yield* %	$[\eta]$ 100ml/g	M.W.** x 10^{-4}
1	14.2	1.54	0.392	62.9	0.578	11.1
2	14.3	1.54	3.31	92.9	0.622	12.4
3	14.3	1.54	16.3	95.1	0.502	9.0
4	14.0	1.54	33.0	96.2	0.416	6.8

* The Reaction Time; 6 Hrs.

** Pepper's Eq., $[\eta]=2.7\times10^{-4}\ M^{0.66}$ in benzene at 25°C, was used.

The molecular weight was inversely dependent upon the concentration of anthracene used and dependent on the initial concentration of styrene as will be discussed later.

The sequence of the polymerization will be given as the following;



(1)

$$\text{II} + \underset{\text{III}}{C_6H_5CH{=}CH_2} \longrightarrow \text{I} + \underset{\text{IV}}{C_6H_5CH{=}CH_2^{\overset{+}{\cdot}}} \qquad (2)$$

$$\text{IV} + \text{III} \longrightarrow \text{Polystyrene} \qquad (3)$$

The evidences for the possibility of the formation of the cation-radical, IV, are:

1. The polymerization cannot be initiated rapidly in the absence of either oxygen or anthracene.

2. An electronic spectrum of the solution gives a λ_{max} at 610 mμ (FIG.1) similar to that of diphenylethylene cation-radical reported by Leftin and Hall[2] which is obtainable from

diphenylethylene adsorbed on silica-alumina or from diphenylethylene dissolved in benzene-trichloroacetic acid mixture[3], while the spectra of anthracene [4,10], the carbonium ion, $C_6H_5\overset{+}{C}HCH_3$ [5], and the growing polymer carbonium ion[6], respecively, are all near at 400 mμ in various solvents.

3. Liquid sulfur dioxide could not be oxidized in the presence of anthracene by oxygen to sulfur trioxide which might otherwise initiate the cationic polymerization.

4. If the sulfur trioxide might be formed by another cause such as by a peroxide of anthracene, a cationic and a radical polymerizations should result simultsneously and the products must involve a mixture of polystyrene and styrene-polysulfone.[7]

5. Anthracene-peroxide was not detected by KI test, when a current of oxygen was passed through liquid sulfur dioxide containing anthracene.

It has been reported by Asami and Tokura[8] that the polymerization of styrene in liquid sulfur dioxide with stannic chloride as the initiator was approximately of living nature, whose D.P. of the product is expressed as,

$$\text{D.P.} = k_1 \ (M) / (C) \quad + \quad a_1 \qquad \text{(A1)}$$

where, (M) and (C) are concentrations of the monomer and the initiator, and k_1 and a_1 are the constants.

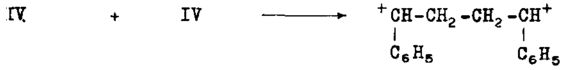
The results of the present experiment also satisfies the similar expression, Eq. (A2), as will be calculated from TABLE 1. So,

$$D.P. = k_2 \; (M) \, / \, (C) \; + \; a_2 \qquad (A2)$$

The present authors are not yet sure whether the initiating carbonium ion is a mono-cation (V) or a di-cation (VI), the latter being an initiating species like the Szwarc's anion-radical initiated polymerization in tetrahydrofuran.

$$IV \; + \; R \longrightarrow R\text{-}CH_2\text{-}\underset{C_6H_5}{CH^+} \quad V \qquad (4)$$

R: a radical scavenenger



$$IV \; + \; IV \longrightarrow {}^+\underset{C_6H_5}{CH}\text{-}CH_2\text{-}CH_2\text{-}\underset{C_6H_5}{CH^+} \qquad (5)$$

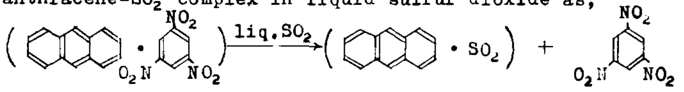
VI

If the polymerization by anthracene and oxygen in liquid sulfur dioxide is to be growing via the di-carbonium ion (VI), resulted by a recombination of the cation-radicals, (IV), k_1/k_2 should be,

$$k_1/k_2 \; = \; 2$$

the found value being 50/28, i.e., approximately 2.

The counter-anion of the polymerizing ion pair may probably be $HS\bar{O}_4$ anion produced from $\bar{O}_2^{\cdot}$, SO_2 and a trace of water in liquid sulfur dioxide. The complex, such as anthracene-sym-trinitrobenzene is also a good initiator of the polymerization in the presence of oxygen, since the comlex replaces its acceptor-component by sulfur dioxide to form an anthracene-SO_2 complex in liquid sulfur dioxide as,[10]



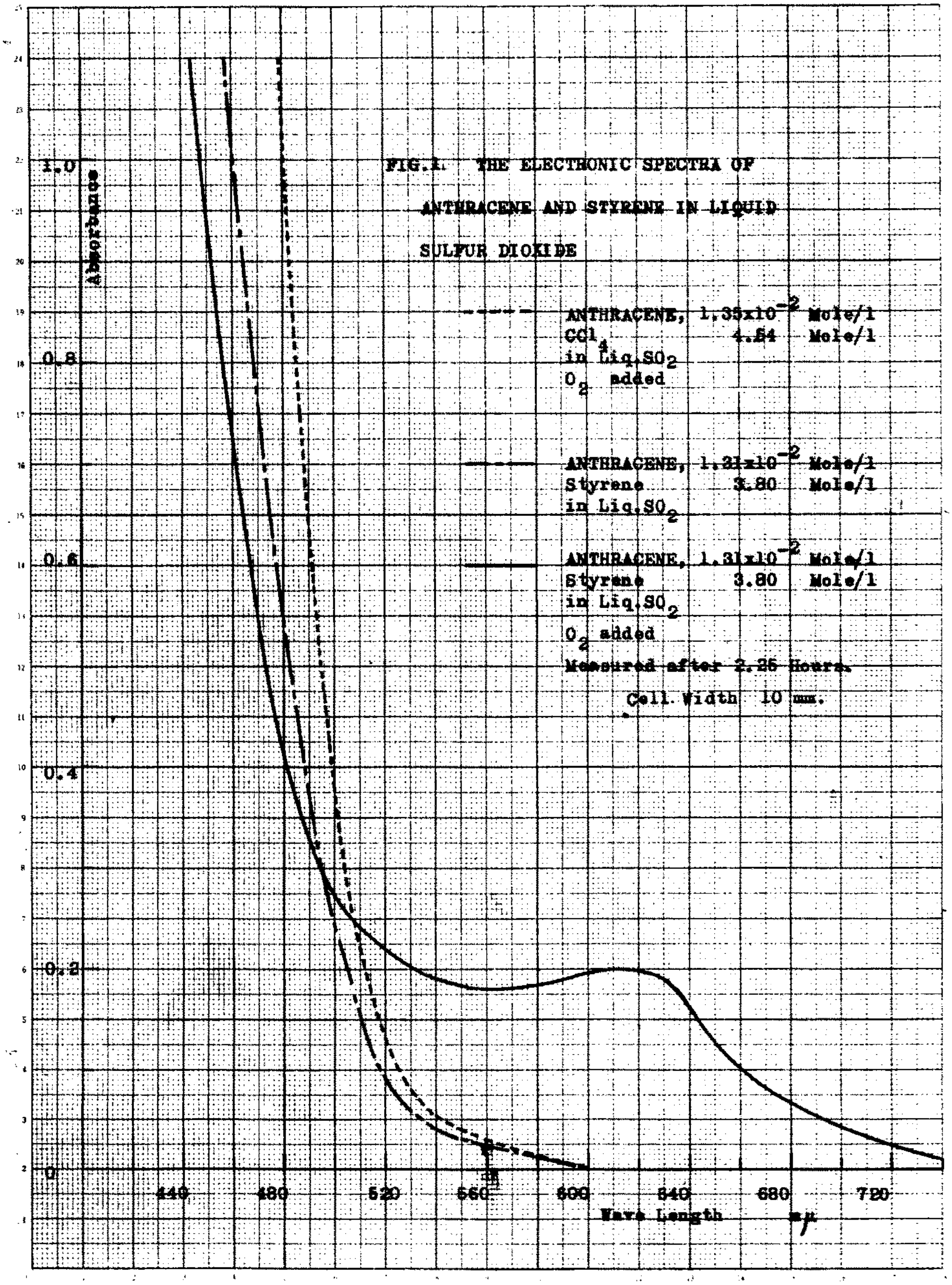


FIG.1. THE ELECTRONIC SPECTRA OF ANTHRACENE AND STYRENE IN LIQUID SULFUR DIOXIDE

REFERENCES

1. a. N.Tokura, M.Matsuda and H.Kichiji, *J.Chem.Soc.,Japan, Industrial Ed.,* (Kogyokagaku Zasshi), **65**, 1636 (1963)

b. N.Tokura, M.Matsuda and Y.Ogawa, *J.Polymer Sci.*,**A1**, 2965 (1963)

2. H.F.Leftin and W.K.Hall, *J.Phys.Chem.*, **66**, 1457 (1962)

3. A.G.Evans, P.M.S.Jones and J.H.Thomas, *J.Chem.Soc.*, 104 (1957)

4. H.Brockmann and G.Budde, *Chem.Ber.*, **86**,432 (1953)

5. D.C.Jordan and F.E.Treloar, *J.Chem.Soc.*, 729 (1961)

6. D.C.Jordan and F.E.Treloar, *ibid*, 734 (1961)

7. R.C.Schultz and A.Banihaschemi, *Makromol,Chem.*, **64**, 140 (1963)

8. R.Asami and N.Tokura, *J.Polymer Sci.*, **42**, 545 (1960)

9. M.Szwarc, M.Levy and R.Milkovich, *J.Am.Chem.Soc.*, **78** 2656 (1956)

10. N.N.Lichtin, R.E.Weston and J.D.White, *ibid*, **74**, 4715 (1952)