Studies on Vinyl Sulfonic Acid*
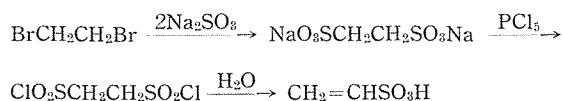
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As the chemistry of vinyl sulfonic acid (VS) has not been studied sufficiently, the authors attempted to study it. In this article the following experimental results are reported.

1. Among the various synthetic methods of VS, it was found that the following process was the best for the laboratory scale:

$$BrCH_2CH_2Br \xrightarrow{2Na_2SO_3} NaO_3SCH_2CH_2SO_3Na \xrightarrow{PCl_5}$$

$$ClO_2SCH_2CH_2SO_2Cl \xrightarrow{H_2O} CH_2=CHSO_3H$$

2. To find the monomer reactivity ratios (MRR), VS was copolymerized with acrylonitrile (AN). By the Fineman-Ross' method MRR were found as $r_1=1.5$ (AN) and $r_2=0.15$ (VS). From these data the Q and e values of VS were estimated as Q=0.09 and e=+1.3.

3. On the quantitative analysis of VS in the AN–VS copolymers, following methods were tried; a) elemental analysis of sulfur by combustion, b) determination of sulfonic group by titration, and c) by infra-red spectroscopic method.

4. The dyeability of AN–VS copolymers to the cationic dye was very good as the authors expected. The initial adsorption rate was very high on the copolymer containing 4.3mole % of VS.
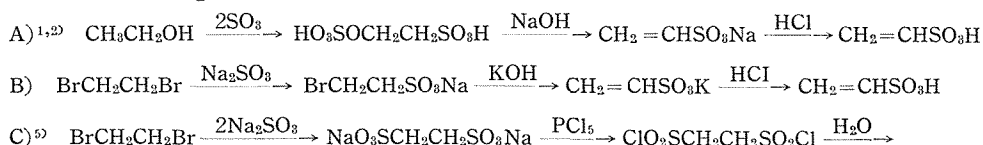
INTRODUCTION

In recent years, the studies on the polymers and the copolymers of the derivatives of VS have been developed in the field of ion-exchange resins, in reformation of elastomers, and in improvement of textile dyeability. Although the salts[1]~[3] and esters[4] of VS have hitherto been studied, we have little information as to the free acid and the synthetic method has not yet been settled.

For these reasons, the authors studied the synthetic methods and the copolymerization with AN.
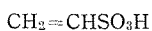
EXPERIMENTAL AND RESULT

1. Syntheses of VS

The following five methods had been studied.

A)[1,2] $CH_3CH_2OH \xrightarrow{2SO_3} HO_3SOCH_2CH_2SO_3H \xrightarrow{NaOH} CH_2=CHSO_3Na \xrightarrow{HCl} CH_2=CHSO_3H$

B) $BrCH_2CH_2Br \xrightarrow{Na_2SO_3} BrCH_2CH_2SO_3Na \xrightarrow{KOH} CH_2=CHSO_3K \xrightarrow{HCl} CH_2=CHSO_3H$

C)[5] $BrCH_2CH_2Br \xrightarrow{2Na_2SO_3} NaO_3SCH_2CH_2SO_3Na \xrightarrow{PCl_5} ClO_2SCH_2CH_2SO_2Cl \xrightarrow{H_2O}$

$CH_2=CHSO_3H$

D) $ClCH_2CH_2OH \xrightarrow{NaHSO_3} NaO_3SCH_2CH_2OH \xrightarrow{PCl_5} ClO_2SCH_2CH_2Cl \xrightarrow{KOH} CH_2=CHSO_3K$

$\xrightarrow{HCl} CH_2=CHSO_3H$

E)[6] $HOCH_2CH_2SO_3Na \xrightarrow{H_4P_2O_7} CH_2=CHSO_3H$

1. 1. Synthesis of VS by Method A[1,2]

This method was developed by D. S. Breslow and his coworkers.

   i) **Preparation of sodium vinyl sulfonate.** 80g. (1 mole) of sulfur trioxide was distilled into a flask containing 45g. (0.98 mole) of absolute alcohol, kept at 0-5°, over a period of 80 minutes with a gentle stirring. The vapor inlet tube was set 2-3 mm. above the surface of alcohol. The temperature of the flask was then raised to 50° and a second mole of sulfur trioxide was distilled into at the same rate, Ethionic acid was obtained as a viscous, dark yellow liquid.

   The ethionic acid was added drop by drop to 500-ml. of 26%-sodium hydroxide solution, kept at 65° and the resulting solution was heated at 70° for two hours. After cooling to room temperature, the solution was neutralized to pH. 8 with sulfuric acid, chilled and filtered. The precipitate of Glauber salt was washed with three 50-ml. portion of ice water. The hydrogen adsorption analysis with the palladium-charcoal catalyst showed that the combined pale yellow filtrate (560g.) contained 17% of sodium vinyl sulfonate, and the yield was 75% based on sulfur trioxide.

   ii) **VS from sodium vinyl sulfonate.** The solution obtained above was concentrated to the half volume of its initial under reduced pressure, chilled with ice water and saturated with hydrogen chloride gas. Precipitated sodium chloride was filtered off and the filtrate was evaporated to dryness on a water bath in the nitrogen atmosphere under reduced pressure. To remove the last trace of hydrogen chloride, two 100-ml. portions of water were added to the residue and distilled by the same manner. The residue was then distilled, 52.5g. (0.485 mole) of crude vinyl sulfonic acid being collected up to 150° at 5mm. Hg. On redistillation, 48.6g (0.45 mole) of transparent and colorless vinyl sulfonic acid were collected at 127-132° at 1.5 mm.Hg.

1. 2. Synthesis of VS by Method B

   i) **Preparation of sodium β-bromoethane sulfonate by Strecker's reaction[7].** In a 1-l. round bottom flask, fitted with a reflux condenser, a mechanical stirrer, and a dropping funnel, was placed 165g. (0.56 mole) of ethylene bromide (b. p. 132°). 208g. of 95% alcohol, and 75-ml. of water. The stirrer was started and the mixture heated to boiling. To the mixture a solution of 20.8 g. (0.17 mole) of anhydrous sodium sulfite in 75-ml. of water was added through the dropping funnel over a period about 30 minutes. The solution was refluxed for two hours after all the sulfite solution had been added. The condenser was then set for distillation, and the alcohol and ethylene bromide were distilled off. The remaining water solution was evaporated to dryness on the water bath. The sodium β-bromoethane sulfonate was extracted from the sodium bromide and unchanged sodium sulfite with hot 95% alcohol. On cooling the solution, the salt crystallized. The prodact was purified

by recrystallizing from 95% alcohol and drying in an oven at 110°. The yield was 29g. (0.14 mole).

ii) **Preparation of VS.** The mixture of 10g. of sodium β-bromoethane sulfonate and 10g. of 50% aqueous solution of potassium hydroxide was kept 100° for two hours. Then the mixture was cooled to 0-5° and neutralized with conc. hydrechloric acid. Precipitated potassium chloride was filtered off. The filtrate containing sodium vinyl sulfonate was treated as the above mentioned manner (1. 1. ii). The yield was 2.5g. (0.023mole).

1. 3 Synthesis of VS by method C[5]

i) **Preparation of sodium ethylene sulfonate by Strecker's reaction.** The apparatus were same as described above (1. 2. i). The saturated aqueous solution of 100g. anhydrous sodium sulfite was placed in a 1-1. flask and heated at 90° on a water bath. Then 94g. (0.5mole) of ethylene bromide was added through the dropping funnel over a period of two hours. The solution was kept at 90° for five hours after all ethylene bromide had been added. The reaction mixture was then condensed to half volume of its original under reduced pressure. Then the residue was evaporated to dryness on a water bath. Sodium ethylene sulfonate was then extracted with hot 90% alcohol. On cooling the solution, the salt crystallized. The product was purified by recrystallizing from 95% alcohol and dried in an oven at 100°. The yield was 93g. (0.4 mole). The product was identified by elemental analysis.

ii) **Preparation of ethylene sulfonyl chloride.** In 100-ml. round bottom flask, fitted with a reflux condenser, was placed 10g. of sodium ethylene sulfonate and 20g. of phosphorus pentachloride, and heated at 180° for one hour. After cooling to room temperature, the product was extracted with two parts of 50-ml. of benzene, and the solution was condensed under reduced pressure. Ethylene sulfonyl chloride crystallized out. The product was purified by recrystallizing from benzene, and drying on a water bath. The product was a pale yellow needle crystal and melted at 98°. The yield was 9.5g. (0.0415 mole).

iii) **Preparation of VS.** 10g. of ethylene sulfonyl chloride and 15 ml. of water were heated at 90-100° under a reflux condenser for three hours. This pale yellow solution was then evaporated to dryness *in vacuo.* To remove the last traces of hydrogen chloride and sulfur dioxide, three 50-ml. portions of water were added to the residue and distilled off *in vacuo.* The residue was then distilled, 3.1 g. (0.029 mole) of VS was collected. These procedures were carried out under the nitrogen atmosphere.

1. 4 Synthesis of VS by Method D

i) **Preparation of sodium isethionate from ethylene chlorohydrin by Strecker's reaction.**[8] The preparation procedures were same as (1. 3. i). 50g. of anhydrous sodium sulfite and 35g. of ethylene bromide were reacted at 90°. The reaction mixture was evaporated to dryness. Sodium isethionate was then extracted with 70% hot alcohol. On cooling, crystalline material separated out. The product was purified by recrystallizing from 70% alcohol and dried in an oven at 110°. The yield was 58g. (0.392 mole).

ii) Preparation of sodium isethionate from ethylene oxide. In 1-l. round bottom flask, fitted with a reflux condenser and a gas-inlet tube, was placed 260g. (1 mole) of 40% aqueous solution of sodium bisulfite. To this solution ethylene oxide was introduced through a gas-inlet tube with stirring at room temperature. Temperature of the reaction mixture rose gradually, and was controlled not to exceed 60°. The solution had light pink color, and as the reaction proceeded, it became colorless. At this time the reaction ended. It took about two hours. This solution was then evaporated to dryness, and sodium isethionate was extracted with 70% alcohol, recrystallized from the same solvent. The yield was 88g. (0.595 mole).

iii) Preparation of β-chloroethylene sulfonyl chloride. In 100-ml. round bottom flask, 10g. of sodium isethionate and 30g. of phosphorus pentachloride were placed, and heated over 150° for two hours under a reflux condenser. The condenser was then set for distillation, and β-chloroethylene sulfonyl chloride was distilled at 93–97°/17mm. Hg. The yield was 6g. (0.037 mole).

iv) Preparation of VS. 10g, of β-chloroethylene sulfonyl chloride was dissolved in 18-ml. of ethylene glycol. To this solution 4.5 g. of potassium hydroxide was added under cooling. It babbled severely, and when babbling ceased, the mixture was heated to 170–180° for 15 minutes. It was then cooled to room temperature, neutralized with sulfuric acid, and filtered. Filtrate was treated as the same manner described in (1.1.iii). The yield was 4.5 g. (0.0415 mole).

1.5. Synthesis of VS by dehydration of sodium isethionate.[6]

In a distilling flask, were placed 20g. (0.135 mole) of sodium isethionate and 100g. of pyro-phosphoric acid, and kept at 220° under reduced pressure (0.5 mm. Hg). Crude VS was distilled off at 107°. The yield was very low: 2.6g. (0.024 mole), since the mixture was kept in a high temperature for a long time and the side reactions such as decomposition and/or polymerization might occur.
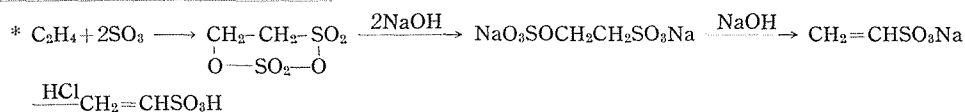
1.6. Results

The yields obtained by the various methods are given in Table 1. From this table, it is concluded that the method C is the most profitable for the laboratory scale. But method A or the other method[4]* seems to be more preferable for the

Table 1. The yield (%) of VS by
various methods,

method	yield
A	45
B	41
C	65
D	37*
E	18*

* Based on sodium isethionate.

* $C_2H_4 + 2SO_3 \longrightarrow CH_2{-}CH_2{-}SO_2 \xrightarrow{2NaOH} NaO_3SOCH_2CH_2SO_3Na \xrightarrow{NaOH} CH_2{=}CHSO_3Na$
$\underset{O{-}SO_2{-}O}{}$

$\xrightarrow{HCl} CH_2{=}CHSO_3H$

This method was not tried by us.

industrial scale, for sulfur trioxide may be used in these two methods, although it is troublesome to handle in a laboratory.

VS is hydroscopic, colorless, and transparent liquid. It boils at 124°/1mm. Hg, and its refractive index is n_D^{23} 1.4493. In the atmosphere, during 10 or 15 minutes it turns color, and becomes dark red in an hour. To prevent it from discoloration, VS must be stored in the dark and cold place under the nitrogen atmosphere. Hydrochloric acid or sulfur trioxide is useful as an inhibitor for the polymerization.

2. Copolymerization of VS and AN

VS, AN, and benzoyl peroxide were dissolved in dimethyl formamide (DMF) and polymerization was carried out at $70\pm1°$ for four hours in the nitrogen atmosphere. The catalyst was used 0.05 wt $\%$ of monomers. After polymerization, copolymers were separated by treating with methanol. DMF and methanol were distilled off and the copolymers were washed several times with methanol and dried over phosphorus pentoxide for two days. The results are shown in Table 2 and Fig. 1.

The Fineman-Ross' plots for the monomer pairs are shown in Fig. 2. The slope gives r_1, for AN as 1.5 and the intersection gives r_2 for VS as 0.15. From these values and Q, e values of AN $(Q=0.37, e=1.3)^{[10]}$, the Q and e values of VS were

Table 2. Copolymerization of AN(M_1) with VS(M_2).
0.05$\%$ benzoyl peroxide : $70\pm1°$, 4 hours

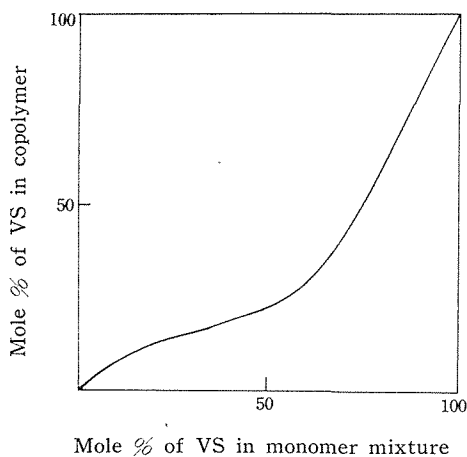| No.	Monomer			Polymer				
	VS(g)	AN(g)	mole $\%$ M_2 in monomer mixture	yield(g)	S($\%$)	VS($\%$)	mole $\%$ M_2 in copolymer	
1	4.3	0.52	80.0	0.8	21.7	74.7	61.0	—
2	4.3	1.05	63.3	1.0	14.2	47.5	31.5	—
3	4.3	1.40	60.0	1.8	12.3	42.3	27.5	0.4
4	4.3	2.10	50.0	2.0	10.8	37.4	23.0	0.5
5	2.15	1.60	40.0	2.0	9.4	32.0	19.0	0.4
6	2.15	2.10	36.7	2.8	8.5	29.1	17.0	0.6
7	2.15	5.25	20.0	5.0	6.9	23.2	13.0	—

Mole $\%$ of VS in monomer mixture

Fig. 1. Copolymerization of VS with AN.

estimated as Q = 0.09, e = +1.3, respectively. There data were compared with those of salt and esters of VS in Table 3.

It was found that the reactivity (polymerization tendency) of VS was inferior to that of sodium vinyl sulfonate. These values agree with the experimental data obtained by Overberger and his coworkers[4].

3. Quantitative analyses of VS in the copolymers with AN

The analyses were carried out by the three methods as follows:
1. Determination of sulfur contents by the combustion-method.
2. The alkali titration of sulfonic group.
3. The infra-red spectroscopic method.

The former two methods are usual ones. The analytical data are shown in Table 4. But among these three methods the spectroscopic method seems to be most reliable, so the last method was studied in detail.

2 gs. of sample were dissolved in 50-ml. of DMF, and 7-ml. of this solution was poured on the 9cm.×9cm. flat glass which was floated on mercury, and dried at 110° for half an hour. The film with the glass was then thrown into water, and the film could be torn off, dried over phosphorus pentoxide for 10 hrs. The thickness was about 1/25 mm. The spectrograms of these samples are shown in Fig. 3. The frequency of CN^- shows at 1250 cm^{-1}, and that of SO_3^- at 1205 cm^{-1}. The base absorption of the bands shows about at 1290 cm^{-1}. Where the transmittances
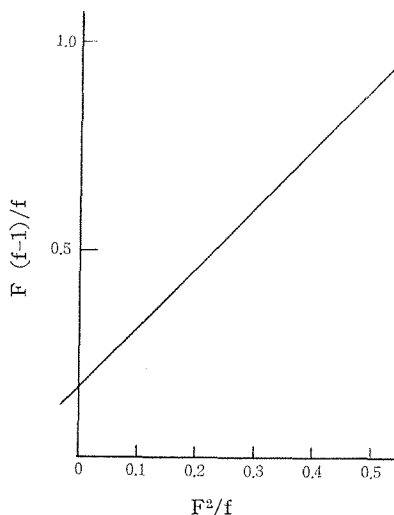

Fig. 2. AN-VS reactivity ratios by the method of Fineman and Ross.

Table 3. Q and e values for related monomers.

Monomer	Q	e
Sodium vinyl sulfonate	0.19	1.51
Butyl vinyl sulfonate	0.021	0.84
Methyl vinyl sulfone	0.07–0.15	1.2–1.3
Vinyl sulfonic acid	0.09	1.3

Table 4. Quantitative analyses of VS in copolymers combustion and titration.

Sample No.	Combustion		Titration*		Mole% of VS
	S(%)	VS(%)	0.05N-NaOH(ml.)	VS(%)	
0+	—	—	—	—	—
1	1.1	3.7	0.34	3.67	1.9
2	2.5	8.4	0.77	8.32	4.3
3	4.3	14.5	1.33	14.36	9.6

+ Sample No. 0 was a poly-AN.

* Titration was carried out as follows : 10mg of sample was dissolved in 50-ml. of DMF, and titrated with 0.05N-NaOH, indicated by phenol phthalein, and was ended after pink color did not fade any more one minute stirring.
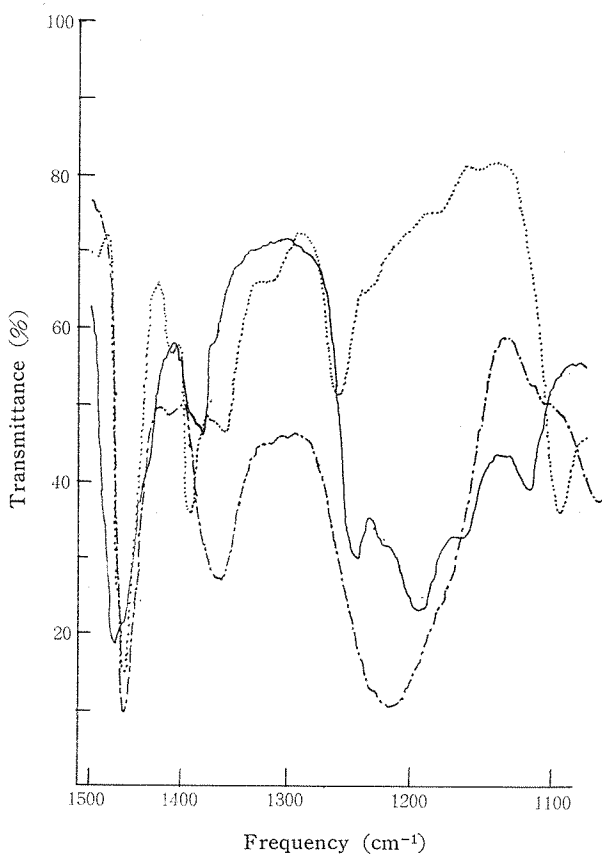
Fig. 3a. Absorption spectra of poly-AN (··········), AN-VS copolymer (—·——·—), and sodium VS in nujol (————).

of poly-AN at 1285cm^{-1} and copolymers at 1290 cm^{-1} are signed by A, and those of poly-AN at 1250 cm^{-1} and coplymers at 1205 cm^{-1} are B, the values of A and B are given in Table 5. Then the value, $\frac{A-B}{A}$, is linear to the mole or the weight per cent of VS in the copolymers. These facts are shown in Fig. 4a and 4b, respectively.

Since this method was very simple but it took a long time, then the sample No. 2 was ground to powder, and the spectrogram obtained by nujol method is
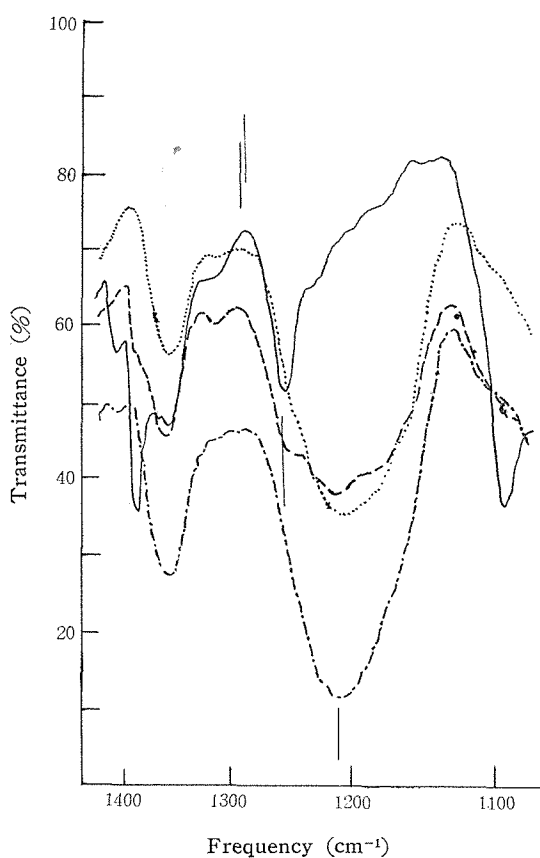
Fig. 3b. Absorption spectra of AN-VS, copolymers: No. 1- (‑ ‑ ‑ ‑ ‑ ‑ ‑),
No. 2-(···············), No. 3- (—·—··) and No. 0- (————).

Table 5. A, B, and $\dfrac{A-B}{A}$ values of samples.

(The same samples cited in Table 4)

Sample No.	A	B	$\dfrac{A-B}{A}$
0	72.5	51.5	0.29
1	62.0	38.0	0.39
2	70.5	35.9	0.49
3	46.5	11.2	0.76

shown in Fig. 5. The $\dfrac{A-B}{A}$ value obtained by this method is equal to that of the film method, is the best analytical method, and the following formulas are used for calculation.

$$VS(wt\%) = 36.6 \left(\frac{A-B}{A} \right) - 11$$

$$VS(mole\%) = 20 \left(\frac{A-B}{A} \right) - 6$$

(222)

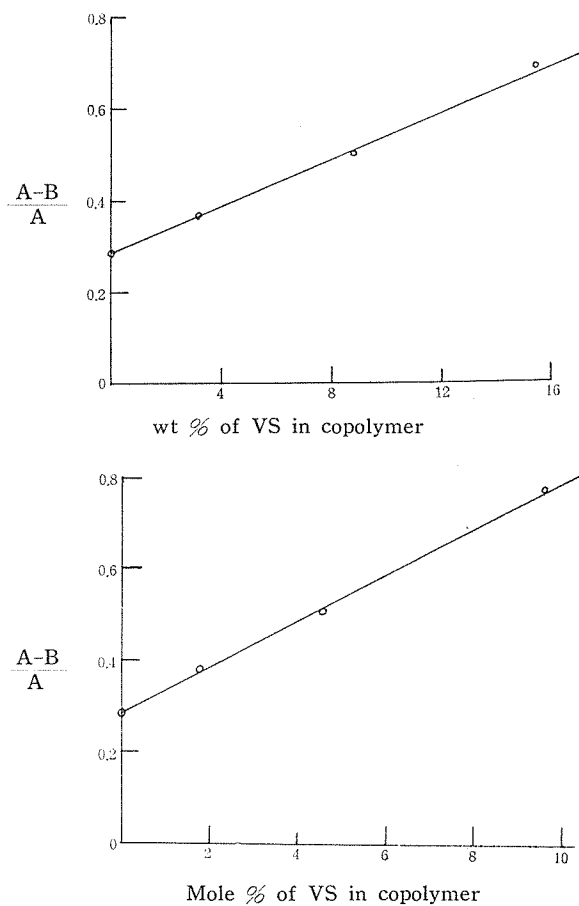wt % of VS in copolymer

Mole % of VS in copolymer

Fig. 4 a, b. Relationship between $\dfrac{A-B}{A}$ and VS contents.
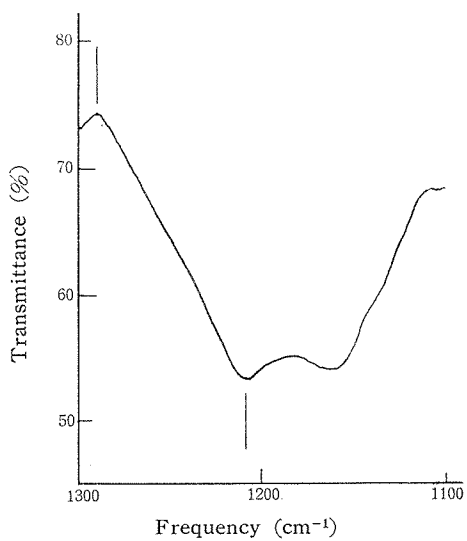

Fig. 5. Absorption spectra of AN-VS copolymer (No. 2) in nujol.

4. Dyeability of AN-VS Copolymers

The determination of dyeability was carried out by using the films which were prepared by the same manner described in the IR analysis. These films were cut to six pieces of 3.5×2.3cm. rectangle.

The dyeing bath was prepared by 1g. of Sevron Blue B (cationic dye : du Pont) 1g. of sodium acetate, and 500-ml. of water.

In a 100-ml. wide-necked flask, was placed 50-ml. of the dyeing solution, kept at 140° to reflux gently. To this boiling bath, six pieces of films were put in simultaneously, and the bath was maintained to boil. After 5, 10, 20, 40, 60, and 120 minutes, the films were taken off from the bath one by one, washed with water, dried over phosphorus pentoxide, and measured the quantities of the dye on the films. The quantities of the dye were measured by the following method. The dyed film was measured its weight, and dissolved to DMF, and made 100-ml. solution. On the other hand, the standard solution was made from the non-dyed film in the same procedure. The absorption intensity at 570mμ of the solution of the dyed film was measured by the Beckmann spectrophotometer. The concentration of the dye was calculated from the calibration formula* which was made preliminarily. From these data, the quantity of the dye on a film was calculated according to the following formula.

The quantity of dye on film

(g./100g. polymer)

$$= \frac{(\text{the weight of the dye})}{(\text{the weight of the dyed film}) - (\text{the weight of the dye})} \times 100$$

The quantities of the dye on various films are shown in Table 6, and the curves of the rate of dyeing are shown in Fig. 6.

From these data the dyeability of AN-VS copolymer to the cationic dye (Sevron Blue B) was very good as the authors expected. The initial adsorption rate was very high on the copolymer containing 4.3 mole % of VS.
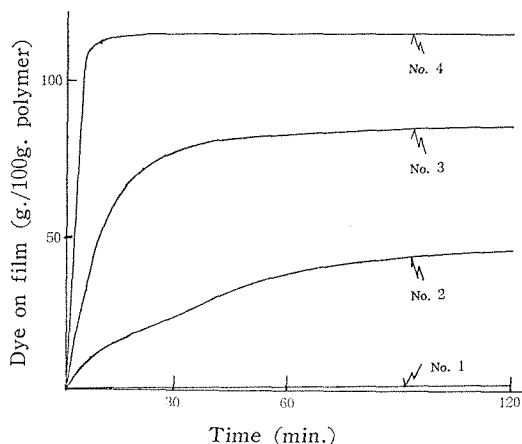

Fig. 6. Rate of dyeing of AN-VS copolymer with Sevron Blue B.

* The calibration formura was given as
   $C = E/50.0$ (C:g/100-ml. E : the intensity of absorption)

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Table 6. Weight of dye on 100g. of the film.

Sample		Weight of dye (g./100g. polymer)					
No.	Mole % of VS	5	10	20	40	60	120
1	0	0.1	0.2	0.2	0.5	0.5	0.8
2	1.9	11.5	15.7	19.8	28.2	38.5	45.0
3	3.1	32.3	56.1	71.5	80.1	81.3	85.2
4	4.3	110.3	113.0	114.5	114.5	114.5	114.5

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