BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 741—745 (1969)

Reactive Fiber. VII. Preparation and Polymerization of Vinyl Sulfonyl (β-Chloroethyl)amide

Yoshio IWAKURA, Keikichi UNO, Nobuo NAKABAYASHI*[1] and Wen-Yen CHIANG

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

(Received June 6, 1968)

Vinyl sulfonyl (β-chloroethyl)amide (III) was prepared from vinyl sulfonyl chloride and aziridine. The monomer reactivity ratios of III (M_2) ($r_1=3.0$, $r_2=0.075$) were determined from the result of copolymerization with styrene (M_1), and Q_2 and e_2 values calculated were 0.13 and 0.42 respectively. Radical polymerization of III gave a polymer with low viscosity and the polymer had good reactivity with nucleophilic reagents. To compare the functional group in polymer chain with that of monomeric compound, methane sulfonyl (β-chloroethyl)amide (IV) was prepared and the reaction between the function and several nucleophiles was studied. Reactive fibers were obtained from copolymers of acrylonitrile and III. Reaction of the fibers with Congo Red was carried out in the presence of pyridine.

The idea of addition reaction was introduced as a reaction species of a reactive polymer which has groups highly reactive to a polymer chain. We reported already several kinds of useful groups to prepare reactive polymers. They are isocyanate,[1] aziridine,[2] epoxide,[3] azlactone,[4] and sulfonyl (β-chloroethyl)amide,[5] *etc.*

In the present paper, the preparation and polymerization of vinyl sulfonyl (β-chloroethyl)amide (III) and the reaction of the resulting reactive polymers are described. Preparation and polymerization of *p*-styrene sulfonyl (β-chloroethyl)-amide have already been published.[6] In order to compare reactive polymer and fiber derived from the styrene derivative with vinyl derivative, we prepared III. The preparation of vinyl sulfonyl aziridine (III′) was unsuccessful because of its unstability. Addition of hydrochloric acid to the crude III′ gave stable III. The reactivity of sulfonyl (β-chloroethyl)amide with several nucleophilic reagents seemed to be similar to that of sulfonyl aziridine with nucleophiles in the presence of bases.

Experimental

Preparation of Vinyl Sulfonyl (β-Chloroethyl)-amide (III). Into a solution of 44.8 g (0.354 mol) of vinyl sulfonyl chloride in 450 m*l* of methylene chloride was added a mixture of 15.3 g (0.354 mol) of aziridine and 35.8 g (0.354 mol) of triethylamine dropwise with stirring at a temperature of −4°C to 0°C during an hour. The reaction was continued at room temperature for another 30 min. Precipitated triethylammonium chloride was filtrated off and 25 m*l* of concentrated hydrochloric acid was added dropwise into the filtrate with stirring at an ice cooling temperature. Fifteen minutes later the organic layer was taken out and was washed by water several times and dried over calcium chloride. After the evaporation of the solvent *in vacuo* the fraction boiling at 139.5−140.5°C/2 mmHg was obtained. The yield was 20.9 g (34.8%).

Found: C, 28.18; H, 4.50; N, 8.40%. Calcd for $C_4H_8SO_2NCl$: C, 28.32; H, 4.75; N, 8.26%.

Preparation of Methane Sulfonyl (β-Chloroethyl)amide (IV). The compound was prepared by the method of Bestian.[7]

Polymerization of III. III and an initiator, AIBN, were sealed in an ampoule under an atmosphere of nitrogen and the polymerization was carried out at 65—70°C for 20—70 hr. The viscous oily polymer was poured into ether to separate poly-III. The purification of the polymer was performed by reprecipitation technique (THF-ether system). The results are listed in Table 1.

Found: N, 8.16%. Calcd for $(C_4H_8SO_2NCl)_n$: N, 8.26%.

Determination of Monomer Reactivity Ratios. About 2.5—3.5 g of a pair of accurately weighed

---

[*1] Present address: The Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Surugadai, Tokyo.

1) Y. Iwakura, N. Nakabayashi and H. Suzuki, *Makromol. Chem.*, **78**, 168 (1964).

2) Y. Iwakura, K. Uno, N. Nakabayashi, T. Tani and W. Y. Chiang, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1222 (1965).

3) Y. Iwakura, T. Kurosaki and N. Nakabayashi, *Makromol. Chem.*, **44**, 570 (1961).

4) Y. Iwakura, F. Toda and Y. Torii, *J. Polymer Sci.*, **A-1-4**, 2649 (1966).

5) N. Nakabayashi and Y. Iwakura, *Makromol. Chem.*, **81**, 180 (1965).

6) Y. Iwakura, K. Uno, N. Nakabayashi and W. Y. Chiang, *J. Polymer Sci.*, **A-5**, 3193 (1967).

7) H. Bestian, *Ann.*, **566**, 210 (1950).

monomers, styrene (M_1) and III (M_2), were mixed with 5 mg of AIBN in an ampoule cooled with Dry-Ice under an atmosphere of nitrogen and the ampoule was sealed. The copolymerization was carried out at 62°C up to a conversion of 10%. After the copolymerization, the viscous mixture was poured into methanol and white flakes were collected. The reprecipitation was repeated three times. The copolymer was dried *in vacuo*. The composition was determined by elementary analyses.

Styrene - III Copolymer. A mixture of 2.07 g of styrene, 1.37 g of III and 0.01 g of AIBN in an ampoule under an atmosphere of nitrogen was heated at 70°C for 25 hr. The copolymer was dissolved in THF and precipitated in methanol. The purification was repeated three times from THF and methanol system. The yield was 2.1 g (60%). $[\eta]=0.54$ (100 m*l* DMF/g at 30°C).

Acrylonitrile - III Copolymer. *(A) Polymerization in THF.* A solution of 53.0 g (1.00 mol) of acrylonitrile, 2.06 g (0.012 mol) of III and 0.015 g of AIBN in 3.5 m*l* of THF was stirred at 65°C for 90 min under an atmosphere of nitrogen. The reaction mass was put into methanol and the resulting white powder was filtered and washed several times by methanol. The yield was 11.0 g (20.0%). $[\eta]=2.7$ (100 m*l* DMF/g at 30°C). The copolymer contained 0.22% (molar) of III unit based on chlorine analysis, 0.15%.

(B) Slurry Polymerization. A suspension of 53.0 g (1.00 mol) of acrylonitrile and 1.7 g (0.01 mol) of III in 1.0 *l* of distilled water and 7.0 m*l* of 0.1 N of sulfuric acid was stirred at 55°C for 10 min with bubbling nitrogen. A pair of initiators, 1.6 g of ammonium persulfate and 0.80 g of sodium metabisulfite, were separately added into the suspension. The copolymerization was carried out for 2.5 hr at the same temperature. The milky mixture obtained was filtered. The collected white powder was suspended into methanol and separated by filtration and washed with methanol several times. The yield was 51.0 g (92.7%). $[\eta]=1.7$ (100 m*l* DMF/g at 30°C).

Wet Spinning of Acrylonitrile - III Copolymer. Copolymer was dissolved in hot DMF and the solution was allowed to stand overnight at room temperature. The dope was extruded into an ethylene glycol coagulation bath at room temperature by a pressure of 1 atm of nitrogen through a spinneret of six holes (0.12 mm diameter). The extruded fiber was drawn three times in a hot water bath kept at 95—98°C.

Polymer Reaction. *Reaction of Poly-III with Thiophenol.* A solution of 0.08 g of poly-III ,0.15 g of triethylamine and 0.15 g of thiophenol in 1 m*l* of THF was sealed into an ampoule. The reaction was carried out at room temperature for a day and at 100°C for another 4 hr. The polymer solution was concentrated by evaporation of THF *in vacuo* and the residue was poured into distilled water to precipitate the polymer. The obtained polymer was dissolved in THF and the solution was poured into water. The collected one was dried *in vacuo*.

Found: N, 5.72%. Calcd for $(C_{10}H_{13}S_2O_2N)_n$: N, 5.76%.

Reaction of Styrene-III Copolymer with p-Toluidine. A solution of the copolymer, *p*-toluidine and pyridine was refluxed for listed interval in Table 7. Methanol was added into the residue to precipitate the polymer after removal of the solvent from the reaction mixture. The reprecipitation (THF-methanol) was carried out three times. The conversion was calculated from chlorine analyses.

Reaction of Methane Sulfonyl (β-Chloroethyl)-amide with Various Nucleophiles. Typical example: A solution of 1.58 g (0.01 mol) of IV, 1.07 (0.01 mol) of *p*-toluidine, 1.01 g (0.01 mol) of triethylamine in 10 m*l* toluene was refluxed for 10 hr under an atmosphere of nitrogen. After separation of precipitated triethylammonium chloride, oily product was obtained by evaporating the solvent from the filtrate. The etheral solution of the oil gave crystals. The melting point was 68.5—70°C. Analytical data are summarized in Table 4.

Reaction of Fiber (Copolymer of III - AN) and Congo Red. The reaction of fiber and Congo Red are carried out at a ratio of 1 : 125 (0.04 g of fiber in 5 m*l* of dye solution) at a temperature of 95°C for 1 hr. The amount of dye combined chemically with the fiber was determined by measuring the unreacted dye in the solution colorimetrically using a Hitachi Photoelectric Photometer, Type EPO-B.

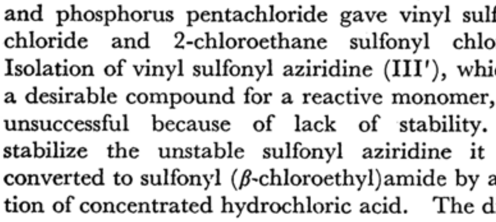
Results and Discussion

Preparation of Vinyl Sulfonyl (β-Chloroethyl)amide. Vinyl sulfonyl (β-chloroethyl)amide was prepared from ethylene bromide according to the following equations[8-10]:

$$BrCH_2CH_2Br + Na_2SO_3 \rightarrow BrCH_2CH_2SO_3Na$$

$$BrCH_2CH_2SO_3Na + NaOH \rightarrow CH_2{=}CH\text{-}SO_3Na \quad (I)$$

$$CH_2{=}CH\text{-}SO_3Na + PCl_5 \rightarrow \underset{(II)}{CH_2{=}CH\text{-}SO_2Cl} + CH_2ClCH_2SO_2Cl$$



The reaction between sodium vinyl sulfonate and phosphorus pentachloride gave vinyl sulfonyl chloride and 2-chloroethane sulfonyl chloride. Isolation of vinyl sulfonyl aziridine (III'), which is a desirable compound for a reactive monomer, was unsuccessful because of lack of stability. To stabilize the unstable sulfonyl aziridine it was converted to sulfonyl (β-chloroethyl)amide by addition of concentrated hydrochloric acid. The direct preparation of III from II and aziridine was tried, and II was recovered. The infrared absorption spectrum of III showed absorptions of NH at 3280 cm^{-1}, SO_2 at 1333 cm^{-1} and 1150 cm^{-1},

---

8) W. F. Whitmore and E. D. Landau, *J. Am. Chem. Soc.*, **68**, 1798 (1964).

9) C. S. Marvel, C. F. Bailey and M. S. Sparbey, *ibid.*, **49**, 1833 (1927).

10) E. F. Landau, *ibid.*, **69**, 1219 (1947).

and CH_2=CH at 3080 cm^{-1}, 3050 cm^{-1}, 1610 cm^{-1}, 970 cm^{-1} and 915 cm^{-1}, respectively.

Polymerization and Copolymerization of III. Poly-III was not obtained by UV irradiation. But using a radical initiator gave only low viscosity polymer even after a prolonged polymerization time. The polymer obtained was soluble in tetrahydrofuran (THF), dimethylformamide (DMF), methanol, benzene and acetone but insoluble in ether, water, and chloroform. The polymer of III decomposed at 95—105°C. The infrared absorption spectrum of poly-III showed no absorptions due to C=C double bond bands. The results of the polymerization are shown in Table 1.

TABLE 1. POLYMERIZATION OF VINYL SULFONYL (β-CHLOROETHYL)AMIDE (III)

Monomer (g)	Initiator AIBN (g)	Temp. (°C)	Time (hr)	Yield g (%)	η_{inh}[a]
4.59	0.006	65	50	0.2(4.4)	0.29
0.92	0.01	70	20	0.05(5.4)	0.32
0.92	UV	r.t.	18	—	—
1.50	0.01	60	70	0.21(14)	0.39

a) 0.25g/100 m*l* DMF at 30°C.

TABLE 2. COPOLYMERIZATION OF STYRENE (M_1) AND III (M_2) AT 62°C

Expt No.	Mol% in monomer		N% of copolymer	Mol% of copolymer	
	$[M_1]$	$[M_2]$		$[m_1]$	$[m_2]$
1	84.73	15.27	0.86	93.33	6.67
2	80.02	19.98	1.00	92.20	7.80
3	69.97	30.03	1.43	88.61	11.39
4	60.03	39.97	1.90	84.50	15.50
5	50.12	49.88	2.31	80.75	19.25
6	40.11	59.89	3.07	73.35	26.65
7	30.00	70.00	3.79	65.76	34.24
8	20.00	80.00	5.09	50.34	49.66

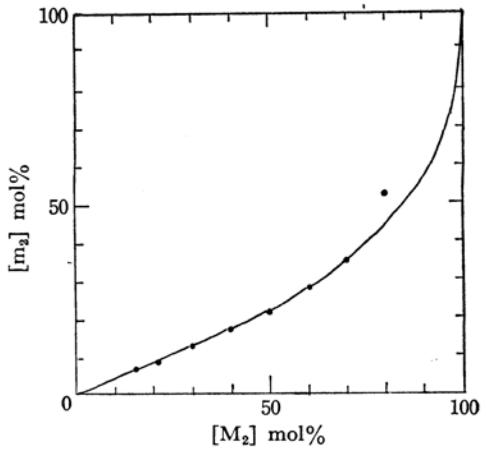
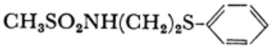
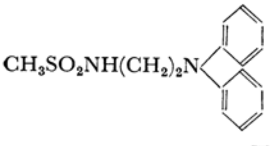
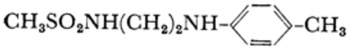
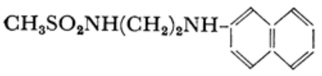
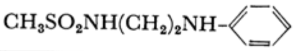


Fig. 1. Copolymerization curve: Styrene (M_1)-III (M_2).
(●) experimental; (—) calculated line based on the r_1, r_2 values

On the copolymerization of III with styrene, monomer feeds and copolymer compositions are shown in Table 2 and Fig. 1. The monomer reactivity ratios of III (M_2) with styrene (M_1) were determined from these data and *Q*, *e* values of III were calculated as follows: $r_1=3.0$, $r_2=0.075$, $Q=0.125$, $e=0.42$.

Reaction of Methane Sulfonyl (β-Chloroethyl)amide with Nucleophiles. As a model of the reaction of poly-III, the reaction of methane sulfonyl (β-chloroethyl)amide (IV) with nucleophiles was carried out. Table 3 shows the results

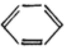
TABLE 3. REACTION OF METHANE SULFONYL (β-CHLOROETHYL)AMIDE

Product	IV (mol)	Reagent (mol)	Base (mol)	Toluene (m*l*)	Temp. (°C)	Time (hr)	Yield[a] (%)	Mp (°C)
 (IV-1)	0.01	0.01	0.01	10	reflux	4	13(65)	66.5—67.5
 (IV-2)	0.01	0.015	—	—	150	7	7(44)	109—110.0
 (IV-3)	0.01	0.01	0.01	10	reflux	10	3(53)	68.5—70.0
 (IV-4)	0.01	0.015	—	—	150	7	17(38)	103—105.0
 (IV-5)	0.01	0.01	0.01	10	reflux	10	23(78)	48—50.0

a) The yield of purified products is described. Values in parenthesis are the yield of crude products. IR spectra of crude compounds were the same as those of purified samples.

TABLE 4. ELEMENTARY ANALYSES OF MODEL COMPOUND

Compound	C%		H%		N%	
	Found	Calcd	Found	Calcd	Found	Calcd
IV-1	47.04	46.73	5.83	5.66	6.20	6.06
IV-2	62.30	62.04	6.24	6.25	9.86	9.65
IV-3	52.25	52.61	6.97	7.06	11.99	12.28
IV-4	59.34	59.29	5.92	5.74	10.76	10.64
IV-5	49.60	50.45	6.34	6.54	13.22	13.07

TABLE 5. THE EFFECT OF TRIETHYLAMINE ON THE PREPARATION OF $CH_3SO_2NH(CH_2)_2NH$-

IV (mol)	Aniline (mol)	Toluene (ml)	Triethyl amine (mol)	Temp. (°C)	Time (hr)	Yield (%)
0.01	0.01	10	0.01	140	4	78
0.01	0.015	—	—	150	6	37

TABLE 6. REACTION OF POLY-III

	Reagent (g)	Poly-III (g)	Solvent THF(ml)	Base[a] (g)	Temp. (°C)	Time (hr)	Yield (%)	Anal. N%	Conversion (%)
Thiophenol	(0.15)	0.08	1	0.15	room 100	24 4	63	5.72	100.7
Aniline	(0.25)	0.07	1	0.20	115	7	70	9.84	32.0
p-Toluidine	(0.05)	0.07	1	0.10	115	6	70	7.97 (Cl)	53.4[b]

a) Triethylamine.
b) Data was calculated from chlorine analysis.

of the reaction. Table 4 shows the elementary analyses of model compounds. From these results, main reaction of IV with nucleophiles may be concluded as a substitution reaction at β-carbon of β-chloroethyl amido group. The reaction is shown as Eq. (1).

$$CH_3SO_2NHCH_2CH_2Cl + RH \rightarrow CH_3SO_2NHCH_2CH_2R + HCl \qquad (1)$$

As shown in Table 5, the reaction of IV with aniline proceeded without triethylamine as an acid acceptor and the fact suggests that aniline itself acts as an acid acceptor. When triethylamine was used, the reaction proceeded more smoothly and a high yield of the product was obtained in a short time.

Reaction of Poly-III and Nucleophiles. Poly-III was found to be reactive with nucleophiles such as phenol, aniline and *p*-toluidine like methane sulfonyl (β-chloroethyl)amide. The results are summarized in Table 6.

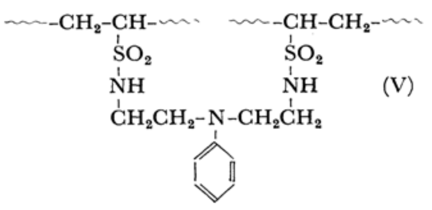
TABLE 7. REACTION OF COPOLYMER OF STYRENE-III WITH *p*-TOLUIDINE IN THE PRESENCE OF PYRIDINE

Exp. No.	Reaction time (min)	Recovered yield (%)	Cl % of reacted polm.	Conversion (%)
1	Original	—	5.42	—
2	5	90	5.28	2.3
3	15	94	5.26	2.7
4	60	75	5.21	3.5
5	120	73	—	6.3[a]
6	240	73	5.08	5.7
7	1800	64	1.05	79.0

a) Conversion was calculated from nitrogen analysis.

Reaction of Copolymer with Nucleophiles. The reaction of styrene-III copolymer with *p*-toluidine was carried out and the results are listed in Table 7. The degree of reaction was calculated by chlorine analysis of the resulting copolymer. The reaction seemed to proceed very slowly. From the values of monomer reactivity ratios of III with styrene, III unit should be placed separately on a copolymer chain. This is very different from homopolymer. The low degree of reaction of the copolymer might reflect the difference of polymer structure.

Polymer of III reacted with thiophenol was soluble in THF, but reaction of polymer III with aniline or *p*-toluidine gave cross-linked polymer. Aniline and *p*-toluidine appeared to act as a bifunctional reagent to make crosslinking as shown in V. The crosslinking presumably disturbs the amine to approach reacting sites and conversion of the reaction becomes low.


(V)

The fiber spun from copolymer of III with acrylonitrile was treated with Congo Red, a kind of amine, in aqueous solution at 95°C for an hour in the presence of pyridine. The amount of dye taken up by the fiber was determined by the colorimetric method. Usual acrylic fibers could not be dyed by Congo Red, a direct dye. The extraction of colored fiber with hot water gave no decoloration. We could conclude that the dye taken up was combined

TABLE 8. REACTION OF POLY-ST-III WITH NUCLEOPHILES

Reagents	Reagent wt. (g)	Poly-St-III[a] (g)	Solvent THF(m*l*)	Base (m*l*) Pyridine	Temp. (°C)	Time (hr)	N% (found)	Conversion (%)
Phenol	0.13	0.20	5	1	reflux	2	1.87	18.4
p-Toluidine	0.21	0.20	5	1	reflux	2	2.30	6.3
Congo Red[b]	0.26	0.20	5	1	reflux	2	2.61	4.2

a) Found 2.18 % (N).

b)

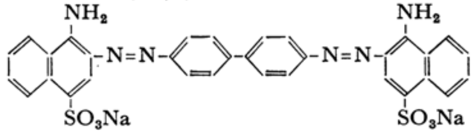


TABLE 9. THE REACTION OF FIBER AND CONGO RED AT VARIOUS CONCENTRATION OF PYRIDINE

Pyridine (%)	Amount of dye (mg/g)	Conversion (%)
2	30	82.3
6	22	60.4
10	25	68.6
14	22	60.4
24	18	49.6
50	14	34.6

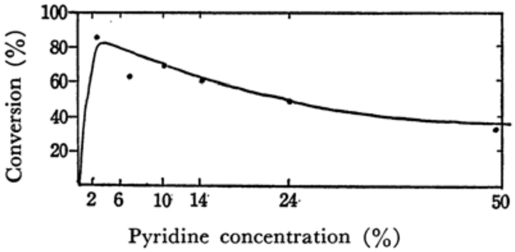


Fig. 2. The effect of pyridine concentration in the dye solution on amount of dye on fiber.

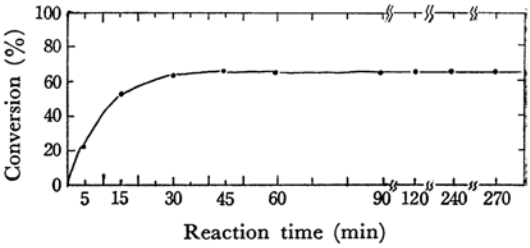


Fig. 3. The relation between the reaction time and the amount of the reaction in the case the dying of the fiber. (Pyridine concn. 10%, at 95°C)

chemically with the fiber. Effect of pyridine concentration in the dye solution on the reaction is shown in Table 9 and Fig. 2. The concentration of pyridine seemed to affect partition coefficient of the dye in the solution and the fiber, which played an important role in the reaction. Finally, we concluded that the reactivity of the sulfonyl (β-chloroethyl)amide groups derivatives of *p*-styrene and vinyl are the same, but the polymerizability and copolymerizability of styrene derivative are better than those of vinyl derivative.