

Reactive Fiber

Part I. Copolymerization and Copolymer of Acrylonitrile with Glycidyl Methacrylate and with Glycidyl Acrylate

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SUMMARY:

As one of the ways to obtain high molecular compounds which have chemical reactivity, the copolymerizations of acrylonitrile with glycidyl methacrylate, and with glycidyl acrylate were examined to prepare the copolymers which are soluble, moldable and spinnable. The homogeneous reaction of the copolymers with amines in dimethylformamide and the heterogeneous reaction of the fibers from copolymers with amines, amino acids, and dyes containing amino, phenolic hydroxyl groups was carried out and it was assumed that the copolymer of acrylonitrile with glycidyl methacrylate was a "Reactive Polymer" having considerable chemical reactivity.

ZUSAMMENFASSUNG:

Als ein Weg zur Darstellung reaktionsfähiger Makropolymerer wurde die Copolymerisation des Acrylnitrils mit Glycidylmethacrylat und Glycidylacrylat untersucht. Die dargestellten Copolymerisate sind löslich, formbar und spinnbar.

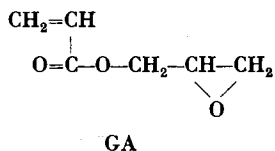
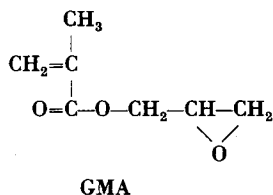
Die homogene Reaktion der Copolymeren mit Aminen in Dimethylformamid und die heterogene Reaktion von Fäden der Copolymerisate mit Aminen, Aminosäuren und Farbstoffen mit Amino- und phenolischen Hydroxygruppen wurden ausgeführt. Nach den Ergebnissen stellt das Copolymer aus Acrylnitril mit Glycidylmethacrylat ein sehr reaktionsfähiges Polymeres dar.

I. Introduction

Many investigations have been carried out dealing with the reactions of the epoxy ring with amino, carboxyl and hydroxyl groups, sodium sulfite and sodium bisulfite¹). In view of the reactivity of the epoxy ring, the copolymers and the graft copolymers containing glycidyl esters of unsaturated carboxylic acid are being investigated in our laboratory to obtain a polymer which has chemical reactivities.

¹) L. SHECHTER and J. WYNSTRA, *Ind. Engng. Chem.* **48** (1956) 86, 94; R. T. E. SCHENCK and S. KAIZERMAN, *J. Amer. chem. Soc.* **75** (1953) 1636; W. C. J. Ross, *J. chem. Soc. [London]* **1950**, 2257.

This paper reports the copolymerizations of acrylonitrile (AN) with glycidyl methacrylate (GMA) and with glycidyl acrylate (GA), and the chemical reactivities of the copolymers and fibers from the copolymers.



One of the present authors, determining the monomer reactivity ratio between glycidyl methacrylate and acrylonitrile, and between glycidyl methacrylate and styrene, has shown that glycidyl methacrylate and acrylonitrile could have been copolymerized²⁾. It has been reported in the U.S.A. that by treating the copolymers of acrylonitrile and glycidyl esters of unsaturated carboxylic acid with amines the epoxy rings contained in the copolymer react with the amines to gain an affinity for acid dyes³⁾. The result offered in this paper show that by using hydroxy amines instead of ordinary amines in the reaction the resulting copolymer from acrylonitrile-glycidyl methacrylate possesses affinity not only for acid dyes but also for direct dyes and for amino acids and amino sulfonic acids, making the copolymer amphotericized. Moreover, in the fiber from the copolymer, epoxy rings, which are components of the fiber, react with dyes which have amino or phenolic hydroxyl groups, to combine chemically in the same way as in the case of the so-called "Reactive Dye".

This copolymer and this fiber from the copolymer having such characteristics as described, may be called "Reactive Polymer" and "Reactive Fiber", respectively.

II. Results and Discussion

I. Synthesis of the Monomer

a) Glycidyl methacrylate

The method of synthesis was mainly according to USP 2,537,981 (1951).

4 moles epichlorohydrin were reacted with 1 mole sodium methacrylate using a catalyzer in the presence of polymerization inhibitor at a temperature of about 110°C. for 1 hr.; b.p. 85°C./15 mm.; n_D^{25} 1.4476.

²⁾ Y. IWAKURA and K. MATSUZAKI, Chem. High Polymers Japan 17 (1960) 187.

³⁾ Brit. Pat. 721, 688 (1955).

b) Glycidyl acrylate

It is possible that commercial methyl acrylate or acrylic acid contain some methyl propionate or propionic acid by the mode of preparation. Glycidyl acrylate was made from acrylic acid, which was prepared by means of dehydration and hydrolysis of ethylene cyanohydrin by 85% sulfuric acid⁴). B.p. 83 °C./20 mm.; n_D^{20} 1.4472.

2. Determination of the Monomer Reactivity Ratio

a) Monomer Reactivity Ratio

In the acrylonitrile-glycidyl acrylate system 15 g. of the mixture of the monomers was diluted to 75 wt.% monomer concentration by adding tetrahydrofuran containing 35 mg. α, α' -azo-bis-isobutyronitrile and copolymerized at 60 °C. The composition of the monomer feed and the copolymer formed are summarized in Table I.

Table I. Determination of the monomer reactivity ratio in the copolymerization system acrylonitrile (M_1)—glycidyl acrylate (M_2)

Mole % in Monomer		N % KJELDAHL	Mole % in Polymer	
M_1	M_2		m_1	m_2
95.23	4.77	23.22	94.60	5.40
90.06	9.94	20.86	90.07	9.93
84.83	15.17	18.70	85.42	14.58
80.34	19.66	16.88	81.04	18.96
73.96	26.04	14.03	75.23	26.77
70.28	29.72	12.77	69.30	30.70
66.23	33.77	11.54	68.40	31.60
59.80	40.20	9.22	59.30	40.70
31.52	68.48	4.28	31.85	68.15
22.32	77.68	2.28	18.55	81.45
10.91	89.09	1.51	12.80	87.20

Table II. Determination of the monomer reactivity ratio in the copolymerization system styrene (M_1)—glycidyl acrylate (M_2)

Mole % in Monomer		C %	Mole % in Polymer	
M_1	M_2		m_1	m_2
93.84	6.16	88.01	90.10	9.90
90.06	9.94	86.42	86.31	13.69
77.97	22.03	80.35	71.26	28.74
58.56	41.44	76.75	61.85	38.15
28.60	71.40	70.71	45.17	54.83
19.59	80.41	69.75	42.42	57.58
8.97	91.03	65.37	29.41	71.59

⁴) USP 2,026,894 (1936).

In the copolymerization of styrene with glycidyl acrylate 30 g. of the mixture of the monomers and 60 mg. α, α' -azo bis-isobutyronitrile were used in each run. Table II lists the experimental data.

From these results, the monomer reactivity ratio were obtained by the method of FINEMAN and ROSS⁵⁾ as follows:

For acrylonitrile (M_1)	$r_1 = 1.01$	$r_2 = 1.02$
For styrene (M_1)	$r_1 = 0.60$	$r_2 = 0.17$

As reported in the previous paper²⁾ the monomer reactivity ratio for the copolymerizations of acrylonitrile-glycidyl methacrylate and of styrene-glycidyl methacrylate systems are $r_1 = 0.14$, $r_2 = 1.32$ and $r_1 = 0.44$, $r_2 = 0.53$, respectively.

Summarizing these results, the concentration of M_2 in the monomer feed was plotted against the corresponding mole-% of m_2 in the copolymer in Fig. 1 and Fig. 2. The lines in the figure were calculated from the monomer reactivity ratio and the spots were from the experimental data.

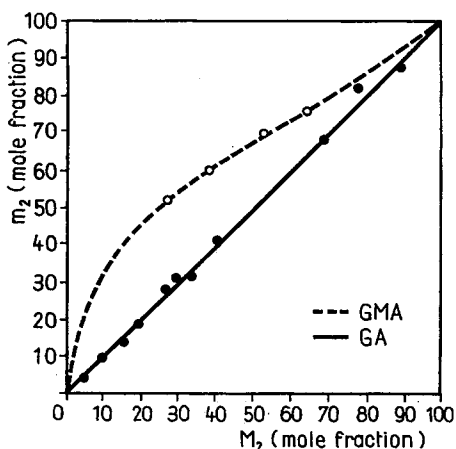


Fig. 1. Copolymer composition curve of glycidyl methacrylate and glycidyl acrylate in the copolymerization with acrylonitrile

b) Q- and e-values

The Q- and e-values according to PRICE⁶⁾, were obtained from their monomer reactivity ratios in the copolymerization with styrene:

Glycidyl methacrylate	$Q = 0.87$	$e = 0.40$
Glycidyl acrylate	$Q = 0.53$	$e = 0.66$

⁵⁾ M. FINEMAN and S. D. ROSS, J. Polymer Sci. 5 (1950) 259.

⁶⁾ C. C. PRICE, J. Polymer Sci. 3 (1948) 772.

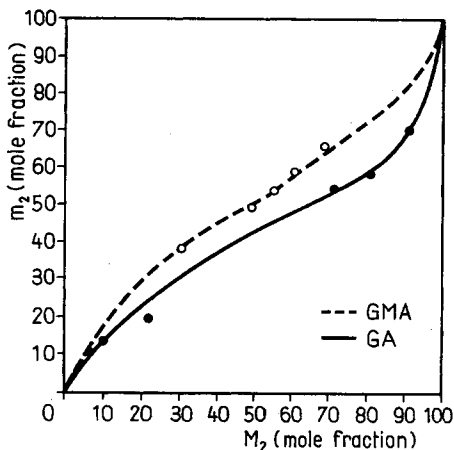


Fig. 2. Copolymer composition curve of glycidyl methacrylate and glycidyl acrylate in the copolymerization with styrene

3. Preparation of the Copolymer

As copolymers containing epoxy rings are apt to be insoluble, due to ring opening, various polymerization methods were examined in order to avoid reaction for the susceptibility of epoxy ring during the polymerization and to obtain a copolymer which is soluble and of a moderate molecular weight for spinning. Table III gives the results found on the solubilities for dimethylformamide of the copolymers obtained by various polymerizations.

The difference of solubility depends on the mode of polymerization, the kind of solvent and whether glycidyl methacrylate or glycidyl acrylate is polymerized under the same conditions. The mechanism of the polymerization is now being investigated in detail.

Table III. Solubility test of copolymers prepared by various methods

Monomer system	Polymerization method				
	Bulk	Emulsion	Slurry in water	Slurry in cyclic ether	Slurry in other solvent
Acrylonitrile-GMA	S	I	S. milky	S. clearly	I
Acrylonitrile-GA	I	I	I	S. clearly	I

S = Soluble I = Insoluble S. milky = Soluble in DMF, giving a milky solution

Cyclic ether = Tetrahydrofuran, dioxane

Other solvent = Benzene, n-hexan, n-dibutyl ether

As transfer to solvent determines the molecular weight in the polymerization in tetrahydrofuran, in order to obtain the suitable molecular weight for spinning, the monomer concentration must be in excess of 80 wt. % as shown in Table IV.

Table IV. Copolymerization of acrylonitrile and glycidyl methacrylate in tetrahydrofuran at 60°C. GMA/AN = 0.05

Monomer wt. %	α,α' -Azo-bis-isobutyronitrile			
	0.17 mol % (of monomers)		0.08 mol % (of monomers)	
	$[\eta]$	\bar{M}_n	$[\eta]$	\bar{M}_n
50	0.5	5,200	0.49	5,100
70	0.92	14,200	0.90	13,000
85	1.52	28,400	1.69	33,000

Comparing the polymerization by slurry polymerization in water with that in tetrahydrofuran in Table V, it is assumed that even the former method can be utilized in preparing the polymer which is spinnable as long as dimethylformamide is used as solvent for the polymer.

Table V. Comparison of copolymer by slurry polymerization in water with that in tetrahydrofuran

Property	Kind of polymer	Copolymer by slurry in water	Copolymer by slurry in THF
	Solubility	DMF KCNS	S. milky I
Content of GMA (wt. %)	by KJELDAHL by DMF-HCl	12.4 8.4	12.4 7.2
	DMF = dimethylformamide I = insoluble	THF = tetrahydrofuran S. = soluble	

In Table V, contents of glycidyl methacrylate determined by KJELDAHL's method are equal to the ester contained in the copolymer and that by DMF-HCl method correspond to contents of the epoxy ring and so the difference between the both indicates the amount of epoxy ring opened during the polymerization.

4. Reaction of the Copolymer with Amines in the Homogeneous State

a) Reaction between nitrile groups in polyacrylonitrile and amines, and aminolysis of ester groups by diethanolamine

The used polyacrylonitrile was made by slurry polymerization in water. 0.5 g. polyacrylonitrile was dissolved in 5 ml. DMF and mixed with

5.0 ml. of 0.4 N amine — DMF solution. The reaction temperature was 70.0 ± 0.1 °C. The results are in Table VI.

Table VI. Reaction of nitrile group with amines

Amine	Reaction time (hrs.)	Conv. (%)
Diethanolamine	24	1.1
Dibutylamine	30	0.8

4.9 g. copolymer which contained 14.53 wt. % methyl methacrylate was dissolved in 25 ml. DMF and mixed with 65 ml. of 0.2N diethanolamine-DMF solution at 70 °C. The results of the reaction at 70.0 ± 0.1 °C. are in Table VII.

Table VII. Reaction of ester group with diethanolamine

Reaction time (hrs.)	Conv. (%)
4	1.6
6	2.0
10	2.9
15	2.2
28	1.8

From the results in Table VI and VII, nitrile groups do not react with amines and the ester is not aminolysed by amines under these conditions.

b) Reaction between diethanolamine and the epoxy ring in the acrylonitrile-glycidyl methacrylate copolymer

0.7 g. copolymer which was made by slurry polymerization in THF and had 11.72 wt. % glycidyl methacrylate and had an intrinsic viscosity of 1.31 was dissolved and mixed with 5.0 ml. of 0.4 N diethanolamine-DMF solution. The reaction was carried out at 70.0 ± 0.1 °C. The results are summarized in Table VIII.

Supposing that this reaction is second order between epoxy ring in the copolymer and amine, the reaction velocity constants are calculated and shown in Table VIII. As it is apparent that the values of the constant in Table VIII remain consistent all over the reaction and as shown

$$\frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)}$$

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Table VIII. Reaction of epoxy ring with diethanolamine and its rate constant

a = Concentration of epoxy ring (mole/l.)
 b = Concentration of amine (mole/l.)
 k = Second order reaction constant (l./mole·sec.)

Reaction time (hrs.)	Conv. (%)	$\frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)}$ (l./mole)	k · 10 ⁴ (l./mole·sec.)
3	18.8	1.17	1.09
	17.1	1.04	0.96
6	33.1	2.38	1.10
	32.3	2.24	1.03
12	50.7	4.15	0.96
	50.4	4.06	0.94
18	65.8	6.52	1.01
	64.9	6.29	0.97
24	66.2	6.59	1.01
	70.4	9.00	1.04
	77.7	9.70	1.12

average of k: 1.02 ± 0.013

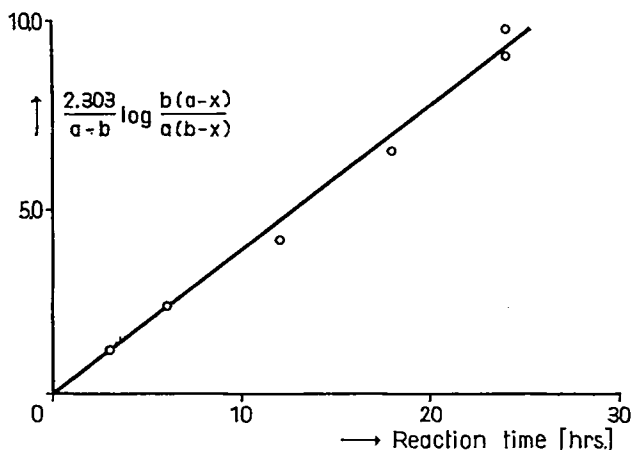


Fig. 3. Reaction constant of the epoxy ring in the acrylonitrile-glycidyl methacrylate copolymer in the reaction with diethanolamine

in Fig. 3 the relationship of against time is linear, the assumption supposing the second order reaction is verified.

In the same way, the reaction constants were obtained for the copolymers of which composition and intrinsic viscosity differed from one another. The compositions and intrinsic viscosities of copolymers and

Table IX. Reactivity of the epoxy ring in various copolymers with diethanolamine

Exp. No.	Copolymer		Mol. ratio Amine/GMA	$k \cdot 10^4$ (l./mole·sec.)
	$[\eta]$ (g./100 ml.)	GMA contents (%)		
2	1.25	9.12	3.9	0.95 ± 0.043
3	0.71	33.93	3.7	0.94 ± 0.025
4	0.99	36.05	3.9	0.94 ± 0.082
5	0.72	37.56	3.8	0.97 ± 0.025
6	1.90	38.41	3.8	0.88 ± 0.091
7	1.32	24.24	3.9	0.88 ± 0.086

the reaction constants are listed in Table IX. From the rate constant, the reactivity of the epoxy ring in the copolymers appears not to change. This means, that the reactivity of the epoxy ring is independent of the molecular weight⁷⁾ but the neighbouring effect which has been mentioned by many authors⁸⁾ as yet cannot be discussed.

c) Reaction between dibutylamine and epoxy ring in the acrylonitrile-glycidyl methacrylate copolymer

4.88 g. copolymer (glycidyl methacrylate contents: 9.12 wt.%, $[\eta]$: 1.25) was dissolved in 25.97 g. DMF and by adding 66.05 g. of 2N DMF solution of dibutylamine the reaction was started at $70.0 \pm 0.1^\circ\text{C}$. The molar ratio of amine to epoxy ring was 3.9. The results are in Table X.

Table X. Reactivity of the epoxy ring with dibutylamine

Reaction time (hrs.)	Conv. (%)	$\frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)}$ (l./mole)	$k \cdot 10^4$ (l./mole·sec.)
2.0	19.0	1.26	1.75
4.0	29.1	2.42	1.67
6.0	38.6	3.80	1.70
10.0	52.5	6.07	1.69
15.2	59.7	7.56	1.41
28.0	85.0	17.55	1.71
			average of k : 1.66 ± 0.031

⁷⁾ L. M. MINSK, W. J. PRIEST, and W. O. KENYON, J. Amer. chem. Soc. **63** (1941) 2715; A. CONIX and G. SMETS, J. Polymer Sci. **15** (1955) 221.

⁸⁾ L. A. HILLER, Jr., J. Polymer Sci. **10** (1953) 385; J. MOENS and G. SMETS, J. Polymer Sci. **23** (1957) 931; E. W. WESTHEAD, Jr. and H. MARAWETZ, J. Amer. chem. Soc. **80** (1958) 237.

The reaction constants where dibutylamine was used were about twice as large as that where diethanolamine was used. As an example of the reaction with diethanolamine, in Fig. 4, Experiment No. 2 is cited to illustrate the difference between the two amines. The difference seems to depend on their basicity.

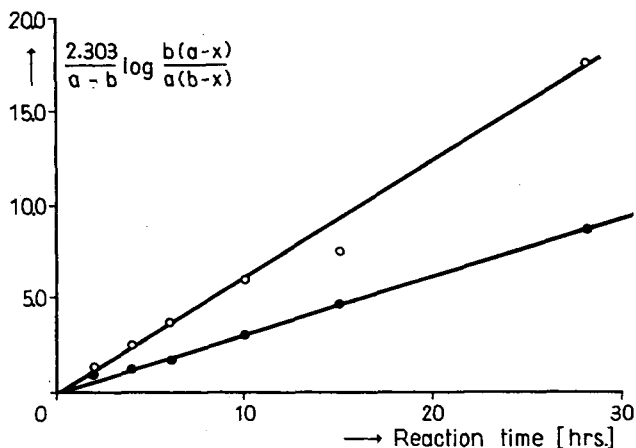


Fig. 4. Reaction constant of the epoxy ring copolymer in the reaction with diethanolamine and dibutylamine

● = Diethanolamine
○ = Dibutylamine

d) Reaction between diethanolamine and the epoxy ring in the acrylonitrile-glycidyl acrylate copolymer.

The used copolymer was made by slurry polymerization in THF and contained 11.23 wt. % glycidyl acrylate and its intrinsic viscosity was

Table XI. Reactivity of the epoxy ring in acrylonitrile-glycidyl acrylate copolymers with diethanolamine

Reaction time (hrs.)	Conv. (%)	$\frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)}$ (l./mole)	$k \cdot 10^4$ (l./mole · sec.)
2.0	12.6	0.63	0.88
4.0	17.2	0.71	0.49
6.0	25.6	1.48	0.69
6.4	27.9	1.73	0.72
8.0	34.2	2.19	0.76
10.0	36.5	2.44	0.68
12.0	41.7	2.96	0.69
			average of k: 0.70 ± 0.115

1.90. 4.92 g. copolymer, 26.30 g. DMF to solute the copolymer and 65.94 g. of 0.2 N DMF solution of diethanolamine were used. The molar ratio of amine to epoxy ring was 4.0. The data are in Table XI.

Comparing these results with Exp. No. 6 in Table IX as the reactivity of the respective epoxy ring for diethanolamine seems to be equal, like

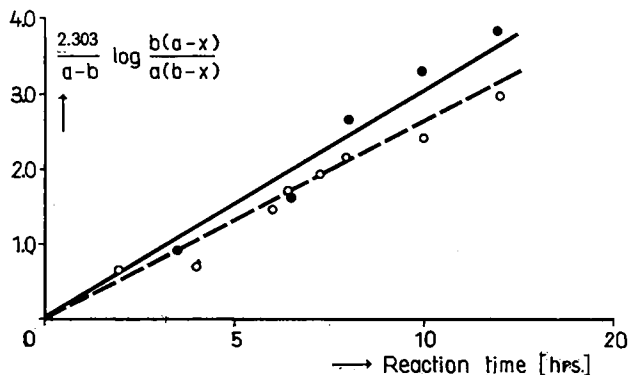


Fig. 5. Reaction constant of the epoxy ring in the acrylonitrile-glycidyl acrylate and acrylonitrile-glycidyl methacrylate copolymer with diethanolamine

- = Glycidyl methacrylate copolymer
- = Glycidyl acrylate copolymer

in Fig. 5, it is assumed the different arrangement of the units along the chain, which is due to the monomer reactivity of acrylonitrile-glycidyl acrylate systems, does not affect the reaction.

5. Wet-spinning of the Copolymer

A concentrated solution of the copolymer might increase its viscosity until gelation due to the presence of the sensible epoxy ring, but unexpectedly, no viscosity change was observed by the Ball-fall test*) in which about 10 wt. % DMF solution of acrylonitrile-glycidyl methacrylate

Table XII. Stability test on 10 wt. % dimethylformamide solution of acrylonitrile-glycidyl methacrylate copolymer by Ball-fall test

Days	1	2	6	7	8
Sec.	730.2	732.0	736.2	733.2	736.2

*) Used steel ball is $\frac{1}{8}$ " diam. and 0.13 g. and measured distance of the fall is 20.0 cm. in a glass tube of 3.0 cm. diam. The test was carried out at 45°C.

copolymer (glycidyl methacrylate contents: 10.19 wt.%), was kept under shielding moisture for 8 days at 45 °C. as shown in Table XII.

Wet-spinning was carried out on three kinds of the copolymers as follows.

Dope concentration (wt. % in DMF)

- 13% (I) Acrylonitrile-glycidyl methacrylate copolymer prepared by slurry polymerization in tetrahydrofuran.
Glycidyl methacrylate contents: 10.67 wt.%. $\bar{M}_n = 33,000$.
- 14% (II) Acrylonitrile-glycidyl methacrylate copolymer prepared by slurry polymerization in water.
Glycidyl methacrylate contents: 10.19 wt.%. $\bar{M}_n = 30,600$.
- 15% (III) Acrylonitrile-glycidyl acrylate copolymer prepared by slurry polymerization in THF.
Glycidyl acrylate contents: 12.0 wt.%. $\bar{M}_n = 29,000$.

The mechanical properties of the fibers obtained are indicated in Table XIII.

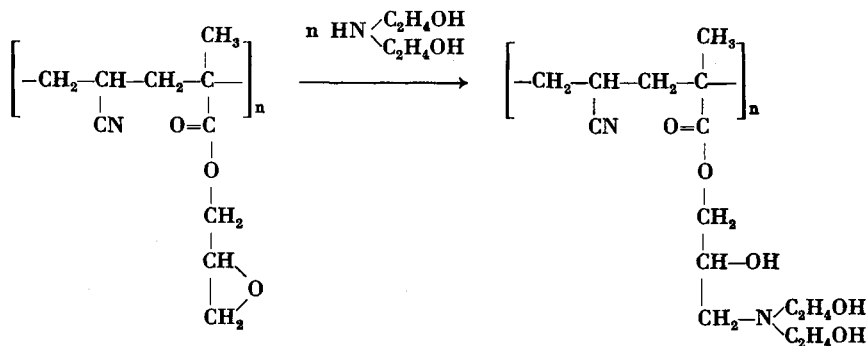
Table XIII. Mechanical properties of the fibers from acrylonitrile-glycidyl ester copolymers

Fiber	I	II	III
Property			
Tenacity (g./d)	2.9	2.9	2.3
Elongation (%).....	13.5	14.5	10.6

6. Reaction of the Fiber from Copolymer with Amines

The fiber from the acrylonitrile-glycidyl methacrylate copolymer (GMA contents: 11.28 wt.%) made by slurry polymerization in water was heated in 20 % acetone solution of amine for a given time at 50 °C. and the extent of reaction of the epoxy ring with amine was determined by KJELDAHL's analysis. As amines, dibutyl- and diethanolamine were used and also in the latter case the test was carried out in the presence of pyridine. The results are shown in Fig. 6.

The reaction between an amine and the epoxy ring in the fiber proceeded effectively at such a low temperature as 50 °C. Thus, the amine combines to the acrylonitrile-glycidyl methacrylate fiber as follows and in doing so produces many possibilities.



On the other hand, in the treatment in 20 wt. % isopropanol solution of diethanolamine at 80 °C., the reaction of epoxy ring did not occur. The reaction of the acrylonitrile-glycidyl acrylate fiber (GA contents: 12.0 %) with amine was carried out in 20 % acetone solution of amine at 60 °C., but no reaction occurred within experimental errors.

In the reaction of the acrylonitrile-glycidyl methacrylate fiber in acetone solution, the rate determining step was the reaction of the epoxy

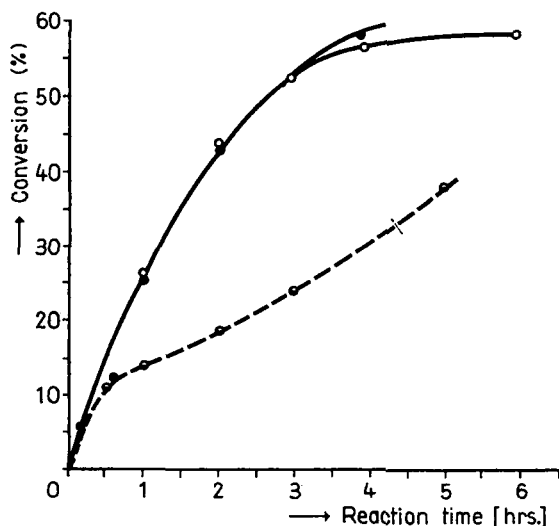


Fig. 6. Rate of epoxy ring in the acrylonitrile-glycidyl methacrylate fiber in the reaction with amines

- = Diethanolamine
- = Diethanolamine in the presence of pyridine (0,3 wt.%)
- = Dibutylamine

ring with amine rather than the diffusion of reagent and in the case of isopropanol solution, no reaction occurs because the reagent does not diffuse into the fiber as isopropanol has very little affinity for the copolymer.

The nonreactivity of the acrylonitrile-glycidyl acrylate fiber is attributed to the difference in the manner in which the glycidyl acrylate units are distributed among the copolymer, as there is no difference in the reactivity of each epoxy ring between the acrylonitrile-glycidyl methacrylate and the acrylonitrile-glycidyl acrylate copolymers in the homogeneous system as described in the previous section. Namely, the acrylonitrile-glycidyl methacrylate copolymer has the distribution of the copolymer compositions calculated by Eq. (1) and Eq. (2)⁹ like Fig. 7.

$$\ln \frac{M}{M_0} = \int_{M_1^0}^{M_1} \frac{dM}{x_1 - M_1} \quad (1)$$

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \frac{r_1(M_1) + (M_2)}{(M_1) + r_2(M_2)} \quad (2)$$

where M_0 = initial total number of moles of both monomers

M = total number of moles of both monomers

M_1, M_2 = mole fraction of the component M_1 and M_2

M_1^0 = initial mole fraction of monomer M_1

x_1 = mole fraction of component M_1 in copolymer

Thus the formed acrylonitrile-glycidyl methacrylate copolymer has a large range of compositions and has a part in which are more glycidyl methacrylate units than there are in the over-all composition. As these parts, perhaps have relatively affinity to acetone, the epoxy ring being in such a segment reacts with the amine.

But in a acrylonitrile-glycidyl acrylate copolymer all the chains have the same composition as suggested by the monomer reactivity ratio and, in this example, all the polymer chains have 12 wt. % glycidyl acrylate homogeneously. Perhaps, acetone cannot diffuse into the portion of such a glycidyl acrylate contents.

⁹ I. SKEIST, J. Amer. chem. Soc. **68** (1946) 1781.

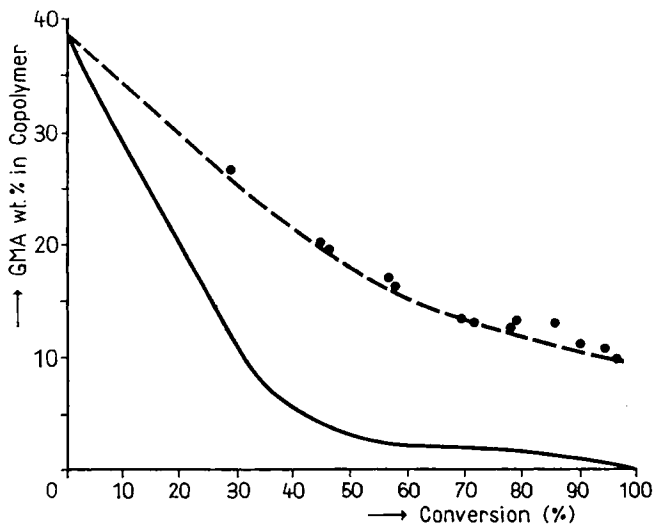


Fig. 7. Variation of copolymer composition with the extent of reaction in the slurry polymerization in water (acrylonitrile: 47.7; glycidyl methacrylate: 5.3)
 — = Copolymer composition formed at every conversion
 - - - = Averaged composition calculated
 ● = Experimental data

7. Dyeability and other Properties of the Aminated Fiber

a) Dyeability

When the acrylonitrile-glycidyl methacrylate fiber was heated in 20 % acetone solution of various amines for 2 hrs. at 60°C., the fiber was aminated. As amines, diethylamine and diethanolamine were used and the aminated fibers obtained were dyed with acid and direct dyes. The degree of exhaustion is as in Table XIV.

Table XIV. Degree of dye exhaustion of aminated fiber (%)

Amines treated	Direct Sky Blue FF	Acid Brilliant Scarlet 3 R
Diethylamine	0	exhausted
Diethanolamine	72	exhausted

Dyeing these aminated fibers with several direct dyes such as Congo Red, Benzopurpline 4B, Direct Black BH and Crysophenine G gave the same results.

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From these results it was assumed that the hydroxyl group was induced when the hydroxyamine reacted with acrylonitrile-glycidyl methacrylate fiber and made it easy to form a hydrogen bond with the direct dye. The acrylonitrile-glycidyl methacrylate fibers were treated with various hydroxyamines synthesized in our laboratory and dyeability of these fibers are listed qualitatively in Table XV.

Table XV. Relation of amines used in treating acrylonitrile-glycidyl methacrylate fibers for dyeability

			Acid Dye	Direct Dye
Hydroxyamine	Aliphatic	$\begin{array}{l} \text{CH}_2\text{-CH}_2\text{-OH} \\ \text{HN} \diagdown \\ \text{CH}_2\text{-CH}_2\text{-OH} \\ \text{CH}_3 \end{array}$	++	+
		$\begin{array}{l} \text{CH}_2\text{-CH-OH} \\ \text{HN} \diagdown \\ \text{CH}_2\text{-CH}_2\text{-OH} \end{array}$	++	+
	Aromatic	$\begin{array}{l} \text{CH}_2\text{-CH}_2\text{-OH} \\ \text{HN} \diagdown \\ \text{CH}_2\text{-CH-OH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	++	-
		$\begin{array}{l} \text{CH}_2\text{-CH}_2\text{-OH} \\ \text{HN} \diagdown \\ \text{CH}_2\text{-CH-O-C}_6\text{H}_5 \\ \\ \text{OH} \end{array}$	++	-
Amine	Aliphatic	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \text{HN} \diagdown \\ \text{C}_2\text{H}_5 \end{array}$	++	-
	Aromatic	$\begin{array}{l} \text{H}_2\text{N-C}_6\text{H}_5 \\ \text{H}_2\text{N-CH}_2\text{-C}_6\text{H}_5 \end{array}$	- ++	- -

++ : The degree of dye bath exhaustion is above 100%;
 bath exhaustion is above 50%
 - : Does not be dyed.

+ : The degree of dye.
 Dyeing condition is in
 experimental part.

According to the data, the presence of phenyl groups in the fiber, not only for steric hindrance but also for hydrophobic property, seemed to affect dyeability of fiber.

b) Moisture regain

On every aminated fiber treated with various amines, moisture regain was tested. The results were as follows:

Amine used	Moisture regain (%) (at 65% R.H., 30°C.)
—	2.03
Diethylamine	2.11
Monoethanolamine	3.01
Diethanolamine	3.83
2-(2'-Hydroxy-2'-phenylethylamino) ethanol	2.67
2-(3'-Phenoxy-2'-hydroxypropylamino) ethanol	2.61

It seems to be more hygroscopic with increasing hydroxyl groups, but for amino alcohols containing phenyl groups the values decreased.

c) Mechanical Properties

The acrylonitrile-glycidyl methacrylate fiber, which was copolymerized in slurry polymerization in water and contained 10.67 wt. % of glycidyl methacrylate, was heated in a mixture of 50 wt. % acetone and 50 wt. % amine for a given time at 60°C. and its mechanical properties were summarized.

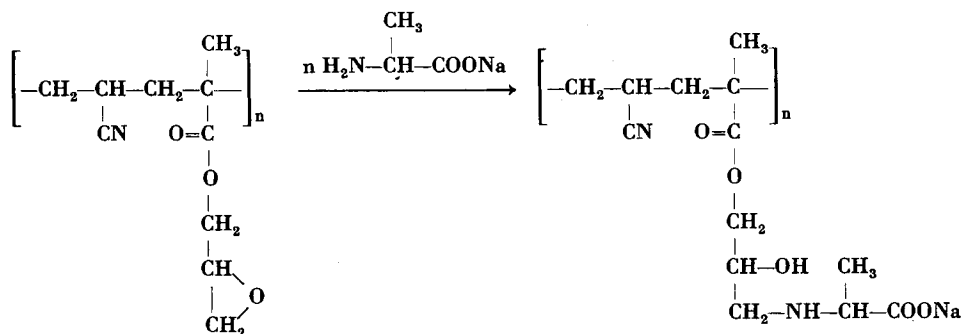
Amine	Time (hrs.)	Tenacity (g./d)	Elongation (%)
—	—	2.9	14.5
Diethanolamine	1	3.0	23.1
Diethanolamine	2	3.0	23.5
Diethanolamine	3	2.7	25.4
Diethylamine	2	2.9	22.4

By treatment with amines no change could be recognized in the tenacity but its elongation increased.

8. Reaction of the Acrylonitrile-Glycidyl Methacrylate Fiber with Amino Acid

When the acrylonitrile-glycidyl methacrylate fiber was immersed [1] in 70% DMF-aqueous solution of the sodium salt of α -amino acid or sodium β -aminoethyl sulfonate and heated for 1 hr. at 100°C. or [2] in 80% acetone-aqueous solution of them for 2 hrs. at 60°C. the polymer reaction proceeded and the fiber was amphoterized.

Reactive Fiber



In the second case, the extent of the reaction of the epoxy ring with the amino acid and the degree of exhaustion of the dyes are shown in Table XVI.

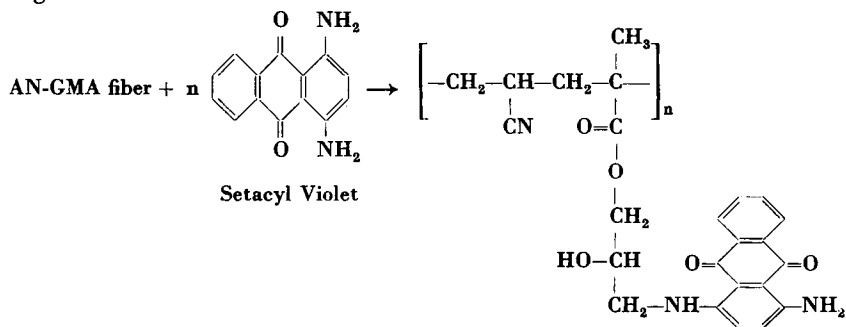
Table XVI. Reactivity of the epoxy ring in copolymer
(fiber from acrylonitrile-glycidyl methacrylate)
with amino acid and dyeability (Dye bath exhaustion %/0) of reaction product

	N (%)	Conv. (%)	Congo Red (Direct dye)	Acid Brill Scarlet 3 R (Acid dye)	Malachite Green (Basic dye)
Taurine-Na	22.7	52	46	40	exhausted
Alanine-Na	22.9	64	23	25	28
Glycine-Na	—	—	36	70	54

AN-GMA fiber: 23.44% N; 11.28 wt.% GMA.

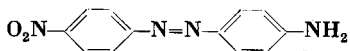
9. Reaction of the Acrylonitrile-Glycidyl Methacrylate Fiber with Dye

The acrylonitrile-glycidyl methacrylate fiber reacted with the amino or phenolic hydroxyl group of dyes giving a chemical bond in the following manner.

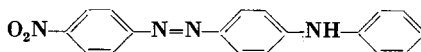


The reaction proceeded in emulsion or in suitable media by heating for 2–3 hrs. at 100°C. The reacted dye could not be extracted by cyclohexanone. The following types of dispersed dyes easily react with the fiber contrary to reactive dyes:

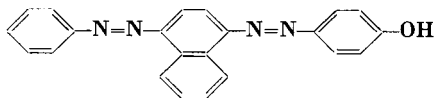
Dispersol Fast Orange G



Setacyl Scarlet 2 GN



Dispersol Fast Orange B



III. Experimental

1. Preparation of the Monomer

Sodium methacrylate	109 pts.
Epichlorohydrin	500 pts.
Benzyltriethylammonium chloride	2 pts.

A mixture of the above ingredients was heated with stirring for 1 hr. at 95–100°C. in presence of a polymerization inhibitor such as α -naphthylamine or hydroquinone. Sodium chloride formed was removed by filtration and then glycidyl methacrylate could be separated from the filtrate by vacuum distillation after distillation of the excess epichlorohydrin whose boiling point is lower than that of the glycidyl methacrylate.

2. Polymerization for Determining the Monomer Reactivity Ratio

Polymerization was carried out by the sealed ampoule technique. The initiator-monomer-solvent systems were taken in ampoules: cooled in acetone – dry ice mixture and sealed under a stream of nitrogen free from oxygen and thermostated at 60°C. until generally from 5% to 10% conversion was obtained. The polymer obtained was dissolved in dimethylformamide and precipitated by methanol. The copolymer was reprecipitated three times and dried under vacuum.

3. Preparation of the Copolymer

In all cases the polymer formed was washed with water and alcohol and dried under vacuum.

a) Bulk polymerization

This method was carried out by the sealed ampoule technique described.

b) Emulsion polymerization

Acrylonitrile	202.0 pts.	Sodium lauryl sulfate	5.0 pts.
Glycidyl methacrylate	20.0 pts.	Dodecyl mercaptane	0.5 pts.

Reactive Fiber

$K_2S_2O_8$	12.4 pts.	Water	1000.0 pts.
$NaHSO_3$	2.1 pts.		

The polymerization proceeded under a stream of nitrogen gas at 40–48 °C.

c) Slurry polymerization in water³⁾

Acrylonitrile	47.7 pts.	$(NH_4)_2S_2O_8$	1.71 pts.
Glycidyl methacrylate..	5.3 pts.	$Na_2S_2O_5$	0.71 pts.
Water	1000.0 pts.	0.1 N H_2SO_4 ..	7.0 pts.

The polymerization was carried out under nitrogen at 25 °C.

d) Slurry polymerization in organic solvent

Acrylonitrile	136.0 pts.
Glycidyl methacrylate	7.0 pts.
α,α' -Azo-bis-isobutyronitrile.	0.15 pts.
Organic solvent	24.0 pts.
Polymerization temp.	50 °C.

4. Determination of the Molecular Weight

Viscosity measurements were carried out in DMF at 30 °C. with an ÜBBELOHDE viscosimeter. The molecular weight was then calculated using the HOUTZ's relationship

$$[\eta] = 1.75 \cdot 10^{-3} \bar{M}_n^{0.65}$$

5. Determination of the Epoxy Value by DMF-HCl

The copolymer containing epoxy ring was dissolved in 0.1 N HCl-DMF solution and after standing for 3 hrs. the polymer was precipitated by adding water and then the excess HCl was titrated with 0.1 N NaOH in the presence of methyl red as indicator.

6. Wet-spinning

Dope concentration:	13–20%, depending on \bar{M}_n
Nozzle:	0.08 mm. diam., 100 holes or 0.07 mm. diam., 200 holes
Coagulation bath:	Ethylene glycol, room temp.
Elongation bath:	Water, 98 °C.
Elongation ratio:	4.6
Winding velocity:	30 m./min.

7. Determination of the Rate in Homogeneous System

The copolymers were dissolved in DMF and then mixed with amine-DMF solution so that the concentration of polymer was about 5% and the molar ratio of amine to epoxy ring remained 4. The reactions were carried out at 70.0 ± 0.1 °C. At a given reaction time, the polymer was precipitated by adding distilled water whilst vigorously stirring. In some cases at every given interval aliquot was pipetted out from the reaction mixture and the polymer was precipitated in the same way. After standing for $1/2$ hr. it was

filtrated and washed with distilled water. Then the excess amine in the filtrate was titrated by 0.1 N H_2SO_4 potentiometrically or in the presence of methyl red as indicator.

8. Dyeing

Dyeing temperature: 90 °C. Dyeing time: 60 min.

Compositions of dye bath per 1 pt. fiber were as follows:

a) Acid dye	0.02 pts.	b) Basic dye	0.02 pts.
Sulfuric acid .	0.02 pts.	Acetic acid (33%)	0.02 pts.
Sodium sulfite	0.04 pts.	Water	50.0 pts.
Water	50.0 pts.		
c) Direct dye			
	0.02 pts.	Sodium chloride	0.08 pts.
		Water	50.0 pts.

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