Reactive Fiber. IV. The Graft Copolymerization of Glycidyl Methacrylate onto Polypropylene and Polyvinyl Chloride Fibers

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In a series of studies of reactive fibers, the epoxide group containing fibers[1] from acrylonitrile-glycidyl methacrylate (GMA), the acrylonitrile-glycidyl acrylate copolymer, the GMA-grafted cellulose fiber[2] and fibers[3] from *N*-*p*-(*N'*-β-chloroethylaminosulfamoyl)phenylacrylamide and *N*-*p*-(*N'*-β-chloroethylaminosulfamoyl)phenylmethacrylamide copolymers were synthesized and their chemical reactivities investigated.

In this paper, the graft copolymer of GMA onto polypropylene (PP) and polyvinyl chloride (PVC) fiber were prepared by the γ-ray pre-irradiation technique in vacuo. The present method avoided the homopolymerization of GMA and the oxidative degradation of PVC fiber, and introduced epoxide groups into the fibers under mild conditions.

The grafted fibers obtained had high chemical reactivities with amines and hydroxyamines.

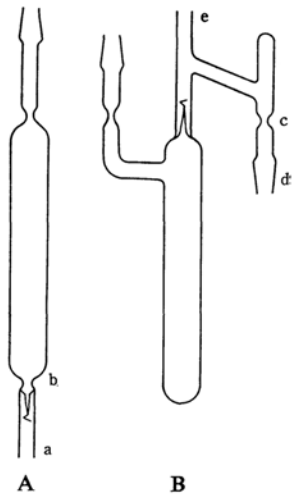


Fig. 1. Ampoules for grafting.

Experimental

Materials. — Polypropylene fiber, the product of Avisun (3—4 deniers), extracted with acetone for six hours in a Soxhlet apparatus.

Polyvinyl chloride fiber, the product of the Teijin Co. (3—4 deniers), was wound on an aluminum plate and extracted with benzene for an hour, and then with acetonitrile for an additional hour in a Soxlet apparatus.

Glycidyl methacrylate (GMA) was purified by distillation under reduced pressure through a column with copper McMahon packing.

Tetrahydrofuran was washed with a mixture of ferrous sulfate and concentrated sulfuric acid in order to remove peroxides, and then distilled.

The other solvents were purified by the usual methods.

Graft Copolymerization.—Graft copolymerization was carried out in the sealed-glass apparatus[4] shown in Fig. 1. Tube A, which contained the fiber, was evacuated at 10^{-3} mmHg for eitht hours, sealed, and then irradiated by γ-ray from 4000 curie ^{60}Co at room temperature. Tube B, which contained a monomer solution, was degassed and sealed. The irradiated tube A was connected to B through a and e, evacuated to 10^{-3} mmHg through d, and sealed at f. The monomer in B was transferred into A by breaking two breakable joints, and then the system was sealed at b and placed in a constant temperature bath for a definite time. The grafted fiber was separated from the system, washed with acetone (in the case of polypropylene) or with acetonitrile (polyvinyl chloride) by means of a Soxhlet apparatus, and dried in vacuo. The grafting ratio was expressed by the ratio of the weight gain to the initial weight.

The Measurement of the Dye Exhaustion.—The fiber was treated in a dyeing bath at 90°C for 60 min. (in the case of polypropylene) or at 60°C for 100 min. (polyvinyl chloride). The extent of dye exhaustion was measured by a spectrophotometer. The dyes used were Direct Sky Blue FF and Benzopurprine 4B (direct dyes), and Acid Orange II, and Acid Brilliant Scarlet 3R (acid dyes). The composition of the dyeing bath was as follows:

For direct dye: 0.02 parts of dye, 0.02 parts of sulfuric acid, 0.04 parts of anhydrous sodium sulfate and 50 parts of water.

For acid dye: 0.02 parts of acid dye, 0.02 parts of acetic acid and 50 parts of water.

One part of the grafted fiber was used for the dyeing bath prepared above.

1) Y. Iwakura, T. Kurosaki and N. Nakabayashi, *Makromol, Chem.*, **44/46**, 570 (1961).
2) Y. Iwakura, T. Kurosaki, K. Uno and Y. Imai, *J. Polymer Sci.*, **4C**, 673 (1961).
3) Y. Iwakura and N. Nakabayashi, *Makromol. Chem.*, will be published.
4) M. Miura and S. Kawamatsu, *Kobunshi Kagaku*, **19**, 175 (1962).

The Determination of the Epoxy Value.—The epoxide value of the grafted fiber was determined by the HCl-Dioxane method.[5] A portion of approximately 100 mg. of grafted PVC fiber was immersed in a solution of 25 ml. of dioxane and 20 ml. of 0.1 N hydrochloric acid - dioxane. The mixture was then allowed to stand overnight, and the excess hydrochloric acid was treated with 0.1 N sodium hydroxide aqueous solution, using phenolphtalein as an indicator.

Results and Discussion

The Graft Copolymerization of Glycidyl Methacrylate to Polypropylene. — When the polypropylene fiber irradiated at dose of 5 Mr. was immersed in undiluted GMA at 30°C, the monomer polymerized into a jelly state. The homopolymer producted was insoluble in acetone and dioxane, which are good solvents for polyglycidyl methacrylate. The cross linking of the homopolymer was prevented by adding a solvent, such as acetone, ethyl acetate, tetrahydrofuran or benzene, in the graft polymerization. The Influence of the solvent on the grafting ratio is given Fig. 2. A solvent such

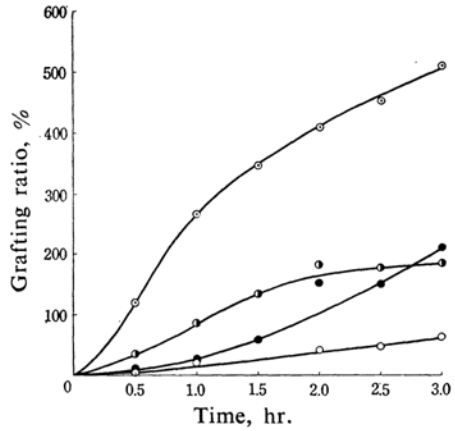


Fig. 2. Influence of solvent on the grafting ratio at the graft polymerization of GMA to polypropylene at 30°C.
Irradiation dose 5 Mr., dose rate 2.7×10^5 r./hr., monomer concentration 20 wt. %

○ Acetone ● Ethylacetate
◑ Tetrahydrofuran ⊙ Benzene

as ethyl acetate or acetone gave a slow initial grafting rate, while benzene gave a higher one. The former two solvents cannot swell as polypropylene fiber, but the latter one can swell the fiber. Figures 3 and 4 show the relation between the grafting ratio and the monomer concentration in benzene or tetrahydrofuran. On all occasions, the addition of a small amount of solvent to GMA increased the

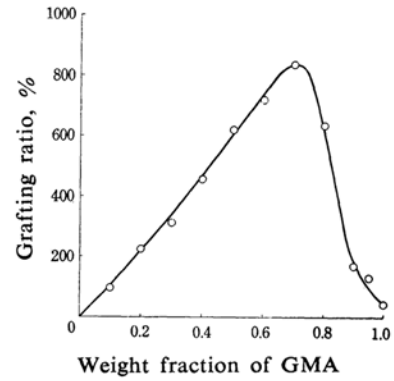


Fig. 3. Influence of monomer concentration on the grafting ratio at the graft polymerization of GMA to polypropylene in benzene.
Irradiation dose 5 Mr., dose rate 2.7×10^5 r./hr., grafting temperature 30°C, reaction time 1 hr.

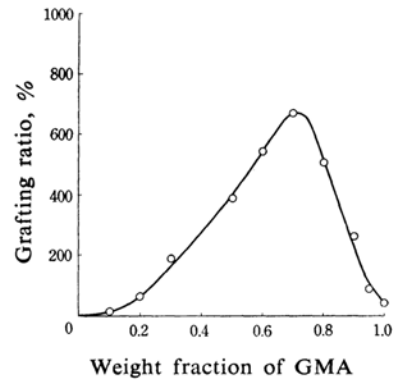


Fig. 4. Influence of monomer concentration on the grafting ratio at the graft polymerization of GMA to polypropylene in tetrahydrofuran.
Irradiation dose 5 Mr., dose rate 2.7×10^5 r./hr., grafting temperature 30°C, reaction time 1 hr.

grafting ratio. The effect of the solvent can be explained by assuming that the monomer molecules could diffuse into the polymer swelled by the solvent.

The Graft Copolymerization of Glycidyl Methacrylate to Polyvinyl Chloride.—The graft copolymerization was carried out at 16°C in a 20 wt. % monomer solution, using benzene, acetone, *n*-hexane, carbon tetrachloride or ethanol as the solvent. It was found that no graft polymerization proceeded in a solvent, such as *n*-hexane, carbon tetrachloride or ethanol, which did not swell the polyvinyl chloride. On the other hand, the graft polymerization did proceed in benzene or acetonitrile. The influence of the temperature on the grafting in benzene is shown in Fig. 6.

5) G. P. King, *Nature*, **164**, 706 (1964).

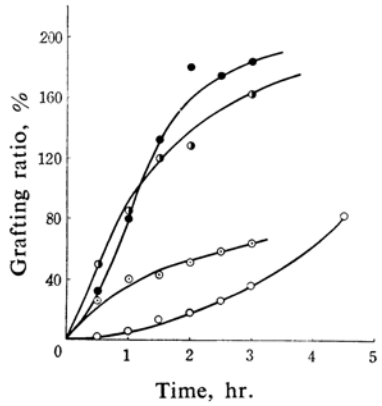


Fig. 5. Influence of temperature on the grafting ratio at the graft polymerization of GMA to polypropylene.
Irradiation dose 5 Mr., dose rate 2.7×10^5 r./hr., solvent tetrahydrofuran, monomer concentration 20 wt. %
○ 15.5°C ● 30°C ◑ 45°C ⊙ 60°C

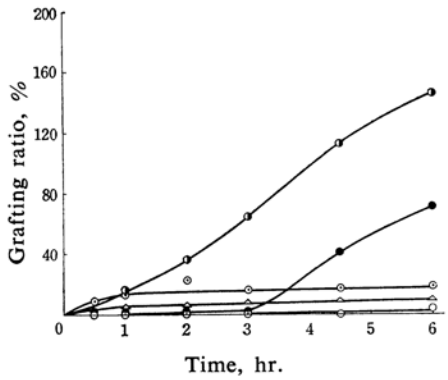


Fig. 6. Influence of temperature on the grafting ratio at the graft polymerization of GMA to polyvinyl chloride in benzene.
Irradiation dose 1.5 Mr., dose rate 7.8×10^4 r./hr, monomer concentration 20 wt. %
○ 5°C ● 8.5°C ◑ 16°C ⊙ 26°C △ 35°C

The optimum temperature for grafting is in a range from 10 to 20°C. Figure 5 shows the influence of the grafting temperature on the grafting ratio when tetrahydrofuran was used as solvent. The preferred temperature range for grafting was 30—45°C. At a temperature lower than 30—45°C, the initial grafting rate decreased because of the slow diffusion of the monomer molecules into the polymer. At a temperature higher than 30—45°C, the termination and the recombination of the trapped free radicals predominated the propagation and the grafting ratio was saturated, as is shown in Fig. 5.

Comparing polypropylene with polyvinyl chloride, the difference in the optimum temperature range for grafting may be explained as follows. In the case of polypropylene, the intermolecular forces in the crystalline regions are strong enough to keep the crystalline state up to a comparatively high temperature, even in the presence of a solvent. In the case of polyvinyl chroride, however, the intermolecular forces at the crystallline region become weak when the monomers diffuse into the amorphous region and the trapped free radicals recombine easily.

The temperature dependency on the grafting rate in acetonitrile is shown in Fig. 7. The grafting rate decreased in a temperature range from 8.5 to 52°C. Figure 8 shows the influence of the monomer concentration on the

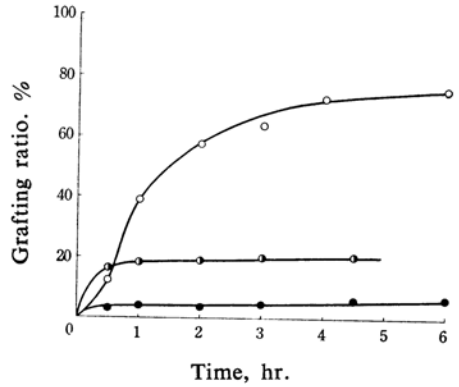


Fig. 7. Influence of temperature on the grafting ratio at the graft polymerization of GMA to polyvinyl chloride in acetonitrile.
Irradiation dose 1.9 Mr., dose rate 7.8×10^4 r./hr., monomer concentration 20 wt. %
○ 8.5°C ◑ 16°C ● 25°C

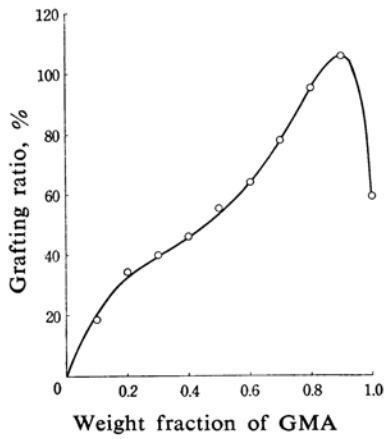
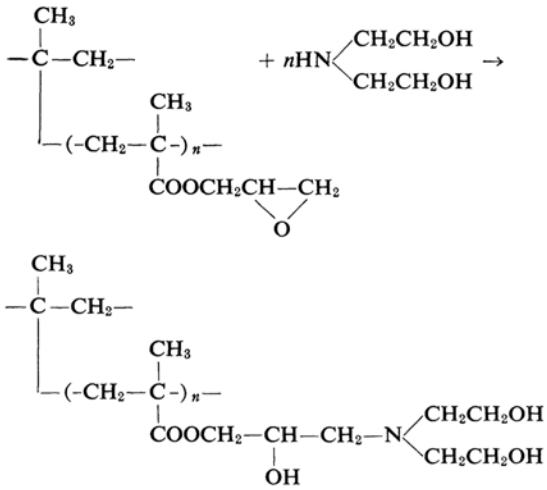


Fig. 8. Influence of monomer concentration on the grafting ratio at the graft polymerization of GMA to polyvinyl chloride at 16°C in benzene.
Irradiation dose 1.9 Mr., dose rate 7.8×10^4 r./hr., reaction time 2 hr.

grafting in benzene. The addition of a small amount of solvent to the monomer increased the grafting ratio, as in the case of polypropylene.

The Reaction of Grafted Polypropylene with Polyhydroxyamines and the Dyeability of the Resultant Polymer. — The epoxide groups are reactive with various reagents, such as amines,[6] acids,[7] phenols,[8] etc. Here, the reaction was investigated with polyhydroxyamine. The polypropylene fibers with a grafting ratio of 40.1% or 76.1% were refluxed in an acetone solution containing a 20 wt. % of diethanolamine.



The extent of the reaction of amine with the epoxide group in the grafted polymer was calculated from the nitrogen values by the Kjeldahl method. As can be seen from Fig. 9, the reaction of the epoxide group with the amine proceeds quantitatively, regardless of the grafting ratio. It has been known that such bases as pyridine catalyze the reaction of epoxide and amine. In this paper, 2.5 mol. % of pyridine was added to the solution of diethanolamine. However, the effect of pyridine was not noticeable, as Fig. 9 shows. Figure 10 shows the infrared absorption spectra of the GMA grafted polypropylene film and of the grafted film treated with diethanolamine.

The grafted polypropylene showed the absorption characteristic of epoxide group at 910 cm^{-1}, but not the absorption around 3500 cm^{-1} characteristic of the hydroxyl group. After it had been treated with diethanolamine, a hydroxyl absorption appeared at 3300 cm^{-1} and the absorption at 910 cm^{-1} disappeared. This indicates the ring opening of the epoxide group.

6) L. Smith, *Kgl. Frusiograf Lund Handl.*, **42**, 1 (1946).
7) M. Imoto, T. Kishida and K. Kho, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*) **56**, 807 (1953).
8) V. Bradley, *J. Chem. Soc.*, **1951**, 1589.

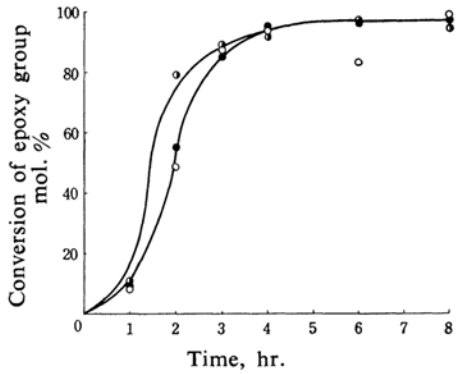


Fig. 9. Reaction of GMA-grafted polypropylene and diethanolamine at 62°C in acetone. Amine concentration 20 wt. %

○ Grafting ratio 40.1%
● Grafting ratio 76.1%
◑ 2.5 mol. % of pyridine was added to amine, grafting ratio 76.1%

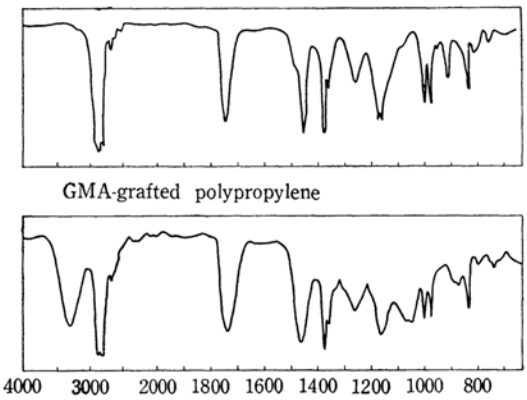


Fig. 10. Infrared absorption spectra of GMA-grafted polypropylene, grafting ratio 25%.

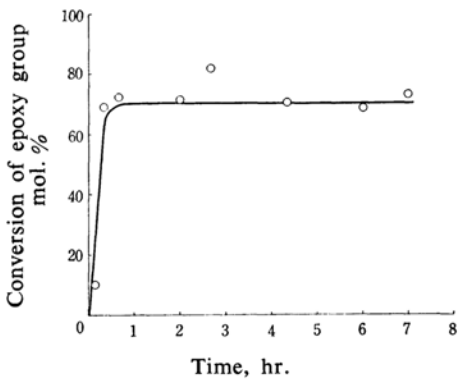


Fig. 11. Reaction of GMA-grafted polypropylene and methylglucamine in dioxane at 100°C.
Grafting ratio 64.7%, methylglucamine concentration 4 wt. %

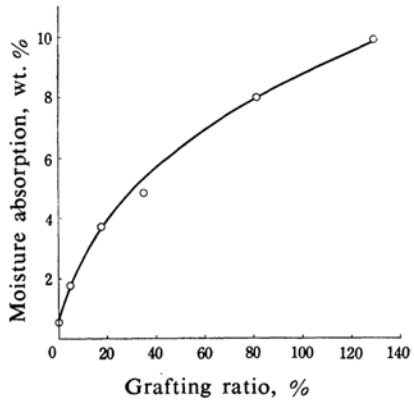


Fig. 12. Moisture absorption of GMA-grafted polypropylene treated with diethanolamine. Amine treatment was carried out for 5 hr. at the same condition as in Fig. 9, relative humidity 60%.

The reaction of methyl gulcamine with the grafted polypropylene fiber was also examined. The grafted polymer was treated with 4 wt. % of methyl glucamine in dioxane at 100°C. The conversion of epoxide groups was 70%, as is shown in Fig. 11.

The moisture absorption of the grafted fiber treated with diethanolamine is given in Fig. 12. The moisture absorption of the polypropylene fiber was increased by grafting. The dyeability of the polypropylene fiber was improved remarkably by treating the grafted fiber with polyhydroxyamine. The results are summarized in Table I.

TABLE I. DYEABILITY OF GMA-GRAFTED POLYPROPYLENE FIBER TREATED WITH POLYOXYAMINES

Grafting ratio, %	Amine	Dyeability	
		Direct dye	Acidic dye
12	Methyl glucamine	+++	++
12	Diethanolamine	++	++
23	Diethanolamine	++	+++
100	Diethanolamine	+++	+++

+++ 100% of dye was absorbed in fiber.
++ More than 50% was absorbed.
+ Less than 50% was absorbed.
Conentration of dye 0.04%, weight ratio of dyestuff to fiber grafted.

The fiber of grafting ratio of 12% had a good dyeability by direct dyes after treatment with methyl glucamine. The diethanolamine-treated fiber of 23% grafted polypropylene showed encough dyeability to acid dyes.

The Reaction of the Grafted Polyvinyl Chloride with Amines. — The epoxide values of GMA-grafted polyvinyl chloride were determined by the HCl-dioxane method. The results are shown in Table II. The epoxide values obtained were more than 90% of the epoxide values calculated from the grafting ratio.

The amine treatment was carried out in a mixture of water and acetone (water 60, acetone 40). The results of the diethanolamine treatment are shown in Fig. 13. The extent of the reaction was 60% for epoxide groups. The addition of pyridine increased the initial grafting rate, but it had no influence on the ultimate conversion. Figure 14 shows the reaction of aniline with the grafted polymer.

Both the reaction rate and the ultimate conversion were lower in the case of aniline than in the case of diethanolamine.

The polyvinyl chloride fiber grafted with GMA were gradually discolored from yellow to brown during treatment with an aliphatic amine such as diethylamine or diethanolamine. Table III shows the nitrogen and chlorine values of the ungrafted PVC fiber treated with

TABLE II. AMOUNT OF EPOXY GROUP IN GMA-GRAFTED POLYVINYL CHLORIDE

Grafting ratio	Amount of epoxy group $\times 10^3$ mol./g.	
	from grafting ratio	from analysis*
20.2	0.7	0.6
50.1	1.5	1.3
68.3	2.0	1.9
105.7	3.1	2.9

* Analysis for epoxy groups were performed by the HCl-dioxane method.

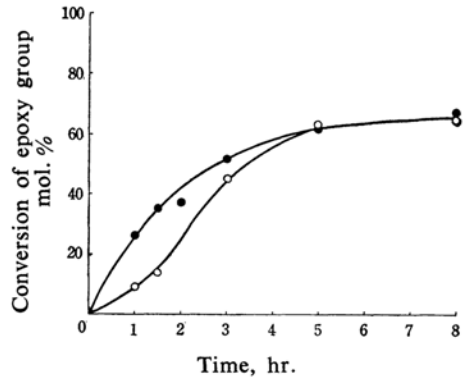


Fig. 13. Reaction of GMA-grafted polyvinyl chloride and diethanolamine at 50°C. Grafting ratio 58.2%, solvent (water 40: acetone 60, wt. ratio), amine concentration 2 mol./l.

○ Without pyridine
● With 0.4 mol./l. pyridine

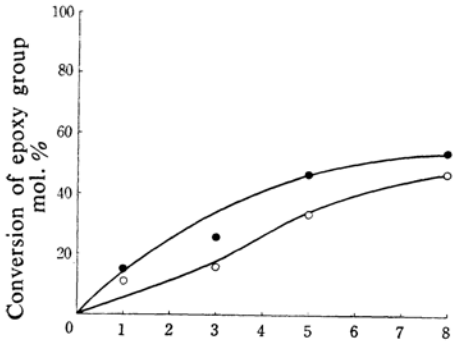


Fig. 14. Reaction of GMA-grafted polyvinyl chloride and aniline at 50°C.
Grafting ratio 64.7%, solvent (water 40: acetone 60, wt. ratio), amine concentration 2 mol./l.
○ Without pyridine
● With 0.4 mol./l. pyridine

TABLE III. CHLORINE AND NITROGEN PERCENT OF POLYVINYL CHLORIDE (UNGRAFTED) AFTER THE TREATMENT WITH AMINES

Amine	Cl, %	N, %
No treatment	56.43	0
Diethanolamine	53.31	0.27
Diethylamine	53.09	0.31

diethylamine or diethanolamine at 50°C. The chlorine values decreased with the treatment, while the nitrogen values increased. Therefore, the substitution of chlorine in polyvinyl chloride with amines seems to occur.

The extent of dye exhaustion was measured using 10% grafted fiber which had been treated with diethanolamine for five hours. The dyes were almost 100% exhausted into the fiber.

Summary

The graft polymerization of glycidyl methacrylate onto polypropylene or polyvinyl chloride fiber has been carried out by the technique of γ-ray pre-irradiation in vacuo, and the reactions of the grafted fiber with amines have been investigated. In the case of polypropylene, the addition of benzene or tetrahydrofuran to the monomer remarkably increases the grafting rate.

The initial grafting rate is slow in acetone or ethylacetate. The epoxide groups of the grafted polypropylene react with diethanolamine quantitatively, but with methyl glucamine partially, with a yield of 70%. In the case of polyvinyl chloride, benzene or acetonitrile is suitable as a grafting solvent. Graft polymerization proceeds in a narrow range of temperature from 10 to 20°C. Diethanolamine or aniline reacts with yields of 50—60% with the epoxide groups of the grafted polyvinyl chloride. Polyhydroxyamine-treated graft fibers have a good dyeability to both direct and acid dyes.

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