Chemical Structure of Cellulose-Styrene Graft Copolymer

Yoshito IKADA, Yasuko NISHIZAKI and Ichiro SAKURADA*

Received December 28, 1971

The chemical structure was determined of a cellulose-styrene graft copolymer prepared by a mutual irradiation method. The grafting was carried out by irradiation with gamma rays of cellulose fibers immersed in monomer solution. The graft fibers were extracted with benzene to remove homopolystyrene and the apparent graft was then acetylated. To remove ungrafted cellulose in the form of cellulose triacetate from the apparent graft, the acetylated product was dissolved in methylene chloride followed by addition of methanol till all the graft copolymer and the remaining homopolystyrene were precipitated leaving cellulose triacetate in solution. Finally the homopolystyrene present in the precipitate was extracted. To separate branches from the graft copolymer, it was hydrolysed. Molecular weights of the graft copolymer and the branch were determined osmometrically.

It was found that the apparent and true percent grafts were 44.0% and 11.0%, re spectively. Only 4.95% of cellulose participated in the grafting. Each graft copolymer molecule carried one branch on the average.

INTRODUCTION

Graft polymerization onto cellulose has been the subject of numerous investigations, and some reviews in this field are available in the literatures.[1,2] Grafting, especially radiation-induced grafting is often carried out in a heterogeneous system. The product is separated after the reaction and extracted thoroughly with a solvent for the homopolymer of the graft side chain. Percent weight increase is conventionally called "percent graft". But everyone has a question whether all nongrafted homopolymers are really extracted or not. It is possible that a part of the homopolymer formed in the matrix of the substrate polymer is occluded in a state that the extraction is hindered, for example, by entanglement of the homopolymer with the substrate polymer.

It is expected that some more homopolymer will be extracted, if we extract the unreacted substrate polymer after extraction of the homopolymer. By continuing such an alternate extraction until no more homopolymer and substrate polymer can be extracted, it is able to obtain true graft copolymer. Stannett and co-workers[3] have carried out such an experiment with cellulose acetate/ styrene, and showed the alternate extraction method to be adequate for the analysis of grafting reaction products. In the case of solution grafting of styrene onto cellulose acetate by a simultaneous irradiation method, they have succeeded to isolate true graft copolymers. The products at 10 Mrads consisted of approximately one grafted polystyrene chain per cellulose acetate molecule. In the case

* 筏　義人, 西崎　靖子, 桜田　一郎 : Department of Polymer Chemistry, Kyoto University Kyoto, Japan.

of heterogeneous grafting onto cellulose no such clear result has yet been obtained.

It was pointed out by Stannett that the cellulose graft copolymers have two advantages from the point of view of composition studies: (1) the solubility difference between the cellulosic backbone and the grafted side chain polymer is sufficiently great to enable adequate separation to be made; (2) the cellulosic backbone can be hydrolysed away, thus enabling the molecular weight of the grafted side chains to be measured. Besides similar advantages as to cellulose, polyvinyl alcohol(PVA) has further advantages that the backbone is easily soluble in water and chemically more stable than cellulose.

We have been engaged in the study of grafting of methyl methacrylate onto PVA as a model substance of cellulose and succeeded to isolate true graft copolymers of PVA/methyl methacrylate. Osmometric molecular weight determination was carried out of these true graft copolymers and number of branches contained in one graft copolymer was calculated.[4]

In the present paper new experimental results on the grafting of styrene onto cellulose will be reported and discussed.

<div align="center">EXPERIMENTAL</div>

a. Preparation of Graft Copolymer

Graft copolymers of polystyrene onto cellulose was prepared by a simultaneous irradiation technique with gamma rays from a Co-60 source. High tenacity rayon $(\bar{P}_v=293)$ was employed as cellulose; the grafting method consisted of placing rayon in the bottom of a small reaction tube, adding a monomer mixture of styrene-methanol-water (20:72:8 by vol.) and carbon tetrachloride (5 mole % to styrene), degassing by freeze-thaw method, and finally sealing off the tube while under vacuum. The irradiation was carried out at 50°C for 20 hr at a dose rate of 1.0×10^4 r/hr.

For isolation of the apparent graft, the reaction product was treated with a large amount of benzene at room temperature to remove homopolystyrene formed in the solution, then washed with water and finally extracted with boiling benzene to obtain the apparent graft. The weight increase after the extraction in percent of the weight of starting cellulose fiber is designated to be apparent percent graft.

b. Acetylation of Cellulose

In order to make easier the separation of unreacted cellulose from the apparent graft, it was acetylated under nondegradative conditions in acetic anhydride-pyridine mixtures. The apparent graft was first soaked in methanol, methanol was replaced by water, and then acetylated with 1:2 acetic anhydride-pyridine mixture for 36 hr at 100°C. After the reaction, the product was precipitated with n-hexane. The precipitate was redissolved in chloroform-methanol and reprecipitated with methanol. The reprecipitation was repeated and finally a purified acetylated product was obtained. When pure cellulose was used for acetylation, it was confirmed that by this procedure cellulose is converted

practically to 100 % (98.5–99.6 %) to triacetate.

c. Isolation of True Graft

It was at first intended to remove remaining homopolystyrene and unreacted cellulose (in the form of triacetate) by alternate extractions with benzene and 1 : 1 methylene chloride-methanol mixture, but it was not successful. Therefore a fractional precipitation method was adopted. The acetylated apparent graft was dissolved in a methylene chloride-methanol mixture (80 : 20 by vol.). Methanol was very slowly added to the solution to precipitate homopolystyrene and true graft copolymer. Dissolution in the methylene chloride-methanol mixture and precipitation with methanol were repeated four times. The final solution contained 45.0–46.3 % methanol.

The above precipitate was extracted with boiling benzene to remove homopolystyrene and finally true graft copolymer was isolated.

d. Separation of Graft Branch

The acetylated true graft copolymer was dissolved in methylene chloride, acetone was added to the solution to obtain 1 : 1 methylene chloride-acetone composition of the solvent, concentrated hydrochloric acid was added to obtain $3 N$ solution and hydrolysis was carried out for 72 hr at 60°C. The hydrolysis proceeded not in a homogeneous but in a highly swollen state. The branch was precipitated by pouring the hydrolysis mixture into methanol. A part of the precipitated branch was dissolved in m-cresol, and filtered. The other part was treated with 1 : 2 acetic anhydride-pyridine mixture for 15 hr at 100°C to acetylate cellulose fragments at the end of polystyrene branches.

e. Molecular Weight Determination

Molecular weight determination of the acetylated true graft copolymer, separated branch after acetylation and acetylated mother cellulose was carried out with High-Speed Membrane Osmometer (Type 502) using chloroform, benzene and chloroform, respectively, as solvents.

f. Chemical Composition of the True Graft Copolymer

Chemical composition of the acetylated graft copolymer was determined by saponification of acetyl groups by $N/20$ NaOH in methanol-H_2O (1 : 1) for 24 hr at 30°C. Residual NaOH was back-titrated using hydrochloric acid.

<div align="center">RESULTS AND DISCUSSION</div>

a. Grafting of Styrene onto Cellulose

The material balance in the course of grafting, separation of the apparent graft, acetylation and isolation of the true graft is shown in Table 1.

Starting from 4.910 g cellulose, 10.666 g acetylated apparent graft copolymer were obtained; when we assume that cellulose is fully converted to triacetate and recovered in the acetylated apparent graft, the calculated weight of the acetylated apparent graft is 10.930 g. The agreement is satisfactory when we

Chemical Structure of Cellulose-Styrene Graft Copolymer

Table 1. Material Balance in the Isolation of True Graft Copolymer of Cellulose.

		Amount in g
Starting cellulose		4.910
Homopolystyrene		7.166
formed out of cellulose	(6.427)	
extracted with boiling benzene	(0.739)	
Apparent graft copolymer		7.070
Acetylated apparent graft copolymer		10.666*
HomoPSt extracted after acetylation	1.520	
Isolated cellulose triacetate	7.517	
Isolated true graft copolymer (acetylated)	0.978	
Loss in the processing	0.651	
Sum of the above figures	10.666	

  * Calculated amount is 10.930 g.

assume a loss of 0.264 g in the separation of the acetylated apparent graft co-polymer. The total loss in the course of the isolation of true graft copolymer was 0.651 g.

Table 2 shows experimental result together with that of grafting in the absence of carbon tetrachloride. It may be seen that the monomer conversion and the apparent percent graft are remarkably decreased by the presence of carbon tetrachloride. Viscosity average degree of polymerization, $\bar{P}_v$, of homo-polystyrene formed in the matrix shows also a much lower value when the reaction is carried out in the presence of carbon tetrachloride. Therefore it is expected that the branch and backbone of the graft copolymers obtained in the presence of carbon tetrachloride will have a balanced length.

The fraction of grafted cellulose was calculated from the composition and the amount of the true graft copolymer. True percent graft is defined as follows:

Table 2. Grafting of Styrene onto Cellulose by Simultaneous Irradiation Method. Cellulose: High tenacity rayon ($\bar{P}_v=293$); Monomer mixture: St: MeOH: $H_2O=$ 20:72:8; Polymerization: 50°C, in vacuum, 20 hr (2×10^5 r).

		[CCl₄]/[St] (mole ratio)	
		0.05	0
Total conversion of monomer	(%)	34.3	95
Apparent percent graft	(%)	44.0	181
True ,,	(%)	11.1	——
Apparent graft efficiency	(%)	25.2	37.7
True ,,	(%)	6.36	——
Wt. fraction of CTA[a] in acetylated graft copolymer	(%)	44.2	——
Fraction of reacted cellulose	(%)	4.95	——
$\bar{M}_v$ of homopolystyrene formed in matrix		1.5×10^5	13.2×10^5

[a] cellulose triacetate.

$$\text{true percent graft} = \frac{\text{wt. of branch after complete extraction}}{\text{wt. of starting cellulose}} \times 100 \qquad (1)$$

As can be seen from Table 2, true percent graft and fraction of cellulose grafted were found to be 11.1 % and 0.0495, respectively.

b. Chemical Structure of the True Graft Copolymer

Results of osmotic pressure measurements are given in Fig. 1. It may be seen that osmotic behavior of the acetylated graft copolymer is quite normal.

As shown in Table 3, the number average molecular weight of the acetylated true graft copolymer, separated branch after acetylation and acetylated mother cellulose were 306,000, 187,000 and 72,400, respectively. Benzene solution of homo-polystyrene formed in the matrix of cellulose exhibited $\bar{M}_n$ of 195,000 which
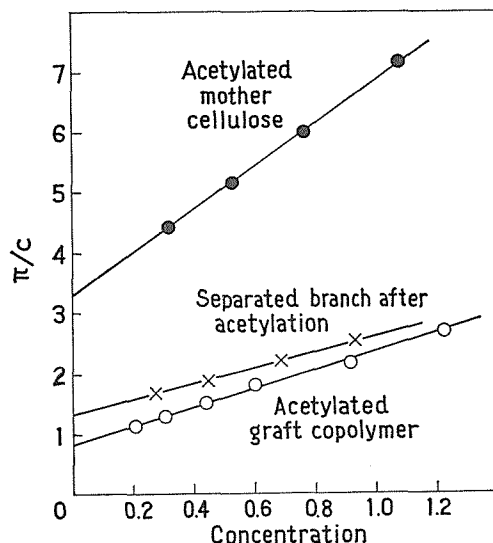

Fig. 1. Osmometry of graft copolymer, mother cellulose and separated branch.

Table 3. Molecular Weight and Chemical Structure of Acetylated Graft Copolymer.

a. *Molecular weight*

	Solvent	temp.	$\bar{M}_n$
Acetylated true graft copolymer	Chloroform	30°C	306,000
Separated branch after acetylation	Benzene	30°C	187,000
Acetylated mother cellulose	Chloroform	30°C	72,400

b. *Composition*

Composition of acetylated true graft copolymer Styrene : Triacetate=0.558 : 0.442	
Molecular weight of polystyrene part	171,000
Molecular weight of triacetate part	135,000

c. *Structure*

Number of branch in one graft copolymer	0.915

agrees practically with $\bar{M}_n$ of the separated branch. Benzene solution of the separated branch was slightly turbid before acetylation and gave a molecular weight of 236,000. IR-spectrum of the separated branch before acetylation exhibited absorptions near the wave number of 3,400 cm^{-1}, which were probably due to OH-groups. Therefore a slightly higher molecular weight of the separated branch before acetylation may be attributed to partial association in benzene.

The determination of chemical composition of the acetylated graft copolymer showed that the graft copolymer consisted of 0.558 parts of polystyrene and 0.442 parts of triacetate by weight. Thus, the number of branch per one graft copolymer molecule can be calculated with the following equation:

$$\text{number of branch} = \frac{\bar{M}_n \text{ of PSt part in acetylated graft copolymer}}{\bar{M}_n \text{ of separated branch}}$$

$$= \frac{\left(\begin{array}{c} \bar{M}_n \text{ of graft} \\ \text{copolymer} \end{array}\right) \times \left(\begin{array}{c} \text{wt. fraction of PSt part} \\ \text{of graft copolymer} \end{array}\right)}{\bar{M}_n \text{ of separated branch}} \qquad (2)$$

Calculated number of branch per one graft copolymer is shown in Table 3. It may be seen from the table that the number of branch is approximately one.

It is interesting to point out that the molecular weight of acetylated backbone part (A) is 135,000, whereas that of acetylated mother cellulose (B) is 72,400, the A/B ratio being 1.87. Some discussion seems to be necessary to interpret the results in detail. The average molecular weight of branch in Table 3 is a value which was actually found by osmometry of the separated branch, and the number of branch is nearly 1±0.1. This is quite reasonable, when we take into account some experimental errors.

Concerning the average molecular weight of the backbone, it is not a value actually determined. If the molecular weight distribution of the mother polymer is homogeneous, the molecular weight of the backbone should be equal to that of the mother polymer, because degradation of cellulose in the course of the grafting can be regarded as negligible. In most cases polymer has molecular weight distribution; if such polymer is subjected to grafting, n-times longer molecule has n-times greater chance to be grafted. Therefore, $\bar{M}_n$ of backbone cellulose in the graft copolymer is expected to be greater than that of the mother cellulose, because only a small fraction of cellulose really participates in the grafting, as seen in Table 2.

When the mother polymer has most probable distribution of degree of polymerization, we can calculate the number average degree of polymerization of the backbone polymer, $\bar{P}_n$ with the following equation:

$$\bar{P}_n = \frac{2\bar{P}_0}{1 + \bar{P}_0 \alpha} \qquad (3)$$

where $\bar{P}_0$ is the number average degree of polymerization of the mother polymer, and α the probability of monomer unit to have been grafted. The order of magnitude of α is 10^{-3} and that of $\bar{P}_0$ is 10^2 in the present case. Therefore it is expected for very small α that $\bar{P}_n \doteqdot 2\bar{P}_0$. In the case of grafting of styrene onto nylon it was found that the experimental result agreed with the theoretical ex-

pectation.[5]

The A/B value of 1.87 may be also interpreted in the present case as to indicate that cellulose molecules of higher molecular weight are preferrably grafted from statistic reason. It is scarcely possible that crosslinking of cellulose molecules has taken place during the reaction and it is also improbable that termination by coupling of growing side chains has occurred to a noticable extent in the presence of a large amount of a chain transfer agent. The most probable conclusion is that the graft copolymer has one backbone cellulose molecule of which the number average molecular weight is 1.87 times that of the mother cellulose molecule.

REFERENCES

(1) E. H. Immergut, in Encyclopedia of Polymer Sci. and Technol., Vol. 3, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., p. 242, New York, Interscience Publishers, 1965.

(2) S. M. Atlas and H. Mark, *Cellulose Chem. and Technol.*, **13**, 325 (1969).

(3) H. Yasuda, J. A. Wray, and V. Stannett, *J. Polymer Sci.*, C2, 387 (1963) ; V. Stannett, J. D. Wellons, and H. Yasuda, *J. Polymer Sci.*, C4 551 (1963) ; J. D. Wellons and V. Stannett, *J. Polymer Sci.*, A3, 847 (1965).

(4) I. Sakurada, S. Matsuzawa, and Y. Kubota, *Makromol. Chem.*, **69**, 115 (1963) ; I. Sakurada, Y. Ikada, and Y. Uesaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 49 (1969) ; I. Sakurada, Y. IKada, H. Uehara, Y. Nishizaki, and F. Horii, *Makromol. Chem.*, **139**, 183 (1970).

(5) To be published.