Characterization of Products Prepared by Homogeneous Grafting of Styrene onto Cellulose in a Sulfur Dioxide–Diethylamine–Dimethyl Sulfoxide Medium*

MICHIKAZU TSUZUKI, IKUO HAGIWARA, NOBUO SHIRAISHI, and TOKUO YOKOTA, *Department of Wood Science and Technology, Faculty of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606, Japan*

Synopsis

Homogeneous graft copolymerization of styrene onto cellulose was carried out using a SO_2–DEA–DMSO cellulose solvent reaction medium and γ-ray mutual irradiation. The yield of grafted side chain polymer and the homopolymer in this reaction system proved to be polysulfone, a styrene–sulfur dioxide copolymer in which the number of sulfur atoms per polymer chain is 3–3.5. Several characterizations of the graft product were attempted. The graft products were extracted with boiling benzene for 24 hr to remove homopolymer, and then the cellulose backbones were hydrolyzed. After hydrolysis, the polysulfone residues were separated by thin-layer chromatography (TLC) into two components, i.e., attendant homopolysulfone and the true side chain polysulfone having some sugar residues at one of the polymer chain ends. The weight fraction of these components for each graft product was determined by a TLC scanner. The molecular weight of the side chain polysulfone remained constant and significantly lower than that of the homopolysulfone throughout the reaction period. By assuming that no scission of cellulose chains occurred throughout the graft reaction, the number of branches per starting cellulose molecule was assessed to be surprisingly large, ranging from 2.4 to 10.6 at a total dose of 1–8 mR of irradiation. It was also found that percent grafting increased with irradiation time because of an increase in the number of branches per cellulose chain. Furthermore, we succeeded in separating the graft product into ungrafted cellulose and the true graft copolymer containing a small amount of attendant hompolysulfone.

INTRODUCTION

In general, it is possible that graft products still contain a greater or lesser amount of homopolymers even after prolonged extraction with a homopolymer-specific solvent, because of the entanglement of the homopolymer with the substrate polymer, and so forth. In fact, by the use of the density-gradient ultracentrifugation technique, Ende and Stannett[1] have pointed out the inevitable difficulty in separating the attendant homopolymer from the graft product. Nevertheless, only a few articles have extended their discussions to this problem, the main reason being that the isolation of the graft copolymer is very difficult.

By repeating alternate extractions until the homopolymer and the ungrafted substrate polymer can no longer be detected in the extract, the true graft copolymer is obtainable. Yasuda et al.[2] have carried out such an experiment in a cellulose acetate–styrene system and have obtained the true graft copoly-

* Presented in part at the 29th Annual Meeting of the Japan Wood Research Society, 17 July 1979, Sapporo, Japan.

Journal of Applied Polymer Science, Vol. 25, 2909–2924 (1980)
© 1980 John Wiley & Sons, Inc.
0021-8995/80/0025-2909$01.60

mer. Sakurada et al.[3] also adopted this method in the analysis of poly(vinyl alcohol)–methyl methacrylate grafting results.

Recently, Inagaki et al.[4] investigated the separation of polymers by thin-layer chromatography (TLC). According to their findings, it is possible to separate copolymers on the basis of their chemical compositions and differences in their chain architecture, such as random, alternating and block structures which even appear on the same composition level.[5] More recently, Taga and Inagaki[6] have used TLC to characterize side chain polystyrenes in a cellulose–styrene copolymer. They applied TLC to separate the polystyrene residue obtained after hydrolysis of the graft product into two components, i.e., the attendant homopolystyrene and the sidechain polystyrene having certain sugar residues at one of the polymer chain ends. Min[7] adopted this technique to separately obtain the true cellulose–styrene graft copolymers and found new information concerning the graft copolymerization of styrene onto cellulose in a heterogeneous system.

In a previous article[8] we reported the graft copolymerization of styrene onto cellulose in a homogeneous system, using a sulfur dioxide (SO_2)–diethylamine (DEA)–dimethyl sulfoxide (DMSO) medium. When the graft products are recovered from the reaction solution using a precipitation technique, it is possible that homopolymers are taken up and that they contaminate the cellulose matrix. We adopted the TLC technique in order to resolve this problem. The present article deals with the separation of two types of polysulfones, i.e., the attendant homopolysulfones and the side-chain polysulfones which are formed by this homogeneous grafting. We also discuss the chemical structure of the graft copolymers.

EXPERIMENTAL

Grafting Procedure

Whatman cellulose powder CF-11 ($\bar{M}_n = 3.69 \times 10^4$) was used as a cellulose sample. Cellulose, 0.2 g, was placed in a 50-ml flask (Kjeldahl type, long neck) to which 20 ml DMSO with 4 mole SO_2–DEA equimolar complex per mole glucose unit was added. After the cellulose was dissolved thoroughly, purified styrene monomer was added to the flask. Freezing, degassing, and melting cycles were repeated three times, and then the flask was sealed. The graft copolymerization was carried out homogeneously throughout the reaction, by utilizing a high-energy irradiation method (mutual irradiation by ^{60}Co γ-ray). The dose rate was 1.0×10^5 R/hr.

After irradiation, the reaction solution was poured into an excess of cold methanol and the precipitate was filtered, dried, and weighed. Then the graft product was extracted with hot benzene for 24 hr to remove homopolysulfone. Apparent percent grafting (Y_a) was calculated according to eq. (1):

$$Y_a = \frac{\text{weight increase after extraction (g)}}{\text{weight of starting cellulose (g)}} \times 100 \quad (1)$$

Acid Hydrolysis

The graft product subjected to the extraction for 24 hr was hydrolyzed to isolate the side chain polysulfone. Hydrolysis was carried out according to the so-called Klason method by immersing the sample at 20°C in 72% H_2SO_4 for 4 hr; the reaction mixture was then diluted with water to an acid concentration of 3% and heated under reflux for 4 hr. The residue after hydrolysis was washed with methanol and dried. The polysulfone residue was purified by dissolving it in chloroform and precipitating it with methanol three times.

TLC Separation Procedure

TLC technique was used to separate the polysulfone residue into two components made up of the attendant homopolymer and the side-chain polymer. Thin layers with a thickness of 0.2 mm were prepared on 5 × 20 or 20 × 20 cm^2 glass plates using Kieselgel G (Merck A.G., Darmstadt, Germany). We also employed commercial TLC plates (DC-Fertigplatten Kieselgel 60, 20 × 20 cm^2, 0.25 mm thick) for TLC scanner measurement. The chromatoplate was developed with methanol, followed by activating it at 110°C for 1 hr just prior to use. Polymerization conditions and characterization of the homopolystyrene and polysulfones used as standard samples for TLC analysis are listed in Table I. The sample polymers were dissolved in chloroform, and 10 μg of the polymer was spotted on a thin layer with a microsyringe. Benzene, chloroform, methyl isobutyl ketone, tetrahydrofuran, methyl ethyl ketone, and acetone were used as developers. After development, the chromatoplate was dried and sprayed with 1% methanol solution of iodine in order to visualize the sample. We also used 18*N* sulfuric acid to stain the sample by heating it to 120°C.

For the quantification of the chromatogram by the use of TLC scanner, 0.4–3.0 μg of the polymer was deposited on a thin layer and methyl ethyl ketone was used as developer. The position of each initial spot is taken at 2 cm above one edge of the plate.

In order to collect the true side chain polysulfone, we employed the preparative TLC technique. Each stock solution of ~40 mg of the graft product obtained after hydrolysis was applied in a band form to a thin layer with a thickness of

TABLE I
Polymerization Conditions and Characterization of Homopolystyrenes Used as Standard Samples for TLC Analysis[f]

Sample code	Irradiation time, hr	SO_2-DEA conc.[d]	$\overline{M}_n \times 10^{-3}$	NSP[e]
P-PSt[a]	10	–	17.6	0
H-PSt-1[b]	80	4	7.6	3.4
H-PSt-2[c]	40	4	4.4	3.1

[a] Obtained as homopolystyrene polymerized in DMSO medium.

[b] Obtained as homopolysulfone polymerized in SO_2–DEA–DMSO medium without cellulose. Concentration of SO_2–DEA was the same as c.

[c] Obtained as homopolysulfone prepared by grafting styrene onto cellulose in a SO_2–DEA–DMSO medium.

[d] Per mole glucose unit.

[e] Number of sulfur atoms per polymer chain.

[f] Dose rate, 1.0 × 10^5 R/hr; styrene content, 33.3 vol%.

1.0 mm precoated on a glass plate of 20 × 20 cm^2. TLC separation was allowed to continue using methyl ethyl ketone as the developer for about 10 hr. After the development, we scraped off each portion of the silica gel layer which had adsorbed only one of the two components, either the side chain polysulfone or the attendant homopolysulfone, from the glass plate and then separately extracted both of the components from the silica gel with acetone or dioxane at room temperature for about 10 hr. The polymers were then purified three times by a precipitation technique using chloroform and methanol.

Identification and Quantification of the Side Chain Polysulfone

In order to identify and determine the two components quantitatively, we employed a Shimadzu TLC scanner model CS-900. The chromatogram was eluted with methanol up to 15–20 cm to remove any impurities involved in the stationary phase, in advance of the spectroscopic quantification. We adopted 215-nm wavelength light as the sample beam and scanned the chromatogram along the direction of TLC development.

Acetylation of Cellulose and Polysulfone Residue

Five milliliters trifluoroacetic anhydride, 2.5 ml acetic acid, and 20 ml chloroform were mixed together and left to stand at 50°C for about 20 min. This solution was added to 0.3 g cellulose or to the same amount of polysulfone residue obtained after acid hydrolysis. The reaction was continued for 7 hr for cellulose and 3 hr for the polysulfone residue. At the end of the reaction, the acetylation mixture was poured into an excess of methanol and the precipitate was filtered. The product was washed thoroughly with distilled water and then methanol and further purified by precipitation with chloroform–methanol.

Molecular Weight Determination

Shimadzu GPC 700 was used to determine the molecular weights of the side-chain polysulfone and the homopolysulfone. Seven columns packed with porous polystyrene gels having pore sizes of 10^2, 10^3, 10^4, 10^4, 10^5, 10^6, and 10^6 Å were used. The eluent was tetrahydrofuran, and the flow rate was approximately 1 ml/min. The molecular weights of the polymers were estimated with the aid of a calibration curve established from narrowly distributed polystyrene samples having known molecular weights.

The molecular weight of cellulose acetate was determined with a Knauel electronic membrane osmometer, from which the corresponding value for cellulose was calculated. The measurement was done at 25°C using chloroform (special reagent for spectrometric usage) as a solvent. Regenerated cellulose film was used as the membrane.

RESULTS AND DISCUSSION

Isolation of the Side Chain Polysulfone

All the generated polymers remaining in the substrate polymers after extraction with a solvent for the homopolyme were regarded as grafted polymers. However, it is possible that the homopolymer in the matrix is not extracted completely by the extraction procedure. In fact, by the use of density gradient ultracentrifugation, Ende and Stannett[1] have revealed the presence of homopolymer in the graft product after extraction. Yasuda et al.[2] and Ikada et al.[3] also pointed out this fact by an alternate extraction using one solvent for homopolymer and another for substrate polymer in a cellulose acetate–styrene and poly(vinyl alcohol)–methyl methacrylate system. By the use of TLC technique, Taga and Inagaki[6] separated the residue obtained after acid hydrolysis of a cellulose–styrene graft product into two components, i.e., the true side chain polystyrene and the attendant homopolystyrene generated in the cellulose matrix. The latter component migrates up to the solvent front on a silica gel support when tetrahydrofuran is used as the developing solvent, whereas the former component remains immobile, probably because of the interaction between hydroxyl groups of the sugar residue at one of the chain ends and active sites on the silica gel. Furthermore, Min et al.[9] examined a similar end group effect upon TLC polymer separation by using three types of polystyrenes with and without one or two carboxyl end groups as samples. It was concluded from their results that if a polymer possesses a polar group at one of the chain ends or at both ends, TLC separation owing to the difference in end or side groups is possible through a polarity-controlled adsorption mechanism, for polymers having molecular weights up to 10^5.

In our previous article[8] we found that a small quantity of sulfur dioxide combines with styrene to form a copolymer during the homogeneous graft copolymerization in a SO_2–DEA–DMSO medium. Though the content of sulfur atoms is very small, that is, 3.0–3.5 atoms per polymer chain having a molecular weight of 7000–8000, we hereafter call the yielded polymer polysulfone to distinguish it from pure polystyrene. Because of the relatively polar nature of the sulfonyl ($-SO_2-$) group, this polymer exhibits an end or side group effect comparable to that described above. Therefore, this polysulfone appears to display a different chromatographic behavior when compared with the pure polystyrene. There is, however, an uncertainty as to whether the side chain polysulfone having the sugar residue is successfully separated from the corresponding homopolymer by the use of TLC with tetrahydrofuran[6] or benzene.[7] Both solvents have been reported as being suitable developers for separation in pure polystyrene grafting cases.

At the beginning, we developed pure polystyrene and two types of polysulfones having molecular weights of 7600 and 4400, as shown in Table I, with solvents which have been reported to be effective developers.[10,11] The results that were obtained by iodine visualization are summarized in Table II. The pure polystyrene (P-PSt) migrated up to the solvent front along with all the developers. However, polystyrenes containing sulfonyl (polysulfone, H-PSt-1, H-PSt-2) also migrated up to the solvent front when tetrahydrofuran, methyl ethyl ketone, and acetone were used as developers. When benzene and chloroform were utilized as developers, however, the samples having sulfonyl remained immobile

TABLE II
Results for TLC Development with Single Solvent

Developer	ϵ^0 [d]	DC[e]	R_f P-PSt	R_f H-PSt-1	R_f H-PSt-2
Benzene	0.32	2.23	1	0	0
Chloroform	0.40	4.81	1	0	0
MBK[a]	0.43	14.75	1	0 and 1	0 and 1
THF[b]	0.45	7.42	1	1	1
MEK[c]	0.51	18.51	1	1	1
Acetone	0.56	20.70	1	1	1

[a] Methyl isobutyl ketone.
[b] Tetrahydrofuran.
[c] Methyl ethyl ketone.
[d] Solvent strength parameter ϵ^0 values for alumina are relative to the solvent n-pentane, for which ϵ^0 is defined equal to zero.
[e] Dielectric constant.

on the starting level. Furthermore, when methyl isobutyl ketone was used as a developer, polysulfones were separated into two components, having $R_f = 0$ and $R_f = 1$, respectively. However, the reason for this separation has not been elucidated. By the use of TLC scanner, the detection of polystyrene components on thin-layer plates becomes possible qualitatively as well as quantitatively.

The three samples were developed by various solvents and detected by TLC scanner. Figure 1 shows the results obtained by TLC scanner after development with methyl isobutyl ketone (A) and methyl ethyl ketone (B). By the former solvent polysulfone (H-PSt-2) was separated into two components, whereas by the latter solvent all polysulfone components were not separated but instead migrated up to the solvent front. These results are completely consistent with those in Table II, which reveal characteristics different from the known TLC results on the separation of the pure polystyrene. It can be concluded from Table II and Figure 1 that the introduction of sulfonyl, which has a much smaller polarity than that of carboxyl groups, into the polymer chain affects the TLC separation in a striking manner, that is, the introduced sulfonyl causes a specific end or side group effect.

Next, we examined whether the polysulfone residue obtained after hydrolysis

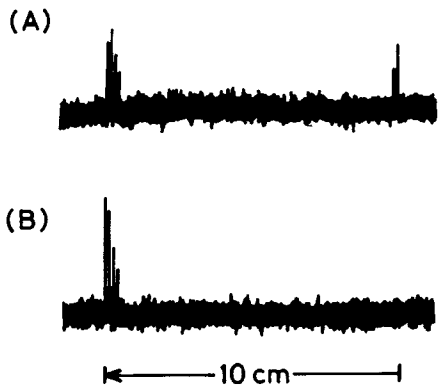

Fig. 1. Chromatograms detected by TLC UV scanning at 215 nm after development with methyl isobutyl ketone (A) and methyl ethyl ketone (B) as developers for homopolysulfone (H-PSt-2).

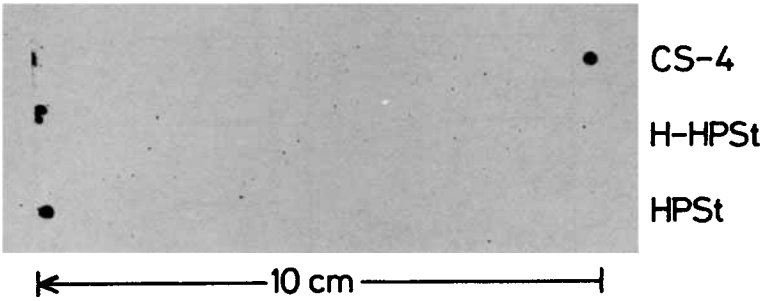

Fig. 2. TLC chromatogram obtained for homopolysulfone (HPSt), hydrolyzed homopolysulfone (H-HPSt), and a polysulfone residue derived after hydrolysis of a graft product (CS-4) using methyl ethyl ketone as developer.

of the graft product can be separated into the true side chain polysulfone and the attendant homopolysulfone as a result of the end group effect of sugar residue at one of the polymer ends. Homopolysulfone ($\overline{M}_n = 4.4 \times 10^3$, NSP = 3.1) was used as the reference sample. Hydrolyzed homopolysulfone was also used as the reference sample in order to investigate the influence of hydrolysis on the polymer. We employed methyl ethyl ketone as the developer. Figure 2 shows the TLC chromatogram thus obtained. Homopolysulfone (HPSt) and hydrolyzed homopolysulfone (H-HPSt) completely migrate up to the solvent front, while the polysulfone residue after hydrolysis of the graft product (CS-4) is separated into two components having $R_f = 0$ and $R_f = 1$, respectively, suggesting that the former component and the latter component are the true side chain polysulfone and the attendant homopolysulfone, respectively. Even though the development was allowed to continue using methyl ethyl ketone for a further 10 hr, the component having $R_f = 0$ remained immobile on the starting level. The IR spectrum of the hydrolyzed homopolysulfone was completely consistent with that of homopolysulfone, and its molecular weight did not change at all in comparison with the molecular weight of homopolysulfone before hydrolysis.

We further confirmed the existence of the polysulfone component in these chromatographic spots by TLC scanner. We detected the polysulfone component on both the solvent front and the starting level for the polysulfone residue after the development, as is shown in Figure 3. At the same time, we recognized the polysulfone only on the solvent front for homopolysulfone and hydrolyzed homopolysulfone after the development.

In order to collect the lower ($R_f = 0$) and the upper ($R_f = 1$) components separately in an amount suitable for following analyses, we employed the preparative TLC technique. The IR spectra taken for the polysulfone components separated by TLC are shown in Figure 4. The IR spectrum of the upper component proved

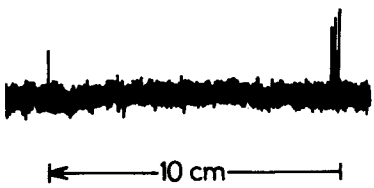

Fig. 3. Chromatogram obtained by TLC UV scanning at 215 nm after development utilizing methyl ethyl ketone as developer for polysulfone residue after hydrolysis (CS-4).

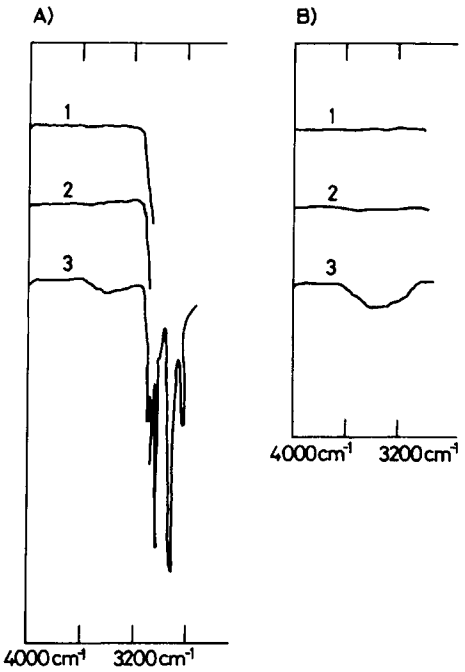

Fig. 4. IR spectra of homopolystyrene and the two components separated from the polysulfone residue derived after hydrolysis of the graft product, CS-4 (upper and lower components) by continuous running development for 10 hr with methyl ethyl ketone as developer. Spectra denoted 1, 2, and 3 are of homopolystyrene, upper component, and lower component, respectively.

to be in agreement with that of homopolystyrene in the frequency range of 4000–400 cm^{-1}, except for 1312 and 1126 cm^{-1} because of stretching vibrations of the S=O group. This confirms that the upper component is homopolysulfone. The IR spectrum of the lower component is slightly different from the spectra of the other polysulfones in the range of 4000–3000 cm^{-1}, as shown in Figure 4. That is, the IR spectrum of the lower component exhibits a broad absorption at around 3400 cm^{-1} which may be attributable to the stretching vibrations of the hydroxyl groups of the sugar residue at one of the polymer ends. This difference in absorbance is more evident among spectra obtained by the film method than those by the KBr disk method. Sakurada et al.[12] have also reported the same observation. However, we did not recognize the sharp peak due to free hydroxyl groups at 3620 cm^{-1} that was reported by Taga and Inagaki.[6]

The interaction between acetyl groups and active sites on silica gel is much weaker than that between hydroxyl groups and active sites on silica gel. If the hydroxyl groups of the sugar residue are changed to the acetyl groups, it is predictable that all polysulfone components having sugar residue will also migrate up to the solvent front with the attendant homopolysulfone. In order to confirm the existence of the hydroxyl groups of the sugar residue at one of the polymer ends, we acetylated the lower polysulfone component by the TFAA method.[19] The sample was developed with methyl ethyl ketone. The nonacetylated lower polysulfone component was used as the reference sample. The TLC chromatogram thus obtained is shown in Figure 5. The nonacetylated lower polysulfone (L-PSt) remained immobile on the starting level, while the acetylated

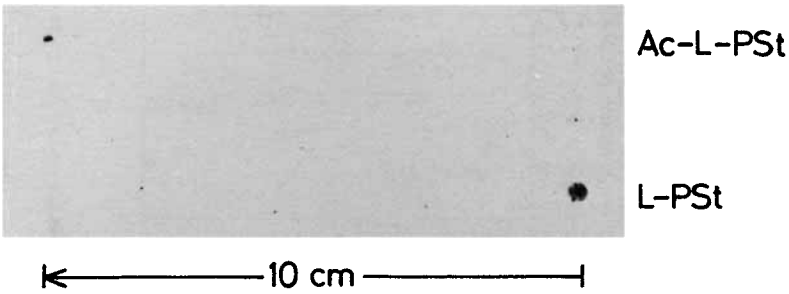

Fig. 5. Effect of acetylation of the lower component separated from the polysulfone residue derived after hydrolysis of the graft product (CS-4) on its TLC chromatographic development (developer, methyl ethyl ketone).

lower polysulfone (Ac-L-PSt) completely migrated up to the solvent front. This result indicates that the lower polysulfone component has a sugar residue with hydroxyl groups at one of the polymer ends.

It can be concluded that in this experiment, in spite of the end or side group effect owing to sulfonyl, the polysulfone residue derived after hydrolysis of the graft product can be separated into two components by TLC: the lower component and the upper component are proved to be the side chain polysulfone and the attendant homopolysulfone, respectively.

Quantification of Chromatogram

The sample polysulfones, just after being applied on an absorbent layer, distribute not only on the layer surface but also within the layer. The polysulfone present within the layer gradually comes up to the surface of the layer with the elevation of the solvent front, probably because of solvent vaporization. Therefore, if the scanning is made in a reflection mode, it is predictable that the scanner response from the final spot derived after development is greater than that from the spot on the starting level. Hezel[13] has pointed out such a phenomenon; that is, the scanner response from the final spot tended to increase with the migration distance of the spot. In order to obtain quantitative data from the chromatogram, we employed a Shimadzu TLC scanner model CS-900. As this scanner model is the reflectional one, we must consider the fact mentioned

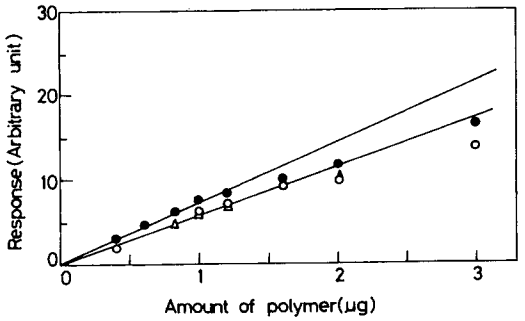

Fig. 6. Calibration curve obtained for homopolysulfone (○, before development; ●, after development up to 10 cm) and the polysulfone obtained after hydrolysis (△, before development) for quantitative analyses of TLC chromatograms.

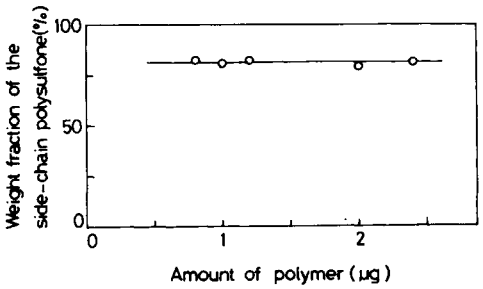

Fig. 7. Weight fraction of side chain polysulfone to total amount of polysulfone present in the graft product after extraction of homopolysulfone. When the maximum sample load of 2.4 μg was applied, the development was repeated three times to avoid tailing effect.

above. Figure 6 shows the calibration curve obtained for homopolysulfone before development and after development up to 10 cm, and the polysulfone residue obtained after hydrolysis of the graft product before development. As was pointed out by Hezel, the scanner response from the final spot derived after development was greater than that from the initial spot before development. As seen in Figure 6, the scanner response is proportional to the amount of the sample up to 1.2 μg.

Next, we examined whether constant quantitative results are obtainable by changes in the amount of the sample load in the range of 0.8–2.4 μg, where the polysulfone residue derived after hydrolysis of the graft product (sample code CS-4) is used as the sample. The results are shown in Figure 7. We developed the chromatographic plate tree times when the maximum sample load of 2.4 μg applied in order to avoid tailing of the sample. As can be seen in the figure, the expected results were realized in the whole range of sample loads from 0.8 to 2.4 μg. From the above results, the amount of the sample for quantitative analyses was kept at 1 μg in this experiment.

From the results of the calibration curve in Figure 6, the value of the true scanner response on the solvent front can be calculated according to the following equation, when the migration distance of the spot is 10 cm:

$$\text{true scanner response on solvent front} = 0.8 \times \text{actual scanner response on solvent front}$$

TABLE III
True Percent graftings calculated from the results of TLC UV-scanning determination

Sample code	Irradiation time, hr	Y_a,[a] %	A[b]	Y,[c] %
CS-1	10	58.3	0.36	21.0
CS-2	20	31.4	0.81	25.5
CS-4	40	65.7	0.84	55.1
CS-6	60	111.4	0.78	86.8
CS-8	80	131.9	0.80	104.6

[a] Apparent percent grafting.

[b] The A value means the weight fraction of the true side-chain polysulfone in the whole amount of the polysulfone component in the graft product.

[c] True percent grafting.

Characterization of Graft Copolymer

By use of the quantitative data obtained by the TLC scanner, we characterized cellulose–styrene graft copolymer produced in SO_2–DEA–DMSO cellulose solvent by the mutual irradiation technique. The true percent grafting is shown in Table III. The A value is the weight fraction of truly grafted side chain polysulfone in the total amount of polysulfone remaining in cellulose after extraction of the homopolysulfone with benzene. Therefore, true percent grafting (Y) is calculated according to eq. (2):

$$Y = A \times Y_a \tag{2}$$

where Y_a is the value of an apparent percent grafting. It can be pointed out from Table III that the A value is approximately 0.8, except for the case of 10-hr irradiation time. This result means that the amount of the homopolysulfone included in cellulose is about 20% of the apparent grafted polysulfone. At the irradiation time of 10 hr, only relatively little grafted polysulfone is generated and a large quantity of homopolysulfone is contaminated in cellulose when the graft product is recovered from the reaction solution, resulting in the larger apparent percent grafting.

True and apparent percent grafting are plotted as a function of the irradiation time in Figure 8. In a previous article[8] we showed that the apparent percent grafting increased linearly with irradiation time, except at 10 hr. However, it is clear in Figure 8 that the true percent grafting obtained by using the TLC scanner is more proportional to the irradiation time than the apparent percent grafting.

In heterogeneous graft copolymerization, it has been revealed that the grafted side chain polymer and the attendant homopolymer both formed in the cellulose matrix have the same molecular weight.[14] On the contrary, Min[7] concluded that the molecular weight of the side chain polymer was significantly higher than that of the attendant homopolymer and that the molecular weight of the side chain polymer became equal to that of the attendant homopolymer when a chain transfer agent was added to the reaction solution. It is also well known that the molecular weight of the grafted polymer is similar to that of the homopolymer in the homogeneous graft copolymerization.[16]

However, more recently Riess et al.[15,16] reported that the molecular weight of grafted polystyrene was systematically higher than that of homopolystyrene

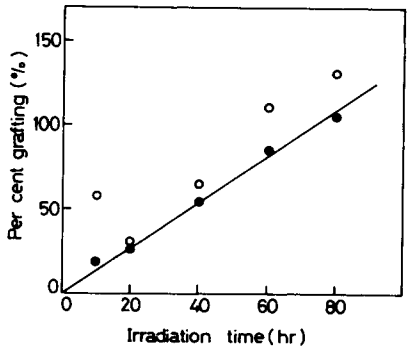

Fig. 8. True (●) and apparent (○) percent grafting. Dose rate, 1.0×10^5 R/hr; SO_2–DEA concentration, 4 mole/mole glucose unit; styrene content, 33.3 vol %.

was systematically higher than that of homopolystyrene in styrene–polybutadiene and styrene–acrylonitrile–polybutadiene homogeneous grafting systems. Figure 9 shows the number-average molecular weights of the truly grafted side chain polysulfone and the homopolysulfone derived in this experiment. The molecular weight of the grafted side chain polysulfone, as well as that of the homopolymer, remains approximately constant in each case throughout the reaction period. However, it is worth noting in Figure 9 that the molecular weight of the side chain polysulfone is significantly lower than that of the homopolysulfone; such a phenomenon has never been reported. This is presumably due to the effect of SO_2–DEA complexes. We have shown that the complexes retarded polymerization of styrene and the molecular weight of the polymer decreased with increase in the concentration of the SO_2–DEA complex.[8] SO_2–DEA complexes are considered to form ternary complexes with hydroxyl groups of cellulose to dissolve cellulose. In this experiment, 4 moles SO_2–DEA complexes per mole glucose unit of cellulose is added to the reaction solution. The amount of free SO_2–DEA complex is considered to be equivalent to 1 mole per mole glucose unit, whereas the other 3-mole equivalents of the complexes are supposed to associate with cellulose. In these circumstances the concentration of SO_2–DEA complex in the vicinity of the cellulose chain is three times higher than in remote locations. Therefore, styrene located in the immediate neighborhood of cellulose is considered to be much more subject to retardation or chain transfer reaction, resulting in the low molecular weight of the grafted side chain polysulfone compared with that of the homopolysulfone.

On the other hand, it is well known that polymers such as poly(methyl methacrylate) degrade under irradiation. Therefore, when methyl methacrylate is used as the monomer, percent grafting of methyl methacrylate levels off or decreases after a certain irradiation time. As shown in Figures 8 and 9, percent grafting increases linearly with irradiation and the molecular weight of the grafted side chain polymer remains constant throughout the experimental period. Although polystyrene is known to be a stable polymer against irradiation, the polymer obtained in this experiment is not merely polystyrene but polysulfone, a styrene–sulfur dioxide copolymer. These results at least show that the polysulfones obtained in this experiment are not polymers of the degrading type.

When characterization of graft copolymers is attempted, it is essentially preferable to isolate true graft copolymers from graft products so that their structures and properties can be examined. However, there is no simple and effective technique to isolate true graft copolymers at the present time. Consequently, the molecular weight of cellulose used as the substrate polymer, as

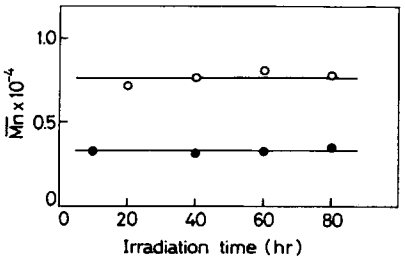

Fig. 9. Number-average molecular weights of true side chain polysulfone (●) and homopolysulfone (○).

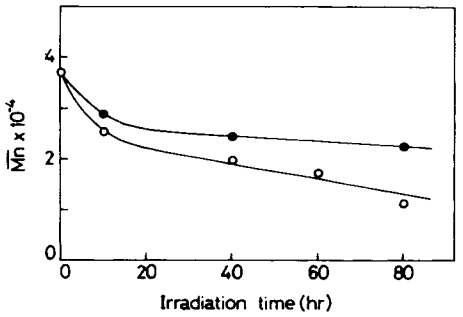

Fig. 10. Comparison of molecular weights of irradiated cellulose (○) with nonirradiated cellulose (●) both in SO_2–DEA–DMSO solution. Dose rate, 1.0×10^5 R/hr; SO_2–DEA concentration, 4 mole/mole glucose unit.

well as that of the grafted side chain polymer, should be determined in order to understand the chemical structure of the graft copolymer in the present experiment. Figure 10 shows that the molecular weight of cellulose drops when it is left standing for a definite time in a SO_2–DEA–DMSO solution with or without irradiation with γ rays. It should be noted that even nonirradiated cellulose degrades slightly on standing in the cellulose solvent. In this case, the number of chain scissions per cellulose molecule at standing times of 10, 40, and 80 hr are 0.29, 0.51, and 0.68, respectively. On the other hand, the molecular weights of irradiated cellulose decrease considerably with increase in the irradiation time in the cellulose solvent. In this case, the number of chain scissions per cellulose molecule at irradiation times of 10, 40, 60, and 80 hr are 0.48, 0.88, 1.15, and 2.40, respectively. However, these values are much lower than those which were obtained by the same irradiation levels under vacuum at room temperature.[17] As SO_2–DEA complex retards polymerization of styrene, it is possible that a part of the radicals generated on the cellulose chain are also trapped by the complex. Therefore, the lower degradation of cellulose found in this experiment might be attributable to this effect of the SO_2–DEA complex.

On the assumption that all the cellulose present in the reaction system takes part in graft copolymerization, the number of branches per the starting cellulose

TABLE IV
Characterization of Graft Copolymers Obtained in the Homogeneous Graft Copolymerization by γ-ray Irradiation Technique

Sample code	Irradiation time, hr	Y,[a] %	$\overline{M}_{ns}$ $\times 10^{-3}$ [b]	$\overline{M}_{nr}$ $\times 10^{-4}$ [c]	N_{sm}[d]	N_{sr}[e]
CS-1	10	21.0	3.3	2.50	2.4	1.6
CS-4	40	55.1	3.2	1.96	6.4	3.4
CS-6	60	86.8	3.3	1.72	9.8	4.6
CS-8	80	104.6	3.7	1.09	10.6	3.1

[a] True percent grafting.

[b] Molecular weight of the side chain polysulfone.

[c] Molecular weight of the cellulose irradiated with γ-ray in a SO_2–DEA–DMSO solution without styrene monomer for a definite period.

[d] Number of branches per cellulose molecule calculated on the basis of the molecular weight of the starting cellulose, 3.69×10^4.

[e] Number of branches per cellulose molecule calculated on the basis of $\overline{M}_{nr}$.

molecule (N_{sm}) and the irradiated cellulose molecule (N_{sr}) are calculated according to eqs. (3) and (4):

$$N_{sm} = \frac{Y/\overline{M}_{ns}}{100/\overline{M}_{nc}} \tag{3}$$

$$N_{sr} = \frac{Y/\overline{M}_{ns}}{100/\overline{M}_{nr}} \tag{4}$$

where Y is the true percent grafting, $\overline{M}_{ns}$ is the number-average molecular weight of the side chain polysulfone, and $\overline{M}_{nc}$ and $\overline{M}_{nr}$ are the number-average molecular weights of the starting cellulose and the irradiated cellulose, respectively. The results are summarized in Table IV. It has been reported that the number of branches per substrate polymer chain is less than 1 or far less than 1 in heterogeneous graft copolymerization systems.[1,3,6,7,12,18] In the present homogeneous graft copolymerization system, however, the number of branches per cellulose chain, especially the value of N_{sm}, is much larger than 1 and increase with increase in irradiation time. As grafting occurring by the heterogeneous graft copolymerization is restricted only to the surface of crystalline regions and in the amorphous regions of cellulose, where the diffusion of monomer into the amorphous regions is the rate-determining step, the number of branches per substrate polymer attained thereby must become very low. In the case of homogeneous graft copolymerization, on the other hand, these disadvantages are eliminated. Consequently, the number of branches per substrate polymer becomes very high.

In order to estimate N_{sm}, we employed the molecular weight of the starting cellulose, assuming that no scission of the cellulose chain occurs throughout the graft reaction; whereas in order to obtain the value of N_{sr}, we used the molecular weight of the irradiated cellulose, assuming that the cellulose chain degrades during the grafting reaction. Accordingly, the difference between the values of N_{sm} and N_{sr} results from the molecular weight of the cellulose employed as the basis for calculating the N_{sm} and N_{sr} values. In actuality, as both the grafting of styrene onto cellulose and the scission of cellulose chain occur from radical sites generated on the cellulose chain, the number of branches per cellulose chain probably reaches an intermediate value between N_{sm} and N_{sr}.

The following equation is obtained for the relation between the true percent grafting (Y) and N_{sm}:

$$Y = \frac{\text{molecular weight of side chain polysulfone}}{\text{molecular weight of starting cellulose}} 100 \times N_{sm} \tag{5}$$

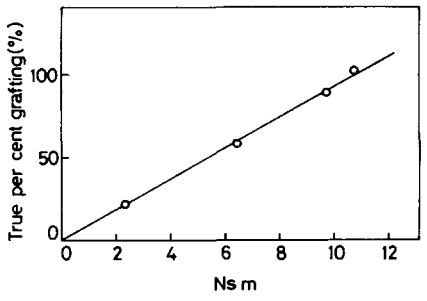

Fig. 11. Relationship between value of true percent grafting and number of branches per starting cellulose molecule, N_{sm}, calculated on the basis of $\overline{M}_n$ value of the starting cellulose, 3.69×10^4.

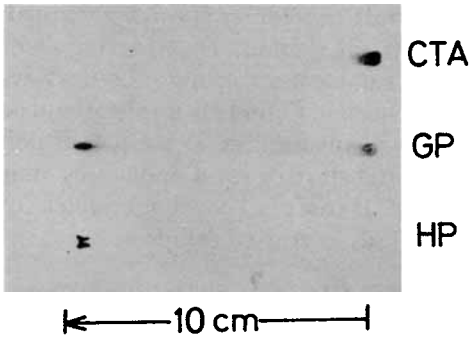

Fig. 12. TLC chromatogram obtained for homopolysulfone (HP), acetylated graft product (GP = CS-4), and cellulose triacetate (CTA) by using a binary solvent mixture of acetone and chloroform (55:45) as developer.

As the molecular weights of the side chain polysulfone are kept constant during the reaction, as shown in Figure 9, Y must be proportional to N_{sm}. True percent grafting versus N_{sm} is plotted in Figure 11. A good linear relationship can be seen between the two values obtained experimentally and independently. This result proves that the increase in the percent grafting with irradiation time arises from the increase in the number of branches per cellulose chain.

Even in the present homogeneous graft copolymerization, it is possible that ungrafted cellulose exists in the graft product. For the purpose of performing a more accurate structural analysis of graft copolymers, we acetylated the graft product to dissolve it and then tried to separate by TLC the acetylated graft product into two components, i.e., the true graft copolymer containing a small amount of the attendant homopolysulfone and the ungrafted cellulose. We employed homopolysulfone (HP) and cellulose triacetate (CTA) as the reference samples. The graft product and the cellulose were acetylated by the TFAA method,[19] because this method was shown not to degrade the cellulose sample used in this experiment, in reaction times up to 6 hr. We used a binary solvent mixture of acetone and chloroform (55:45 by volume) as the developer. After development the chromatogram was dried and sprayed with 18N sulfuric acid and then visualized by heating at 120°C for about 20 min.

The chromatogram is shown in Figure 12. The spot at 0 cm is assignable to cellulose triacetate, i.e., ungrafted cellulose. The spot at 10 cm appears to be due to the true graft copolymer containing a small amount of the attendant homopolysulfone. Furthermore, a large fraction of the cellulose molecules in the reaction system takes part in the graft copolymerization. In addition, the chromatogram was scanned by using a TLC scanner to ascertain whether the

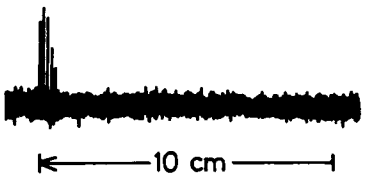

Fig. 13. Chromatogram obtained by TLC UV scanning at 215 nm after development with a binary solvent mixture of acetone and chloroform (55:45) for acetylated graft product (CS-4) in Fig. 12.

homopolymer and the graft copolymer species remained at the starting level before the chromatogram was visualized. To accomplish this, a 215-nm wavelength light was used as a sample beam, while a 300-nm wavelength light was used as a reference beam. As seen in Figure 13, no absorbance at 215 nm appears on the starting level. This result implies, at least, that none of the polystyrene components remains at the starting level, indicating that the graft product is completely separated into (1) true graft copolymer which contains a small amount of the homopolymer and (2) ungrafted cellulose.

The authors thank Professor T. I. Min, Institut Supérieur de Technologie, Suweon, Korea, for his valuable advice. Dr. Nishinaga and Mr. Tomita, Faculty of Engineering, Kyoto University, are also acknowledged for their suggestions on the TLC scanner.

References

1. H. A. Ende and V. T. Stannett, *J. Polym. Sci. Part A*, **2**, 4047 (1964).
2. H. Yasuda, J. A. Wary, and V. T. Stannett, *J. Polym. Sci. Part C*, **2**, 387 (1963).
3. I. Sakurada, Y. Ikada, and F. Horii, *Makromol. Chem.*, **139**, 171 (1970).
4. H. Inagaki, H. Matsuda, and F. Kamiyama, *Macromolecules*, **1**, 520 (1968).
5. F. Kamiyama, H. Matsuda, and H. Inagaki, *Makromol. Chem.*, **125**, 286 (1969).
6. T. Taga and H. Inagaki, *Angew. Makromol. Chem.*, **33**, 129 (1973).
7. T. I. Min, Dissertation, Kyoto University, 1977.
8. M. Tsuzuki, I. Hagiwara, N. Shiraishi, and T. Yokota, *J. Appl. Polym. Sci.*, **25**, 2721 (1980).
9. T. I. Min, T. Miyamoto, and H. Inagaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **53**, 381 (1975).
10. F. Kamiyama, H. Matsuda, and H. Inagaki, *Polym. J.*, **1**, 518 (1970).
11. H. Inagaki, Thin layer chromatography, in *Fractionation of Synthetic Polymers*, L. H. Tung, Ed., Marcel Dekker, New York, 1977, Chap. 7
12. I. Sakurada, Y. Ikada, and Y. Nishizaki, *J. Polym. Sci. Part C*, **37**, 265 (1972).
13. V. Hezel, *Angew. Chem.*, **85**, 334 (1973).
14. I. Sakurada, Y. Ikada, H. Uehara, Y. Nishizaki, and F. Horii, *Makromol. Chem.*, **139**, 183 (1970); I. Sakurada, Y. Ikada, and T. Kawahara, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2329 (1973).
15. J. L. Locatelli and G. Riess, *Angew. Makromol. Chem.*, **28**, 161 (1973).
16. J. L. Refregier, J. L. Locatelli, and G. Riess, *Eur. Polym. J.*, **10**, 139 (1974).
17. Y. Kusama, E. Kageyama, M. Shimada, and Y. Nakamura, *J. Appl. Polym. Sci.*, **20**, 1679 (1976).
18. R. Huang and P. Chandramouli, *J. Appl. Polym. Sci.*, **12**, 2549 (1968).
19. M. Tsuzuki, N. Shiraishi, and T. Yokota, *J. Appl. Polym. Sci.*, **25**, 2567 (1980).

Received March 11, 1980
Revised April 28, 1980