

Isolation of Polystyrene Branches from Grafted Cellulose

INTRODUCTION

The graft copolymerization of styrene to cellulose by gamma irradiation is currently being studied in a detailed manner in our laboratory. In order to correlate the mechanism with the length and dispersity of the polystyrene branches, characterizations of the copolymer and the branches themselves are being made by viscometry and light scattering. This communication is concerned with some noteworthy effects encountered in the isolation of polystyrene branches from the copolymer.

Several methods,¹⁻⁵ most of which entail acid hydrolysis of the backbone to water-soluble glycosidic residues, are available. Initially, method A in the following experimental section was employed, but the results obtained necessitated the use of an alternative procedure (method B).

EXPERIMENTAL

Materials

Cellulose strips, dioxan, water, and styrene were purified as described previously.⁶ Other materials used were reagent-grade products.

Irradiation

Grafted cellulose was obtained by the mutual irradiation method at 30°C using a dose rate of 20 rad/min. Films immersed in a mixture of dioxan-water-styrene (78:2:20 by volume) were irradiated for known times in vacuo. Grafted films were extracted with benzene in a Soxhlet apparatus, washed in methanol, and dried at 40°C in vacuo.

Isolation of Branches from Graft Copolymer

A. The procedure specified by Huang and Chandramouli⁷ was utilized, viz., approximately 2 g copolymer (grafted to 53%) was swollen in N,N-dimethylformamide and then transferred to a flask containing 70 ml acetic anhydride, 70 ml benzene, and 12 ml sulfuric acid (72%). Reaction at 60°C was carried out for 72 hr with continuous shaking. The product was precipitated in an excess of methanol, dissolved in methylene chloride, reprecipitated in methanol, and dried at 60°C in vacuo.

B. The technique of Morris, Blouin, and Arthur⁸ was employed, which consisted of dispersing 2 g copolymer overnight in 200 ml of 75% w/w aqueous zinc chloride with continuous shaking. An equal volume of 6*N* HCl was added and the mixture stirred for 1-2 hr, at which point the dispersion of the sample was complete. After subsequent heating for 4 hr at 100°C, the product was poured into an excess of methanol and the precipitated polystyrene was filtered. Final purification was as in method A.

Analysis

The percentage composition of sulfur in the isolated branches was determined microanalytically by Weiler and Strauss, Oxford, England.

Viscometry

Measurements were conducted in an Ubbelohde suspended level viscometer, and dilution was made in situ.

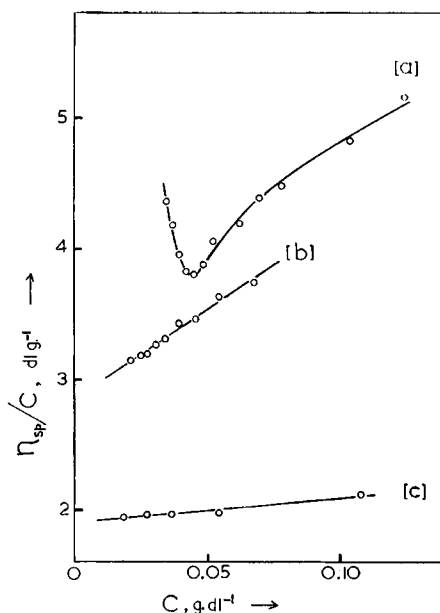


Fig. 1. Reduced viscosity versus concentration plots for branches: (a) isolated according to method A, degree of grafting of initial copolymer = 42%, solvent chloroform; (b) as for (a), but solvent was $10^{-3} M Cl_3CCOOH$ in chloroform; (c) isolated according to method B, degree of grafting of initial copolymer = 52%, solvent chloroform.

RESULTS

Intrinsic viscosities $[\eta]$ of the polystyrene homopolymer produced simultaneously during the irradiation were measured at $30^\circ C$ in toluene. It was intended to compare these values of $[\eta]$ with those of the branches isolated by method A. However, only partial solubility was observed in toluene even after prolonged stirring and warming. On the other hand, the polymer was found to be completely soluble in methylene chloride and chloroform, which suggests that it is more polar than polystyrene.

Possible polyelectrolyte behavior was investigated viscometrically at $25^\circ C$ using a solution of the polymer in chloroform. Figure 1(a) demonstrates typical polyelectrolyte behavior, i.e., a marked increase in η_{sp}/C at low concentration. The reaction conditions in method A do not preclude the possibility of sulfonation of the polystyrene occurring during hydrolysis of the cellulose. Support for this was afforded through a positive acid/base titration and a positive sulfur determination. Furthermore, it may be seen from Figure 1b that the polyelectrolyte behavior can be suppressed by the use of $10^{-3} M$ trichloroacetic acid in chloroform as solvent for the viscosity measurements.

In contrast, the branches isolated by method B were completely soluble in toluene. Figure 1c demonstrates that the viscometric behavior in chloroform was quite normal for this product.

DISCUSSION

In method A, the acetic anhydride is included to promote acetolysis of the cellulose with an efficiency which was amply verified. However, the concentration of the sulfuric acid and the reaction conditions are similar to those utilized in standard methods⁹ for the para-sulfonation of toluene. Hence, it is likely that sulfonic acid groups are introduced at the para positions of the polystyrene. The analytical result of 1.02% by

weight of sulfur corresponds to a sulfonation of approximately 1 in 27 of the styrene segments, which is in good accord (1 in 29) with the result obtained by titration.

Schurz and his co-workers¹⁰ have obtained toluene-soluble polystyrene by acetolysis of cellulose tricarbonyl grafted with polystyrene, but it is noteworthy that the concentration of the sulfuric acid was considerably less than that used in method A.

Although method A is suitable for the hydrolysis of cellulose grafted with monomers which cannot be attacked by sulfuric acid, e.g., methyl methacrylate, its use for cellulose-styrene copolymers should be approached with caution, and the procedure involving $ZnCl_2-HCl$ is more advisable for such systems.

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REFERENCES

1. Kh. U. Usmanov, B. I. Aikhodzhaev, and U. Azizov, *J. Polym. Sci.*, **53**, 87 (1961).
2. Y. Kobayashi, *J. Polym. Sci.*, **51**, 359 (1961).
3. V. Stannett, J. D. Wellons, and H. Yasuda, *J. Polym. Sci. C*, **4**, 551 (1963).
4. F. A. Blouin, N. J. Morris, and J. C. Arthur, Jr., *Text. Res. J.*, **36**, 309 (1966).
5. L. A. Gugliemelli, M. O. Weaver, and C. R. Russell, *J. Polym. Sci., Polymer Letters*, **6**, 509 (1968).
6. J. T. Guthrie, M. B. Huglin, and G. O. Phillips, *Angew. Makromol. Chem.*, **13**, 199 (1970).
7. R. Y. M. Huang and P. Chandramouli, *J. Appl. Polym. Sci.*, **12**, 2549 (1968).
8. N. J. Morris, F. A. Blouin, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **12**, 373 (1968).
9. A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, Green & Co., London, 1948.
10. J. Schurz, M. Rebek, and H. Spork, *Angew. Makromol. Chem.*, **1**, 42 (1967).

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