Preparation of Starch 2-Hydroxy-3-Mercaptopropyl Ethers and Their Use in Graft Polymerizations

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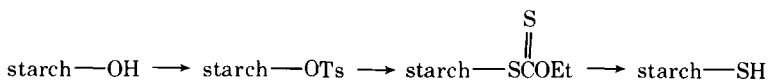
Synopsis

Starch 2-hydroxy-3-mercaptopropyl ethers of degree of substitution (DS) up to 0.34 were prepared as follows: starch was reacted with epichlorohydrin to give 3-chloro-2-hydroxypropyl ethers which were treated with thiosulfate to displace chloride ion followed by reduction of the resulting thiol-sulfonates with sodium borohydride. These mercapto ethers formed graft copolymers with acrylonitrile, styrene, acrylic acid, and dimethylaminoethyl methacrylate (DMAEMA) under hydrogen peroxide initiation. The resulting graft copolymers, after treatment with sodium borohydride to regenerate thiol groups from disulfides formed by peroxide oxidation, could then be reacted with additional monomer and peroxide to increase add-on of the synthetic moiety. Graft copolymers containing about 60% polyacrylonitrile or 70% polystyrene were thus obtained. Repeated graftings were carried out successfully with two, three, or four different monomers added sequentially. Hydrophobic monomers graft polymerized more readily onto graft copolymers containing hydrophobic chains, whereas hydrophilic monomers graft polymerized more readily onto hydrophilic graft copolymers. Graft copolymers prepared from acrylic acid and DMAEMA precipitated near the isoelectric point upon neutralizing their acidic or basic solutions.

INTRODUCTION

Interest at the Northern Regional Research Center in developing new products based upon annually renewable agricultural commodities has led to the development of starch xanthates for increasing the wet and dry strength of paper,[1] producing powdered rubber,[2] removing heavy metals from waste waters,[3] and encapsulating pesticides for slow release.[4] Faessinger and Conte[5,6] have shown that starch xanthates and other thiolated polysaccharides undergo graft polymerization with vinyl monomers and hydrogen peroxide. It has been claimed that such graft polymerizations can proceed in high yields with minimal homopolymerization under a careful choice of reaction conditions and that the grafted chains become attached to the starch through stable carbon-carbon bonds following radical formation and rearrangement.[7] However, instances have been found in which alkali labile xanthate esters can form the grafting linkages.[8,9]
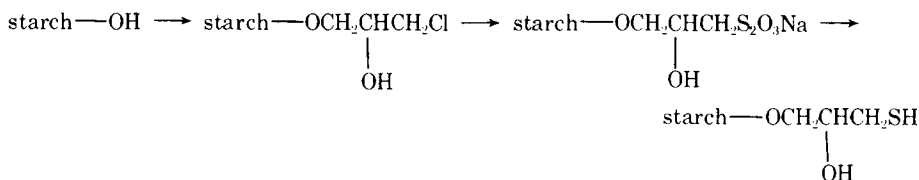
We are interested in preparing a variety of thiol-containing starches and subjecting them to graft polymerization reactions to explore the full potential of this type of grafting. Hopefully the grafts attach to starch via stable linkages. Many grafting reactions, such as starch with styrene, are difficult to perform by ordinary radical polymerization processes but are readily obtained in high yields in thiol-peroxide systems.

Previously, we replaced starch hydroxyl groups with thiol groups by the sequence[10]

$$\text{starch}-\text{OH} \longrightarrow \text{starch}-\text{OTs} \longrightarrow \text{starch}-\overset{\displaystyle S}{\overset{\|}{\text{SC}}}\text{OEt} \longrightarrow \text{starch}-\text{SH}$$

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and formed thiolstarches of degree of substitution (DS) up to 0.16 which are useful in graft polymerizations. Thiol groups introduced into polysaccharides through analogous displacements of sulfonates with thiolacetate anions have found use in imparting wrinkle recovery and wool-like properties to cotton fibers.[11,12]

In continuing our research for methods to introduce thiol groups onto starch we have modified the recently reported method of Axén et al.[13] We reacted starch with epichlorohydrin under acid rather than alkaline catalysis to form the chlorohydrin instead of the epoxide. The chlorohydrin was then reacted with sodium thiosulfate[14] and the resulting thiolsulfonate reduced to the thiol:

$$\text{starch}\!-\!\text{OH} \longrightarrow \underset{\underset{\text{OH}}{|}}{\text{starch}\!-\!\text{OCH}_2\text{CHCH}_2\text{Cl}} \longrightarrow \underset{\underset{\text{OH}}{|}}{\text{starch}\!-\!\text{OCH}_2\text{CHCH}_2\text{S}_2\text{O}_3\text{Na}} \longrightarrow$$

$$\underset{\underset{\text{OH}}{|}}{\text{starch}\!-\!\text{OCH}_2\text{CHCH}_2\text{SH}}$$

These products were reacted with acrylonitrile (AN), styrene (Sty), acrylic acid (AA), and the acetate salt of dimethylaminoethyl methacrylate (DMAEMA· HOAc) to form graft copolymers. Combinations of these monomers were sequentially grafted onto the thiolated starch ethers after reducing disulfides with sodium borohydride following each grafting.

EXPERIMENTAL

Materials

Pearl corn starch, 10%–12% moisture (CPC International, Inc.), epichlorohydrin (Aldrich Chemical Company, Inc.), 37% hydrochloric acid (Mallinckrodt Chemical Works), 70% perchloric acid (Fisher Scientific Company), and sodium borohydride (Alfa Products, Ventron Corporation) were used without further purification. Monomers (AN, Sty, AA, and DMAEMA) and hydrogen peroxide (30%) were as previously described.[10]

Methods

Sulfur and chlorine in starch samples were determined by the method reported by White.[15] Nitrogen was determined by the Kjeldahl method.[16]

Acid Catalyzed Etherification of Starch

Starch (30.0 g) was suspended in epichlorohydrin (100 ml) and refluxed under constant stirring at 100°–120°C. Runs were made 5 hr with no catalyst, 37% hydrochloric acid, and 70% perchloric acid catalysts. The reaction mixture was protected from atmospheric moisture with a calcium chloride tube. Starch was used undried (11.3% moisture) or vacuum dried 2 hr at 100°C (0.5% H_2O). Products were isolated by filtration and washed with acetone. The products were divided in half: one-half was air dried overnight, the other was suspended

in 350 ml water and centrifuged three times. The insoluble material was washed with acetone and air dried overnight. Percent chlorine (% Cl) was determined on the first half and on the water-washed half. Chlorohydrin DS was calculated from percent chlorine by the formula

$$DS_{Cl} = 162 \, (\% \, Cl)/[3550 - 92.5 \, (\% \, Cl)]$$

where 92.5 is the equivalent weight of the 3-chloro-2-hydroxypropyl substituent less 1.0 for hydrogen replacement, 162 is the equivalent weight of the anhydroglucose unit (AGU) of starch, and 3550 is the equivalent weight of chlorine ×100.

Starch 2-Hydroxy-3-Mercaptopropyl Ethers

The starch 3-chloro-2-hydroxypropyl ethers (about 30 g) were suspended in water (180 ml) and sodium thiosulfate pentahydrate (120 g) was added. The mixture was neutralized with acetic acid and stirred 1–12 hr on the steam bath. After cooling and dialysis against distilled water overnight and concentration by evaporation of water, the products were precipitated by pouring into excess ethanol. After filtration, the products were washed with ethanol, acetone, and hexane. Portions of the products were vacuum dried 1 hr at 100°C and the sulfur and chlorine contents were determined. The treatment with sodium thiosulfate was repeated when necessary to bring the chlorine content under 0.1%. Thiolsulfonate DS was determined from percent sulfur (% S) by the formula

$$DS = 162 \, (\% \, S)/[6400 - 192 \, (\% \, S)]$$

where 192 is the equivalent weight of 2-hydroxy-3-thiolsulfonate sodium salt substituent less 1.0 for hydrogen replacement, and 6400 is the equivalent weight of the two sulfurs ×100.

The thiosulfonates were suspended in water (500 ml), and sodium borohydride (5.0 g) was added in small increments with constant stirring. After 3 hr at 50°C the mixtures were dialyzed and concentrated by evaporation of water. Following precipitation by alcohol and drying, thiol DS was calculated from % S by the formula

$$DS = 162 \, (\% \, S)/[3200 - 90 \, (\% \, S)]$$

where 90 is the equivalent weight of the 2-hydroxy-3-mercaptopropyl substituent less 1.0 for hydrogen replacement. It was necessary to repeat the sodium borohydride treatment several times with the higher DS thiolsulfonates to bring about complete reduction. Thiol DS's determined by the Ellman method[10] both for the thiols and thiolsulfonates were found to be in good agreement with DS from sulfur analyses when all of the chlorine had been displaced.

Grafting Reactions

Suspensions of thiolated starch ethers (5.0 g) in water (100–500 ml) were warmed to 75°C while bubbling nitrogen through the mixture. Sodium borohydride (1.0 g) was added in small portions, and after 15 min the medium was cooled to room temperature. Excess borohydride was destroyed with HCl (2.5 ml). Nitrogen bubbling was continued until hydrogen sulfide evolution ceased as shown by lead acetate test paper. The mixture was buffered to pH 5 with a

mixture of acetic acid (6 ml) and sodium hydroxide solution (12.5N, 4 ml). Monomer (5–20 ml) and hydrogen peroxide (1 ml) were added and stirring was continued 4 hr at room temperature. Products were isolated by filtration and washed with water, ethanol, and hexane.

Where DMAEMA was used in the reactions, sufficient acetic acid was added to buffer the mixtures at pH 5 and convert the DMAEMA to the acetate salt.

In recycling reactions, the products were resuspended in water and the grafting process was repeated with the same or a different monomer.

In graft polymerizations with AN, two grafting cycles were carried out in which extractions of homopolymer were performed after each cycle. Sty was then grafted onto this product and the resulting material was extracted with benzene to remove ungrafted polystyrene. DMAEMA·HOAc was grafted onto an extracted polyacrylonitrile containing graft copolymer, then Sty and AA were grafted. A benzene-extracted graft copolymer containing polystyrene was also grafted with DMAEMA·HOAc. AN was grafted in two more cycles onto a thiolated starch ether-Sty-DMAEMA·HOAc terpolymer. In four sequences a thiolated starch ether was grafted with the monomers AA, DMAEMA·HOAc, Sty, and AN. Sty did not graft polymerize onto an AA-thiolated starch ether copolymer.

Graft copolymers containing only polyacrylonitrile or polystyrene (1.0 g) were kept on the steam bath in HCl (1N, 100 ml) 4 hr to hydrolyze the starch portion. The insoluble grafted side chains were isolated and the intrinsic viscosities determined in N,N-dimethylformamide for polyacrylonitrile and in benzene for polystyrene. Molecular weights ($\overline{M}_n$) were calculated using the Mark-Houwink equations $[\eta] = 3.92 \times 10^{-4}M^{0.75}$ for polyacrylonitrile[17] and $[\eta] = 1.13 \times 10^{-4}M^{0.73}$ for polystyrene.[18]

AGU/grafted chain = $\overline{M}_n \times (100 - \% \text{ P})/162 (\% \text{ P})$, where 162 is the equivalent weight of the AGU and % P is the percent of synthetic polymer in the grafted copolymer.

RESULTS AND DISCUSSION

The reaction of hydroxyl compounds with epichlorohydrin in the absence[19] or presence[20] of acid catalysis to form 3-chloro-2-hydroxypropyl ethers was applied to starch, and the results are shown in Table I.

The highest chlorine contents were obtained when undried pearl starch (11.3% H_2O) was refluxed in epichlorohydrin containing small amounts of hydrochloric or perchloric acid. The reaction was less when the starch had been vacuum dried at 100°C for 2 hr to 0.5% H_2O. At the higher acid levels starch degradation occurred, which was indicated by the presence of water-soluble fractions and lower chlorine contents.

Starch and epichlorohydrin appeared to form unstable adducts when no catalyst or HCl catalysis was used, since the chlorine content of the product (Table I, No. 3) was lowered substantially from an initial 4.8% Cl to 1.1% Cl upon washing with water. The proposed adduct may be similar to the unstable Lewis acid-ether adducts of epichlorohydrin[21] which decompose to alcohols and chlorohydrins under aqueous conditions. When $HClO_4$ was used as the catalyst, more chlorine could be introduced into the products, and the products were stable to water washing. The amount of chlorine introduced into the product by this method varied considerably depending upon the amount of moisture present in the starch.

TABLE I
Reaction of Starch with Epichlorohydrin

Starch	Acid	acid, ml	% Cl[a]	% Cl[b]	DS_{Cl}[b]
Undried[c]	None	—	5.6	0.7	0.03
Undried	HCl	1.0	5.0	0.8	0.04
Undried	HCl	3.0	4.8	1.1	0.05
Undried	$HClO_4$	0.2	12.8	12.6	0.85
Undried	$HClO_4$	1.0	2.9	3.1	0.15
Dried[d]	None	—	0.4	0.2	0.01
Dried	HCl	1.0	0.9	0.4	0.02
Dried	HCl	3.0	3.6	0.9	0.04
Dried	$HClO_4$	0.2	0.3	0.2	0.01
Dried	$HClO_4$	1.0	0.5	0.4	0.02

[a] % Cl was determined on acetone washed product that was air dried overnight.

[b] % Cl and DS_{Cl} were determined after washing a portion of the original product with water and then with acetone, and air drying overnight.

[c] 11.3% H_2O.

[d] 0.5% H_2O.

The conversion of the starch-epichlorohydrin reaction product to the thiol-sulfonate is shown in Table II. Sulfur content increased as chlorine content decreased, and thiol DS approached thiolsulfonate DS when most of the chlorine had been displaced. However, in products containing the higher percentages of chlorine, thiol DS was somewhat lower than thiolsulfonate DS. These lower values may have been due to sulfide formation through displacement of chlorine by thiol.[10] Complete sequences for the preparation of starch 2-hydroxy-3-mercaptopropyl ethers are summarized in Table III.

The starch-epichlorohydrin products prepared by perchloric acid catalysis were converted to thiolsulfonates and thiols of higher DS than those products prepared without catalyst or with hydrochloric acid catalysis. The DS_{SH} achievable was dependent upon DS_{Cl}, which in turn varied with the amount of $HClO_4$ reaction time, and the % H_2O of the original starch. The thiols undergo air oxidation to disulfide, but the thiol is completely restored without loss of sulfur upon treatment with sodium borohydride. The sulfur content does not change upon storage for several months at room temperature. The acid catalyst used in the first step caused some degradation of the starch, and the product may be separated into fractions of varying water solubility and sulfur content.

TABLE II
Reaction of Starch-Epichlorohydrin Adduct with Sodium Thiosulfate[a,b]

Time (hr)	% Cl	DS_{Cl}	% S	$DS_{S_2O_3Na}$[c]	DS_{SH}[d]
0	1.1	0.05	—	—	—
1	0.7	0.03	1.6	0.04	0.02
2	0.4	0.02	1.7	0.05	0.04
4	0.2	0.01	2.0	0.05	0.05
9	0.1	0.005	2.1	0.06	0.06

[a] About 30 g starch-epichlorohydrin, 120 g sodium thiosulfate in 180 ml water neutralized with acetic acid. Mixture kept on steam bath and sampled hourly.

[b] Product of Table I, No. 3, washed with water.

[c] Calculated from sulfur content.

[d] Determined by Ellman test.

TABLE III
Preparation of Starch 2-Hydroxy-3-Mercaptopropyl Ethers[a]

| Catalyst | Reaction with epichlorhydin | | Reaction with $Na_2S_2O_3$ | | |
	Time (hr)	DS_{Cl}	Time (hr)	$DS_{S_2O_3Na}$	DS_{SH}
None	5	0.03	12	0.08	0.05
HCl[b]	4	0.05	9	0.06	0.06
$HClO_4$[c]	2	0.10	8	0.09	0.09
$HClO_4$[c]	4	0.21	8	0.19	0.19
$HClO_4$[c]	5	0.47	6	0.31	0.30
$HClO_4$[c]	8	0.61	8	0.53	0.34

[a] Catalyst with 30 g undried, ungelatinized starch refluxed the indicated time to give DS_{Cl}. The resultant product kept on steam bath with sodium thiosulfate as in Table II to give $DS_{S_2O_3Na}$. This product reduced with sodium borohydride and DS_{SH} determined by Ellman test.

[b] 3.0 ml.

[c] 0.2 ml.

The results of grafting various monomers onto starch 2-hydroxy-3-mercaptopropyl ethers is shown in Table IV.

Graft copolymers of acrylonitrile and thiolated starch ethers of DS 0.06 and 0.30 contained 40%–59% polyacrylonitrile and had grafting frequencies of 104–247 AGU/chain. Molecular weights of the grafted chains were 20,300–26,100. These results are similar to those reported previously[10] for thiolstarch of DS 0.16 prepared by a different method. At DS 0.06, only 7% of the thiol groups were used as grafting sites for acrylonitrile, and at DS 0.30, only 3% were used. These results were obtained by multiplying the number of chains per AGU by 100 and dividing by the thiol DS. The usable grafting sites appeared to be in the same range regardless of the thiol DS.

Table IV shows increases in amounts of synthetic polymer and grafting frequencies upon reducing the copolymers with sodium borohydride and additional graft polymerizations with acrylonitrile and styrene. The average molecular weight of grafted chains increased on recycling. When homopolymer was extracted after each grafting cycle, the grafting frequency increases were

TABLE IV
Graft Polymerization of Vinyl Monomers onto Starch 2-Hydroxy-3-Mercaptopropyl Ethers[a]

DS_{SH}	Monomer	Cycle	Add-on (%)	AGU/grafted chain	$\overline{M}_n$/grafted chain
0.06	Acrylonitrile	1	40[b]	247	26,100
0.30	Acrylonitrile	1	46[b]	146	20,300
0.30	Acrylonitrile	1	46	146	20,300
		2	59[c]	104	24,700
0.30	Styrene	1	57	1410	298,000
		2	72[c]	1095	456,000
0.30	Acrylonitrile	1	45[d]	123	16,200
		2	53[d]	118	21,800
	Styrene	3	68[d]	—	[e]

[a] Starch 2-hydroxy-3-mercaptopropyl ethers at 1% concentration in water.

[b] Synthetic portion contains about 20% homopolymer.

[c] Homopolymer extracted only after second cycle.

[d] Homopolymer extracted after each cycle. Values determined from weight increases.

[e] $[n] = 0.82$ in dimethylformamide.

less and the increases in add-on were due more to increases in the average molecular weight of the side chains.

Styrene was copolymerized onto a polyacrylonitrile grafted thiolated starch ether and the product, after extracting with benzene, contained 68% total grafted polymer (polystyrene plus polyacrylonitrile). After acid hydrolysis to remove the starch portion, the remaining grafted side chain mixture contained 25% benzene-soluble polystyrene. The remaining portion was mostly soluble in dimethylformamide and was a mixture of polystyrene and polyacrylonitrile (infrared spectroscopy) that could not be separated. These results suggested that polymerizations in successive cycles took place on grafted chains as well as on thiol sites of the thiolated starch ethers. Polyacrylonitrile is known to contain trapped free radicals, formed under certain free radical conditions, which are capable of initiating block polymerization with styrene.[22]

Several combinations of monomers were grafted in sequence onto starch 2-hydroxy-3-mercaptopropyl ethers, and the results are shown in Table V.

Homopolymer was extracted and thiol groups were regenerated prior to each successive grafting. Percent compositions shown in the last column of Table V are based upon weight increases and nitrogen analyses.

The results in Table V show that the hydrophobic monomer Sty graft polymerizes efficiently (33%) onto a copolymer containing hydrophobic polyacrylonitrile (55%) but that the hydrophilic monomer DMAEMA·HOAc grafts poorly (14%) onto polyacrylonitrile (39%) copolymer. Similarly, DMAEMA·HOAc grafts poorly onto copolymers containing polystyrene; amounts grafted decrease from 11% to 3% as polystyrene in the copolymer increases from 29% to 56%.

If the hydrophilic AA is first grafted onto a thiolated starch ether (43%), hydrophilic DMAEMA·HOAc grafts efficiently (43%), but hydrophobic Sty grafts

TABLE V

Repeated Grafting Cycles of Monomers onto Starch 2-Hydroxy-3-Mercaptopropyl Ethers

DS_{SH}	% N in graft copolymer	Monomers grafted in sequence	Compositions (%)[a]				
			PAN	PSty	PDMAEMA·HOAc	PAA	Starch
0.30	14.6	AN	55[b]				45
	9.8	Sty	37	33[b]			30
0.06	10.4	AN	39[b]				61
	9.8	DMAEMA·HOAc	34		14[b]		52
	8.8	AA	30		13	10[b]	47
0.05	0.1	Sty		29[c]			71
	0.7	DMAEMA·HOAc		26	11[b]		63
0.05	0.1	Sty		56[c]			44
	0.2	DMAEMA·HOAc		54	3[b]		43
	1.0	AN	3[b]	53	3		41
	4.5[d]	AN	17[b]	45	2		36
0.05	0.1	AA				43[c]	57
	2.8	DMAEMA·HOAc			43[b]	25	32
	2.6	Sty		7[b]	40	23	30
	9.4	AN	29[b]	5	28	16	22

[a] PAN, polyacrylonitrile; PSty, polystyrene; PDMAEMA·HOAc, poly-(2-methacryloyloxyethyldimethylammonium acetate); PAA, polyacrylic acid.

[b] Determined from % N in copolymer.

[c] Determined by weight increase.

[d] AN regrafted using four times the usual amount of monomer.

poorly (7%). Thus, hydrophilic monomers graft efficiently to hydrophilic co-
polymers and hydrophobic monomers graft to hydrophobic copolymers, but
difficulty is encountered in grafting where there are large differences in polarity
between monomer and copolymer.

The terpolymer which contained poly-DMAEMA·HOAc (43%), thiolated
starch (32%) and polyacrylic acid (25%) was soluble in acidic or basic solutions
but coagulated under neutral conditions near the isoelectric point of the carboxyl
and substituted ammonium groups.

References

1. C. R. Russell, R. A. Buchanan, C. E. Rist, B. T. Hofreiter, and A. J. Ernst, *Tappi*, **45**(7), 557
(1962).

2. E. B. Bagley and R. J. Dennenberg, *Rubber Age*, **105**(6), 41 (1973).

3. R. E. Wing, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **19**, 847 (1975).

4. B. S. Shasha, W. M. Doane, and C. R. Russell, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 417
(1976).

5. R. W. Faessinger and J. S. Conte, U.S. Patent No. 3,359,224, December 19, 1967.

6. R. W. Faessinger and J. S. Conte, U.S. Patent No. 3,330,787, July 11, 1967.

7. H. E. Teichmann, W. J. Brickman, R. W. Faessinger, C. G. Mayer, and H. A. Krässig, *Tappi*,
57(7), 61 (1974).

8. P. Lepoutre, S. H. Hui, and A. A. Robertson, *J. Appl. Polym. Sci.*, **17**, 3143 (1973).

9. H. Krässig, *Svensk Papperstidn.*, **74**(15), 417 (1971).

10. D. Trimnell, E. I. Stout, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **21**, 655
(1977).

11. R. F. Schwenker, J. L. Lifland, and E. Pacsu, *Text. Res. J.*, **32**, 797 (1962).

12. M. Sakamoto, Y. Yamada, and H. Tonami, *J. Appl. Polym. Sci.*, **13**, 1845 (1969).

13. R. Axén, H. Drevin, and J. Carllson, *Acta Chem. Scand.*, **B29**, 471 (1975).

14. H. Distler, *Angew. Chem., Int. Ed. Engl.*, **6**, 544 (1967).

15. D. C. White, *Mikrochim. Acta*, **807** (1962).

16. C. O. Willits, M. R. Coe, and C. L. Ogg, *J. Assoc. Off. Agric. Chem.*, **32**, 118 (1949).

17. V. Hornof, B. V. Kokta, and J. L. Valade, *J. Appl. Polym. Sci.*, **19**, 545 (1975).

18. C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 1107
(1950).

19. M. Wittwer, U.S. Patent No. 1,976,677, October 9, 1934; German Patent No. 595,174, April
10, 1934.

20. R. E. Wing, W. M. Doane, and C. E. Rist, *Carbohydr. Res.*, **12**, 285 (1970).

21. H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83
(1939).

22. Y. Minoura and Y. Ogata, *J. Polym. Sci., A-1*, **7**, 2547 (1969).