

Sulfonation Studies of Copolymers, Graft Copolymers, and Polymeric Gels Using Phase Transfer Catalysts*

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Synopsis

A new sulfonation method using phase transfer catalysts was applied to sulfonate a number of polymer matrices in an aqueous two-phase system. The polymer matrices included in this study are (1) styrene (Sty) and acrylonitrile (AN) copolymers with glycidyl methacrylate (GMA), (2) graft copolymers of cellulose with GMA, and (3) polystyrene and polyacrylate gels containing GMA as comonomer. The presence of polar groups such as AN in the polymer matrix makes the sulfonation easier. For cellulose graft copolymers, the extent of sulfonation was not much affected by the phase transfer catalysts, presumably due to the high polarity and high water uptake capacity of the cellulose base. For other polymer gels, the following factors influence the extent of sulfonation: (1) the method of gel synthesis, i.e., gels synthesized by delayed addition of GMA give a higher degree of sulfonation; (2) the nature of the crosslinking agent, i.e., gels with ethylene glycol diacrylate (EGDA) gives a higher degree of sulfonation than gels with divinylbenzene (DVB); (3) the pore size of the gels, i.e., gels with larger pore sizes gave higher degree of sulfonation; (4) increasing polarity of the backbone structure of gels favors increased sulfonation, e.g., MMA-GMA-EGDA gels give 54% sulfonation, whereas Sty-GMA-EGDA gives only 38%.

INTRODUCTION

Polymers containing sulfonic acid groups can generally be synthesized by either of the following two methods: (1) by copolymerization with sulfonated monomers such as ethylenesulfonic acid or sodium ethylenesulfonate, or (2) by sulfonation in solution of a preformed polymer. Both methods have their limitations. The former results in the introduction of only small amounts of water-insoluble monomers when copolymerized with sulfonated monomers in aqueous medium. In the direct sulfonation method, it is difficult to control the quality of the sulfonated product because of crosslink formation between pendent sulfonate groups on the polymer chains. Moreover, the sulfonation involves reactive sulfonating agents which give handling problems during the process.

To alleviate the above-mentioned difficulties, we have developed a new sulfonation method.¹ It makes use of preformed copolymers and involves a sulfonation reaction carried out under very mild conditions in a heterogeneous aqueous phase. Our method uses sodium sulfite (Na_2SO_3) as sulfonating agent and as phase transfer catalysts quaternary ammonium salts such as *tetra-n*-butylammonium bisulfate (TBABS) and *tetra-n*-butylammonium bromide (TBAB).

Due to the wide application of polymers containing sulfonic acid groups in many fields, e.g., as aqueous thickeners, impregnants, adhesives, polyelectrolytes,

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and ion exchange resins, the method was used to study the sulfonation of a number of commercially available polymers. This article summarizes the results obtained.

EXPERIMENTAL

Materials

The monomers were purified by distillation under vacuum within 24 h before use and stored at -30° . Crosslinking agents such as EGDA and DVB were used as supplied without further purifications. DVB was of technical grade and had an active content of 55%. Sty, AN, DVB, and EGDA were obtained from KEBO, Stockholm, and GMA from Polysciences, U.S.A. All the solvents used (xylene, dioxane, hexane, and toluene) were of pro analysi grade and obtained from KEBO, Stockholm. Phase transfer catalysts *tetra-n*-butylammonium bisulfate (TBABS) and *tetra-n*-butylammonium bromide (TBAB) were used without further purification as supplied from Labkemi, Stockholm. The radical polymerization initiator 2,2-azobisisobutyronitrile (AIBN) was purified by double recrystallization from absolute alcohol.

Sty-GMA Copolymers

Styrene, 8.74 g (70 mol %), 5.11 g GMA (30 mol %), 40 ml xylene, and 0.1928 g AIBN were placed in a three-neck flask and polymerization was carried out at 60°C for 6 h under nitrogen. In all cases, polymer yield was kept under 10%. Polymers were then isolated by precipitating twice in petroleum ether and then drying at 50°C under vacuum. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) of the polymers were determined by GPC and found to be 37,000 and 22,000, respectively. Polymers were even analyzed for epoxy content and found to have 38.6 mol %.^{2,3}

AN-GMA Copolymers

AN, 15.93 g (70 mol %), 18.30 g GMA (30 mol %), 143 g dioxan, and 0.0342 g AIBN were mixed and polymerization carried out as described in Ref. 2 at 60°C for 3 h. Polymers were isolated again by precipitating twice from petroleum ether and drying at 50°C under vacuum. GMA content was analyzed to be 55 mol %.

Cellulose-GMA Graft Copolymers

Among the different methods used for graft copolymerization onto cellulose, only initiation by Ce^{4+} complex functioned well.⁴ The main reason why the other methods did not function under acidic conditions was perhaps the epoxy ring-opening reaction. The reaction mechanism through Ce^{4+} complex has been described elsewhere.⁵ Grafting was carried out on cellulose beads obtained by the courtesy of Prof. Stramberg. Bead cellulose was used for sulfonation because such a modified product was intended to be used as ion exchange resins, which has many advantages over fiber cellulose because of flow characteristics.⁶ The

beads used had a particle diameter between 0.5 and 1.0 mm. For carrying out graft copolymerization, 2 g cellulose was first swelled in 180 ml distilled water in a three-neck flask overnight and then 11.54 ml GMA and 9.94 ml of a 0.1M aqueous solution of ammoniumcerium(IV) nitrate was added to flask under N_2 gas atmosphere. The contents were heated at 30°C for 90 min under constant stirring. Graft copolymer was isolated by filtration and drying. Unreacted monomers and the homopolymers formed was eliminated by extracting the product first with acetone for 30 h followed by chloroform for 24 h. The degree of grafting and grafting efficiency was determined to be >250 and 76.6%, respectively.

Synthesis of Gels

Sty-GMA and MMA-GMA gels using both DVB and EGDA as crosslinking agents were prepared according to the method described in Ref. 7; 1% of benzoyl peroxide on the monomer basis was used as an initiator. Gels were prepared in two different ways: in one, all the monomers were mixed together and initiation started; in the other, delayed addition technique was used where GMA was added to the reaction mixture after the polymerization reaction had started. Gels were then purified by extractions with $CHCl_3$ for 8 h, dried, and meshed. For the synthesis of MMA-GMA-EGDA gels, 7 g cyanamer 370 (a modified sodium polyacrylate, Cynamid International), 4 g Na_2HPO_4 , and 0.5 g NaH_2PO_4 were added to 600 ml distilled water in a flask. Polymerization was initiated by using 1% on monomer basis of benzoyl peroxide. Solubility parameter of the gels in the reaction medium was controlled by varying the amounts of hexane and toluene.

Sulfonation

Sulfonation was carried out as described earlier¹ at 80°C under an inert gas atmosphere.

Polymer Characterization

Epoxy content of the copolymers was determined as described earlier.^{2,3} Degree of sulfonation was estimated by sulfur analysis discussed earlier,⁸ where sulfur present in the samples was converted to H_2S by reduction. This was then converted to ethylene blue by reacting with *N,N*-diethylphenyldiamine in the presence of Fe^{3+} . Reaction was stopped at 66% conversion by the addition of EDTA which resulted in a complex formation with Fe^{3+} . Salicylate was added to form an ion pair with ethylene blue which was then extracted over to the organic phase. From the measurement of the absorbance of the organic phase in a spectrophotometer, sulfur content in the sample was estimated. Gel morphology was determined by scanning electron microscope. Pore volume and pore diameter were determined by a Micromeritics porosimeter. Gel size and gel size distribution were determined from mesh analysis.

TABLE I
Sulfonation of Sty-GMA Copolymer

Reaction time, h	% Sulfur	% Sulfonation of GMA units
3	0.28	4.27
4	1.10	16.79
5	0.87	13.28
6	1.55	23.66
24	2.75	41.98

Results and Discussion

Sulfonation results of Sty-GMA and AN-GMA copolymers with phase transfer catalyst are summarized in Table I and II, respectively. These tables show that the degree of sulfonation is higher for AN-GMA copolymers than for Sty-GMA copolymers. This is presumably due to the higher polarity of the AN-GMA copolymers than the Sty-GMA copolymers. High polarity would increase the interaction between the sulfite ions in the aqueous phase and the epoxy groups on the polymer chains. This was probably the reason why Svec et al.⁹ could sulfonate poly(GMA) gels to about 18% directly with Na_2SO_3 even without using any phase transfer catalyst.

Sulfonation of cellulose-GMA graft copolymers has earlier been carried out by using Na_2SO_3 - NaHSO_3 .¹⁰ We have investigated the application of our method also to such polymers. It is evident from Table III that the use of phase transfer catalysts such as TBABS and TBAB does not make any remarkable change in the degree of sulfonation after 5 h of reaction. This has been attributed to the very high hydrophilic nature and water uptake capacity of the anhydroglucose moieties in cellulose. It is further evident from Table III that the use of TBAB resulted in a slight decrease in the degree of sulfonation. In order to find a suitable explanation of this behavior as compared to our earlier findings,¹ where a higher degree of sulfonation was obtained with TBAB, the pH of the

TABLE II
Sulfonation of AN-GMA Copolymer

Reaction time, h	% Sulfur	% Sulfonation of GMA units
2	2.54	29.5
5	5.55	64.3

TABLE III
Sulfonation of Cellulose-GMA Graft Copolymers

Type of phase transfer catalyst	% Sulfur	% Sulfonation of GMA units
TBABS	7.4	65.6
No catalyst	7.0	62.5
TBAB	6.85	60.7

TABLE IV
Characteristic Properties of Gels Used for Sulfonation

Gel No.	Gel composition	Crosslinking agent	Hexane amount	Pore volume, cm ³ /g
1	Sty/GMA/DVB (58.3/34.1/8.1)	DVB	44,5 g	1,07
2	Sty/GMA/EGDA (65/30/5)	EGDA	40 ml	0,494
3	MMA/GMA/EGDA (65/30/5)	EGDA	20 ml	1,116
4	MMA/GMA/EGDA (67/30/3)	EGDA	40 ml	0,998

reaction mixture after modification was determined. It was found that when TBAB was used as a catalyst instead of TBABS for sulfonation, a strong basic solution having pH > 10 was obtained. This caused perhaps degradation of cellulose molecules resulting in a lower degree of sulfonation. However, such a degradation is not expected in the case of acrylate copolymers since they are very stable toward alkaline hydrolysis.

This sulfonation method was also used to sulfonate gels. The characteristics of the gels used in our experiments are summarized in Table IV. From sulfonation studies of the polystyrene gels, it has been found that even after 10 h of reaction, the degree of sulfonation was as low as about 5%. When the sulfonation was carried out on gels synthesized by delayed addition of GMA, about 20% sulfonation was obtained already after 2 h of reaction. This shows the role played by the location of the epoxy groups contained in the GMA on the gels. When GMA units are present in larger amounts on the surface of the gels, a higher degree of sulfonation is achieved.

Table V summarizes the sulfonation results on gel type 2 which has been synthesized in a polymerization medium having different solvent composition. Since the reaction is diffusion controlled, a decrease in the % sulfonation may be attributed to the decrease in the pore volume of the gels. It was shown in Table IV that the pore volume decreases with increasing hexane content in the polymerization medium.

TABLE V
Sulfonation of Sty-GMA-EGDA Gels (cf. Type 2 in Table IV)

Polymerization medium (hexane/toluene)	Sulfonation time					
	4 h		6 h		24 h	
	% S	% Sulfonation	% S	% Sulfonation	% S	% Sulfonation
10/10 ml	0.81	11.98	0.83	12.27	2.55	37.72
20/20 ml	0.105	1.55	0.15	2.21	1.2	17.75
40/0 ml	0.34	5.02	0.37	5.57	0.78	11.53

TABLE VI
Sulfonation of MMA-GMA-EGDA Gels (cf. Type 3 in Table IV)

Reaction time, h	% Sulfur	% Sulfonation
4	2.8	41.4
6	2.5	37.0
24	3.65	54.0

From sulfonation studies of gel type 3 (cf. Table IV), as shown in Table VI, it was found that even an increased polarity of the backbone structure of the gels resulted in an increased degree of sulfonation.

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