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Swelling Ratios and Rates of Sulfonation of Solvent Modified Copolymers of Styrene Cross-Linked with Pure m- and Pure p-Divinylbenzene

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Summary

Solvent-modified (toluene) copolymers have been prepared from styrene cross-linked with commercial divinylbenzene, m-divinylbenzene, and p-divinylbenzene at divinyl monomer contents of 16 mole % and 32 mole % at $F_M = 0.50$. The resultant copolymers have been characterized by swelling-ratio determinations and rates of sulfonation at 60 and 80°C. The solvent-modified 16 mole % cross-linked copolymers sulfonated at rates slightly greater than those characterizing the 8 mole % cross-linked copolymers prepared in the absence of diluent. The order of decreasing sulfonation rates for both the conventional 8 mole % cross-linked systems and for the solvent-modified 16 mole % cross-linked copolymers is commercial divinylbenzene/styrene, p-divinylbenzene/styrene, m-divinylbenzene styrene. The 32 mole % cross-linked systems exhibit a different order of decreasing sulfonation rates: commercial divinylbenzene/styrene, m-divinylbenzene/styrene, p-divinylbenzene/styrene. The swelling ratios of the 32 mole % solvent-modified copolymers were comparable to those of the conventional 8 mole % cross-linked systems.

We have previously reported the swelling ratios [1] and rates of sulfonation [2] of polystyrene cross-linked with pure m-, pure p-, mixtures thereof, and commercial divinylbenzene. We have obtained similar data for a series of comparable resins prepared by solvent-modified bead copolymerization techniques [3], which we wish to report herein.

EXPERIMENTAL

Styrene

This was supplied by Distillation Products Company and was purified by vacuum distillation over potassium hydroxide with 2, 6-di-t-butyl-4-methylphenol as inhibitor (N_D^{20} = 1.5468; reported value (25), N_D^{20} = 1.5465).

Commercial Divinylbenzene

This was supplied by the Dow Chemical Company and was purified by vacuum distillation (b.p. 52–53°C at 1 mm) to obtain an inhibitor-free sample (N_D^{20} = 1.5552; reported value, undistilled, N_D^{25} = 1.5585). The analysis provided by the Dow Chemical Company showing the components of the commercial mixture in weight per cent is as follows: m-diethylbenzene, 0.7; p-diethylbenzene, 1.3; m-ethylvinylbenzene, 24.9; p-ethylvinylbenzene, 11.2; m-divinylbenzene, 37.8; p-divinylbenzene, 20.5; mass 144 and 146, 1.8; naphthalene, 1.2; indene, 0.6. This was confirmed by vapor-phase chromatographic analysis in this laboratory [4]. Based upon this composition the divinyl monomer content was calculated and used in determining the amount of cross-linking agent per unit weight of commercial divinylbenzene. The ethylvinylbenzene was taken as added styrene.

m-Divinylbenzene

This monomer was prepared by preparative scale vapor-phase chromatographic fractionation of commercial divinylbenzene supplied by the Dow Chemical Co. Separation was accomplished by use of a Perkin-Elmer R column consisting of 80% Chromosorb W as support and 20 wt. % Ucon LB-550X polypropylene glycol as liquid phase as previously described [4]. The m-divinylbenzene monomer used in the present study was 99.4% pure (N_D^{25} = 1.5755).

p-Divinylbenzene

This was purified by preparative scale vapor-phase chromatographic fractionation of a 91% p-divinylbenzene sample obtained from the Cosden Petroleum Corporation. Separation was performed on a chromatographic column as previously described [5]. The p-divinylbenzene monomer used in this study was 99.2% pure (m.p., 29.5°C, N_D^{35} = 1.5855; reported values [1], m.p., 29.5–30.0°C, N_D^{35} = 1.5857).

Initiator

Dibenzoyl peroxide was purified by recrystallization from a concentrated chloroform solution with methanol addition and carefully dried under vacuum at room temperature.

Dispersion Agent

Carboxymethyl cellulose ether sodium salt supplied by the E.I. DuPont de Nemours and Company was used without further treatment as the dispersion agent for all the bead copolymers prepared for this study. Specifications given by the supplier are as follows: premium refined grade (p-75-H); degree of substitution, 0.65–0.85; Brookfield viscosity (dry basis) for 1% solution at 25°C, 1300–2200 cp.

Diluent

Toluene, Baker "analyzed" reagent, obtained from the J. T. Baker Chemical Company was further purified by distillation.

Copolymerization Procedures

The non-solvent-modified beads were prepared as previously described [1]. For the 16 mole% compositions the charge consisted of 3.8462 g of pure DVB isomer (or 6.5972 g of commercial DVB); 16.1538 g of styrene (or 14.2778 g using commercial DVB); and 0.0400 g of dibenzoyl peroxide (0.0418 using commercial DVB). A suspending solution of 0.5 g of dispersion agent in 280 ml of distilled water was used in a 300-ml flask. The polymerization was run at 80°C, with a Thyrotron controlled, eccentric stirrer at 300 rpm, and for 20 hr. The solvent-modified runs were made using the same quantities except for the addition of 20 g (20.8705 g for commercial DVB runs) of toluene (to give $F_M = 0.50$) to the monomer–initiator solution. The beads were decanted, sieve-sized, washed with water (and then acetone for the solvent-modified types), and finally air-dried at 100°C for 30 min.

Swelling Ratios

Swelling ratios were determined as previously described [1] using the process developed by Freeman [6]. The values are given in the discussion section.

Sulfonation and Capacity Measurements

These were conducted as previously described [1, 2]. The capacities were determined on resins dried (5 days, 110°C, 2 mm vac.) in the acid form by titration of the acid liberated on addition of excess potassium chloride. The data are recorded as milliequivalents of exchange capacity per gram of dry weight of the resins and are presented in Figs. 1–4.

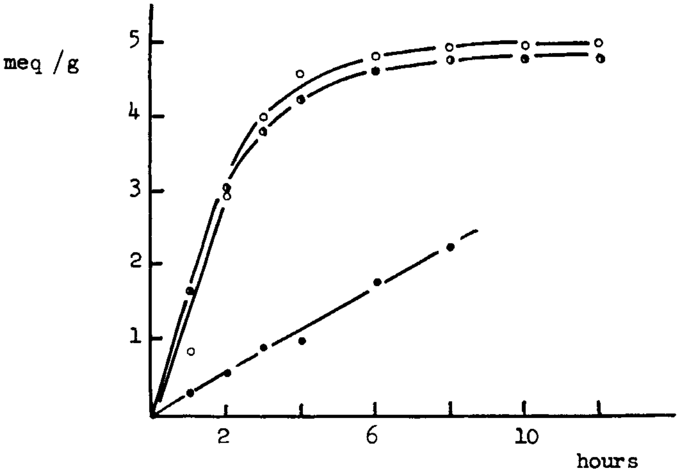

FIG. 1. Rate of sulfonation of solvent-modified styrene/divinylbenzene (16 mole%) bead copolymers at 60°C. O, commercial-DVB; ◑, p-DVB; ●, m-DVB.

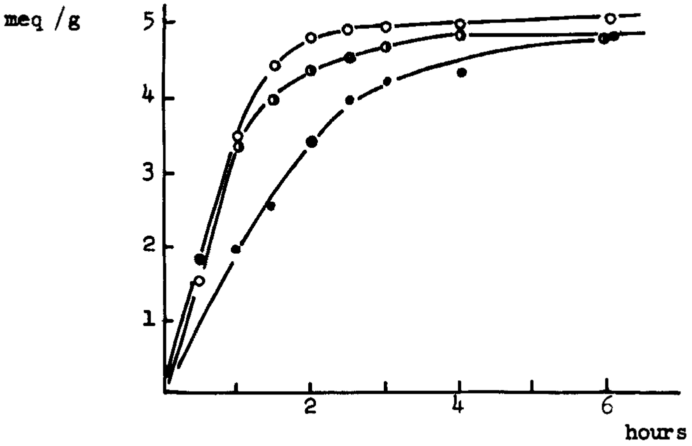

FIG. 2. Rate of sulfonation of solvent-modified styrene/divinylbenzene (16 mole%) bead copolymers at 80°C. O, commercial-DVB; ◑, p-DVB; ●. m-DVB.

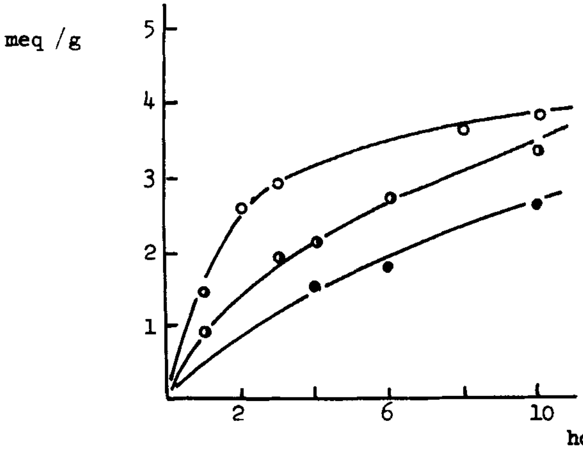

FIG. 3. Rate of sulfonation of solvent-modified styrene/divinylbenzene (32 mole%) bead copolymers at 60°C. ○, commercial-DVB;◑, m-DVB;●, p-DVB.

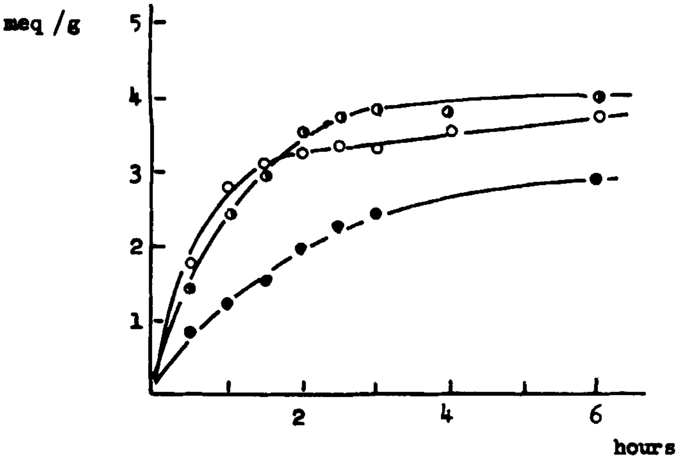

FIG. 4. Rate of sulfonation of solvent-modified styrene/divinylbenzene (32 mole%) bead copolymers at 80°C. ○, commercial-DVB;◑, m-DVB;●, p-DVB.

DISCUSSION

We have previously discussed [7, 8] the evidence indicating the possibility that polymers of polystyrene cross-linked with divinylbenzene have different network structures. This difference derives from the kinetics of the copolymerization, which establish that p-DVB enters the growing polymer chain more rapidly than does m-DVB. The result is a network with, presumably, either clustered p-DVB units or spaced m-DVB units and, from this, differences in the available interstices in the network. The differences, although small, are nonetheless real, and the question now arises as to whether such effects can also be observed in beads with expanded networks prepared by solvent-modified techniques [3]. The data we now have do, in fact, establish such differences.

The swelling ratios of the DVB cross-linked, solvent-modified polystyrene beads show differences similar to those observed for resins prepared without solvent. The swelling ratios of the 32 mole % cross-linked, solvent-modified polymers are 1.88 (meta), 1.58 (para), and 2.10 (commercial). These values stand in the same order but are slightly greater than those previously observed for the 8% non-solvent-modified copolymers; e.g., 1.77 (meta), 1.53 (para), and 1.84 (commercial). The 16 mole % cross-linked, solvent-modified beads show swelling ratios of 1.95 (meta), 2.10 (para), and 2.13 (commercial). It is noted that the order of rate of swelling of the meta and para solvent-modified copolymers is reversed at these two concentrations (16 and 32) and that the commercial DVB resins show little change in swelling ratio. It appears that below a minimum concentration of DVB the structural differences are not operative in either the solvent-modified copolymers or in the non-solvent copolymers, as previously noted [1].

The rates of sulfonation of the solvent-modified beam copolymers are given in Fig. 1–4. Comparisons of the rate data for the 16% solvent-modified DVB resins with the data for non-solvent-modified, 8% cross-linked resins, as previously recorded [7, 8], show that (1) the 16% solvent-modified beads sulfonate more rapidly than the 8% nonsolvent-modified beads both at 60 and 80°C except that at 80°C there is little difference in the rates for solvent-modified and non-solvent-modified beads cross-linked withe commercial-DVB; (2) the order of decreasing rates at both 60 and 80°C is commercial $>$ para $>$ meta cross-linked structures for both solvent-modified and non-modified and non-solvent-modified resins; and (3) at 32% DVB the the order of rate of sulfonation of the meta and para isomers is reversed (meta faster than para) and the rate of the 32% para is less than that of the 16% para. The data for the comparisons, stated as slopes of the initial portions of the rate curves, are given in Table 1.

TABLE 1

Initial Slopes of the Sulfonation Rate Curves

Cross-linking monomer[a]	8 mole% conventional[b]		16 mole% solvent-modified[c]		32 mole% solvent-modified[c]	
	60°C	80°C	60°C	80°C	60°C	80°C
c-DVB	1.7	6.9	2.7	7.0	2.9	7.0
p-DVB	0.1	1.9	3.8	6.5	0.8	3.0
m-DVB	nil	nil	0.6	3.5	2.7	6.0

[a] c-DVB, commercial divinylbenzene; p-DVB, p-divinylbenzene; m-DVB, m-divinylbenzene.

[b] From data previously reported [2].

[c] From Figs. 1–4.

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Zusammenfassung

Losungsmittelmodifizierte (Toluol) Copolymere wurden aus mit handelsüblichem Divinylbenzol, m-Divinylbenzol, und p-Divinylbenzol verzweigtem Styrol hergestellt, wobei der Divinylmonomerengehalt zwischen 16 Mol% und 32 Mol% variiert wurde, bei einem F_M Wert von 0.50. Die erhaltenen Polymeren wurden durch Messungen des

Quellungsverhältnisses und der Sulfonierungsgeschwindigkeiten bei 60 und 80°C charakterisiert. Die lösungsmittelmodifizierten, mit 16 Mol% verzweigten Copolymeren konnten etwas schneller sulfoniert werden als die mit 8 Mole% in Abwesenheit eines Lösungsmittels verzweigten Copolymeren. Folgende Reihe abnehmender Sulfonierungsgeschwindigkeiten für das übliche 8 Mol% verzweigte System als auch für das lösungsmittelmodifizierte, 16 Mol% verzweigte Copolymer wurde gefunden: handelsübliches Divinylbenzol/Styrol, p-Divinylbenzol/Styrol, m-Divinylbenzol/Styrol. Die mit Mol% verzweigten System ergeben eine andere Reihe abnehmender Sulfonierungsgeschwindigkeiten: handelsübliches Divinylbenzol/Styrol, m-Divinylbenzol/Styrol, p-Divinylbenzol/Styrol. Die Quellungsverhältnisse der mit 32 Mol% lösungsmittelmodifizierten Copolymeren und jene des üblichen, mit 8 Mol% verzweigten Systems sind einander ähnlich.

Résumé

On a preparé des copolymères, modifiés par le solvant (toluène), à partir du styrene réticulé avec le divinylbenzène commercial, le meta-divinylbenzène et le para-DVB, à des taux du monomère vinylique de 16% et 32% en mole, à $F_m = 0.5$. Les copolymères obtenus ont été caracterisés par des déterminations du taux de gonflement et des vitesses de sulfonation à 60 et 80°C. Les copolymères, modifiés par le solvant, avec 16% mole de réticulation étaient sulfonés avec des vitesses légèrement superieures que celles caractérisant les copolymeres 8% reticulés, en absence du diluant. L'ordre de vitesses de sulfonation décroissantes pour les deux-le système conventionel réticulé à 8% et les copolymères, modifiés par le solvant, à 16% en mole de réticulation est: divinylbenzène commercial/styrène, para-divinylbenzène/styrène, métadivinylbenzène/styrène. Le système avec le 32% de réticulation montre un ordre différent des vitesses de sulfonations decroissantes: divinylbenzène commercial/styrène, méta-DVB/styrène, para-DVB/styrène. Les taux de gonflement des copolyméres reticulés 32% en mole, modifiés par le solvant, étaient comparables à ceux des systèmes conventionels à 8% de réticulation.