

## Irradiation Stability of Sulfonated Styrene Resins Crosslinked with Various Divinylbenzene Isomers and Mixtures Thereof

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### Synopsis

The  $\text{Co}^{60}$ - $\gamma$ -irradiation-induced degradation of sulfonated styrene resins crosslinked with 4 and 8 mole-% *m*- or *p*-divinylbenzene isomers, or mixtures thereof including commercial divinylbenzene have shown a loss in capacity of 5–12.8% at radiation intensities of ca. 290,000 r./hr. and total doses of  $0.91$ – $1.90 \times 10^8$  rad in the presence of water. The loss is less for the 8% crosslinked resins and is less (2–6%) if irradiated dry. The resins crosslinked with commercial divinylbenzene show a slightly higher loss of capacity (11.2–11.9%) than do others (10.2–10.7%), presumably due to the ethylphenyl contamination. The moisture content also increases on irradiation; 13–16% for the 8% and 2.7–3.0% for the 4% resins at  $1.90 \times 10^8$  rad. The *meta* crosslinked resin shows somewhat lower moisture content increase (1.5% for 8%; 0.8% for 4%), indicative of a more stable cross-linkage. The results are discussed in terms of the reactions involved: desulfonation, hydroxylation, and cleavage of crosslinkages.

### Introduction

This report describes  $\text{Co}^{60}$   $\gamma$ -irradiation stability studies with sulfonated resins of polystyrene crosslinked with various divinyl monomers. The resins were prepared as previously described<sup>1</sup> from styrene and divinyl monomers of specified purity and composition. Comparisons have been made with resins prepared with 4 and 8 mole-% of pure *p*-divinylbenzene, pure *m*-, and pure 2:1/*m*:*p*-mixtures of divinylbenzene (DVB) as separated by preparative vapor phase chromatography from the commercial divinylbenzene mixture. Radiation studies, both wet and dry, have been made and changes in weight loss, loss of capacity, and variation in water content have been noted. The data are presented in Tables I and II. The amount of degradation we have observed is comparable to that reported from other laboratories.<sup>2–6</sup>

### Experimental

The resins were prepared by copolymerization, at 80°C. with 0.5% benzoyl peroxide, of purified styrene and divinylbenzenes: commercial (Koppers Co.); pure *meta*-; pure *para*-; and pure 2:1/*m*:*p*-divinylben-

TABLE I  
 $\text{Co}^{60}$  Irradiation of Sulfonated Polystyrene Resins  
 Crosslinked with 8% Divinyl Monomer

Resin	Dose $\times 10^{-3}$ , rad	Weight loss, %	Moisture content, % water	Capacity, meq./g. <sup>a</sup>	Capacity loss, %	Acid in wash, meq./g. <sup>a</sup>
Dowex 50-X8 (initial) <sup>b</sup>			51.6	5.03		
Dowex 50-X8 (wet)	0.91	3.6	53.3	4.64	7.7	0.23
	0.92		53.5	4.65	7.5	0.32
	1.82	5.7	56.9	4.45	11.5	0.73
	1.90			4.43	11.9	
Dowex 50-X8 (dry)	0.88	1.9	50.4	4.80	4.6	0.21
	0.89	1.9	48.6	4.80	4.6	0.22
	1.73	2.8	50.3	4.74	5.7	0.27
	1.75	2.9	50.4	4.72	6.2	0.27
8% Commercial DVB resin (initial) <sup>c</sup>			44.0	5.29		
8% Commercial DVB (wet)	0.91	4.1	49.7	4.94	6.6	0.34
	1.82	7.2	50.3	4.72	10.8	0.65
	1.90		51.0	4.70	11.2	0.78
8% Commercial DVB (dry)	0.88	2.3	47.2	5.04	4.7	0.21
	0.89	2.9	49.9	5.06	4.3	0.21
	1.73	3.7	48.1	5.00	5.5	0.29
	1.75	3.7	47.6	4.99	5.7	0.35
8% 2:1/m:p- DVB resin (initial) <sup>d</sup>			42.00	5.29		
8% 2:1/m:p- DVB (wet)	0.91	6.5	46.0	4.98	5.8	0.37
	0.92		45.8	5.07	4.2	0.44

(continued)

zene. The vapor-phase characterization of these materials and the preparative techniques used in their separation have been described previously.<sup>8</sup> The details of the bead copolymerization and sulfonation have also been described previously.<sup>1</sup> Beads of 30 mesh sulfonated at 100°C. were used for the present studies. The sulfonated resins were washed repeatedly with distilled water and dried (5 days, 110°C., 1 mm.) to constant weight. Samples (0.5–0.7 g.) were weighed in glass tubes and flushed with oxygen-free nitrogen. Samples to be irradiated dry were sealed under nitrogen. Those to be irradiated wet were treated with distilled water to equilibrate with water, drained, and sealed under air.

Radiations were run at ca. 290,000 r./hr. in a previously described source.<sup>9</sup> After irradiation the samples were washed by decantation to remove water-soluble material until no further acidity was present in the

TABLE I (continued)

Resin	Dose $\times 10^{-3}$ , rad	Weight loss, %	Moisture content, % water	Capacity, meq./g. <sup>a</sup>	Capacity loss, %	Acid, in wash, meq./g. <sup>a</sup>
	1.82	7.8	46.8	4.80	9.3	0.66
	1.90		47.4	4.75	10.2	0.81
8% 2:1/ <i>m</i> : <i>p</i> - DVB (dry)	0.89	2.3	45.6	5.12	3.2	0.23
	0.90	2.2	46.2	5.16	2.5	0.20
	1.73	3.5	44.4	5.02	5.1	0.26
	1.75	2.8	43.8	5.05	4.5	0.26
8% <i>p</i> -DVB (initial) <sup>c</sup>			43.8	5.33		
8% <i>p</i> -DVB (wet)	0.91	5.3	46.9	4.95	7.1	0.34
	1.14		59.6	4.87	8.6	0.38
	1.82	7.1	49.2	4.76	10.7	0.71
8% <i>p</i> -DVB (dry)	0.88	2.8	46.7	5.15	3.4	0.21
	0.90	2.5	45.0	5.15	3.4	0.22
	1.73	3.6	46.6	5.05	5.2	0.31
	1.75	3.2	46.5	5.09	4.5	0.31
8% <i>m</i> -DVB (initial) <sup>f</sup>			49.1	5.30		
8% <i>m</i> -DVB (wet)	0.91	3.1	48.7	5.00	5.8	0.40
	1.14	4.4	49.0	4.92	7.2	0.42
	1.80	4.9	49.8	4.75	10.4	0.41
	1.90		50.5			0.51
8% <i>m</i> -DVB (dry)	0.84	2.3	48.9	5.14	3.1	0.24
	1.73	3.6	48.0	5.02	5.3	0.28
	1.75	3.0	47.2	5.03	5.2	0.26

<sup>a</sup> On dry resin.

<sup>b</sup> Commercial resin (Baker Analyzed).

<sup>c</sup> Resin from styrene and 8 mole-% commercial divinylbenzene based on 55% divinyl content.

<sup>d</sup> Resin from styrene and 8 mole-% 2:1/*m*:*p* divinylbenzene.

<sup>e</sup> Resin from styrene and 8 mole-% *p*-divinylbenzene.

<sup>f</sup> Resin from styrene and 8 mole-% *m*-divinylbenzene.

wash water. The washings were titrated to determine the amount of acid removed and the resins were dried as before to determine weight loss. Moisture content was determined as described previously.<sup>2</sup> Capacities were determined by treatment with potassium chloride and back-titration.<sup>10</sup>

## Results

The data reported herein on loss in capacity on irradiation for four types of resins are in accord with previously reported values. Thus, for 8% crosslinked wet resins at a total dose of  $1.9 \times 10^8$  rad at ca. 290,000 r./hr. our data show a loss in capacity of 10–11%. Capacity losses in this same range and at similar dose rate levels, but apparently dose rate-dependent,

TABLE II  
Co<sup>60</sup> Irradiation of Sulfonated Polystyrene Resins  
Crosslinked with 4% Divinyl Monomer

Resin	Dose × 10 <sup>-3</sup> , rad	Weight loss, %	Moisture content, % water	Capacity, meq./g. <sup>a</sup>	Capacity loss, %	Acid in wash, meq./g. <sup>a</sup>
Dowex 50-X4 (initial) <sup>b</sup>			66.3	5.00		
Dowex 50-X4 (wet)	0.91 1.82	2.0 6.1	66.0 68.5	4.75 4.50	5.0 10.0	0.20 0.51
Dowex 50-X4 (dry)	0.85 1.66	1.4 4.2	65.4 64.5	4.88 4.77	2.4 4.6	0.21 0.36
4% Commercial DVB resin (initial) <sup>c</sup>			67.5	5.32		
4% Commercial DVB (wet)	0.91 1.82	3.7 6.4	67.7 69.7	4.91 4.55	7.7 12.8	0.34 0.73
4% Commercial DVB (dry)	0.85 1.66 1.70	2.1 3.2 3.1	67.5 66.2 66.4	5.20 5.05 5.05	2.3 5.1 5.1	0.16 0.31 0.31
4% 2:1/ <i>m</i> : <i>p</i> - DVB (initial) <sup>d</sup>			63.0	5.34		
4% 2:1/ <i>m</i> : <i>p</i> - DVB (wet)	0.91 1.76 1.80	3.7	63.1 64.3 64.6	5.04 4.70 4.68	5.6 12.0 12.3	0.30 0.60 0.69
4% 2:1/ <i>m</i> : <i>p</i> - DVB (dry)	0.85 1.67 1.70	2.1	62.9 63.3 62.1	5.23 5.09 5.09	2.1 4.8 4.8	0.16 0.27 0.23
4% <i>p</i> -DVB (initial) <sup>e</sup>			60.8	5.34		
4% <i>p</i> -DVB (wet)	0.91 1.76	4.3 7.9	61.4 62.5	4.96 4.70	7.1 12.0	0.37 0.59
4% <i>p</i> -DVB (dry)	0.85 1.66 1.70	2.8 2.9 2.7	61.1 61.6 61.9	5.23 5.10 5.08	2.1 4.5 4.9	0.16 0.26 0.23
4% <i>m</i> -DVB (initial) <sup>f</sup>			62.6	5.32		
4% <i>m</i> -DVB (wet)	0.91 1.80	3.3 5.9	62.7 63.1	5.04 4.68	6.5 12.0	0.37 0.65
4% <i>m</i> -DVB (dry)	0.84 1.66	1.8 2.4	61.7 61.4	5.18 5.07	2.6 4.7	0.21 0.22

<sup>a</sup> On dry resin.

<sup>b</sup> Commercial resin (Baker Analyzed).

<sup>c</sup> Resin from styrene and 4 mole-% commercial divinylbenzene based on 55% divinyl content.

<sup>d</sup> Resin from styrene and 4 mole-% 2:1/*m*:*p*-divinylbenzene.

<sup>e</sup> Resin from styrene and 4 mole-% *p*-divinylbenzene.

<sup>f</sup> Resin from styrene and 4 mole-% *m*-divinylbenzene.

have been reported by others.<sup>4</sup> The data are summarized in the following paragraphs and presented in detail in Tables I and II.

**Resins Irradiated in the Wet State.** The weight loss varies from 2.0 to 7.9% and increases from 2.0 to 6.5% and from 4.9 to 7.9% with increase in total dose from  $0.91 \times 10^8$  to  $1.90 \times 10^8$  rad for various resins of 4 and 8% divinyl content.

The loss in capacity varies from 5% to 12.8% and is greater for resins with less crosslinking. Thus, under comparable conditions, resins of 8% divinyl content show 10.2% loss and resins of 4% divinyl content show 12.3%. There is a difference in loss of capacity in the various 8% divinyl resins. The Dowex 50-X8 and commercial divinylbenzene resins lose 11.2–11.9% of their capacity under conditions which give 10.2–10.7% loss in resins prepared with other divinylbenzenes.

The moisture content of the resins increases. Thus, the 8% divinyl resins show an increase of 13–16% after  $1.90 \times 10^8$  rad irradiation dose. For the 4% resins the increase is less: 2.7–3.0%. The *m*-divinylbenzene-crosslinked resins show less moisture content increase: 1.5% increase for 8% and 0.8% for 4%-*m*-divinyl.

**Resins Irradiated in the Dry State.** The weight loss is 2–3.5% over the dose range of  $0.85$ – $1.75 \times 10^8$  rad and is, thus, significantly less than that for the wet resins. The loss in capacity varies from 2.1 to 6.2% over the dose range of  $0.85 \times 10^8$ – $1.75 \times 10^8$  rad and is again less than that for the wet resins. There is, however, not much difference in loss of capacity at 4 and 8% divinyl content for the dry resins. Thus, the loss for the 4% divinyl resins is 2.1–5.1% and for the 8% resins is 3.1–6.2%. The Dowex 50-X8 and 8% commercial divinylbenzene resins show a 6.2% loss and thus appear to be somewhat more sensitive to loss of capacity on irradiation than do the other resins for which the loss is 4.5–5.2%.

The moisture content in most cases decreases (from 1.5 to 3.0%) with increase in total irradiation dose. There is an increase of 2–6% for some resins which is, however, less than that for the wet resins (13–16%).

### Discussion

These data show some differences which may be related to structural alterations in the polymer network structure. The Dowex 50-X8 and 8 mole-% commercial divinylbenzene-crosslinked resins (both wet and dry) are somewhat more sensitive to irradiation decomposition than are the other resins. At a total dose of  $1.9 \times 10^8$  rad these two lose 11.2–11.9% of their exchange capacity when irradiated wet and 6.2% when irradiated dry as compared to 10.2–10.5% and 4.5–5.2%, respectively, for the other resins under comparable conditions. It thus appears that there is present among the eight to ten components of the commercial divinylbenzene mixture a material which enhances irradiation instability of the copolymers prepared therefrom. Presumably, this is the ethylvinylbenzene.

The absence from these irradiation data of a difference in rate of loss of capacity between the *m*- and *p*-divinylbenzene-crosslinked structures

requires explanation. Irradiation-induced loss of capacity involves a loss of sulfonic groups or desulfonation reaction. The same structural factors which presumably create the difference in rate of sulfonation<sup>7</sup> for the *meta* and *para* structures should be operative in the irradiation-induced desulfonation. The fact that the difference does not appear in the data indicates that other irradiation-induced reactions, such as hydroxylation and breaking of crosslinkages, obscure the distinctions. It is possible that resins prepared at 80°C. (as used in the sulfonation studies) rather than at 100°C. (as used in the irradiation studies) would show differences. Correlations with kinetic data for other types of degradation reactions are to be reported.

There is a difference in the increase in water content of the *m*-divinylbenzene-crosslinked resins. The *meta* resins show less increase: 1.5 instead of 13% for 8% divinyl; 0.8% instead of 3.0% loss for 4% divinyl. This may be a result of a decrease in rate for the irradiation-induced hydroxylation reaction or, more likely, a decreased cleavage of the *meta* type of crosslinkages.

The lesser increase in water content after irradiation of the dry resins as compared to the wet resins requires comment. One would have expected that the decreased loss of sulfonic groups (decreased loss of capacity) would be reflected in an increased moisture content. Apparently, the crosslinkages are more stable in the dry resins, or additional crosslinkages, perhaps of the sulfone type, are formed to give or leave a tighter network.

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### Résumé

On a étudié la dégradation des résines styréniques sulfonées, pontées au moyen de 4 et 8 mole-% d'isomères *mé*ta- ou *para*-de divinylbenzène ainsi qu'au moyen de mélanges comprenant du "divinylbenzène" commercial. Cette dégradation a été réalisée par irradiation-gamma au moyen de cobalt-60 et a montré une perte de capacité de 5 à 12.8% pour des intensités de radiation d'environ 290.000 r/hr et pour des doses totales de 0.91 à  $1.90 \times 10^8$  rad en présence d'eau. La perte est moindre pour les résines pontées à 8% et moindre encore (2-6%) si l'irradiation se fait à l'état sec. Les résines pontées avec du divinylbenzène commercial montrent une perte de capacité un peu plus élevée (11.2-11.9%) que les autres (10.2-10.7%), due probablement à la contamination par l'éthylbenzène. La teneur en humidité augmente aussi par irradiation: 13-16% pour les résines à 8% et 2.7-3.0% pour celles à 4% sous  $1.90 \times 10^8$  rad. Les résines pontées en *mé*ta montrent un accroissement de la teneur en humidité quelque peu plus faible (1.5% pour les résines à 8%, et 0.8% pour celles à 4%), ce qui indique un pontage plus stable. On a discuté les résultats sur la base de réactions telles que la désulfonation, l'hydroxylation et la rupture du pontage.

### Zusammenfassung

Der durch Kobalt-60-Gammastrahlung induzierte Abbau von sulfonierten Styrolharzen, welche mit 4 und 8 Mol% *meta* oder *para*-Divinylbenzolisomeren oder ihren Mischungen einschliesslich des handelsüblichen "Divinylbenzols," vernetzt waren, führte bei Strahlungsintensitäten von etwa 290.000 r/h und Gesamtdosen von 0,91 bis  $1,90 \times 10^8$  rad in Gegenwart von Wasser zu einem Kapazitätsverlust von 5 bis 12,8%. Der Verlust ist bei dem zu 8% vernetzten Harzen und bei Bestrahlung im trockenen Zustand geringer (2-6%). Die mit handelsüblichem Divinylbenzol vernetzten Harze zeigen wahrscheinlich wegen des Äthylphenylgehaltes einen etwas höheren Kapazitätsverlust (11,2-11,9%) als andere (10,2-10,7%). Der Feuchtigkeitsgehalt nimmt bei der Bestrahlung ebenfalls zu; 13-16% für die 8%- und 2,7-3,0% für die 4%-Harze bei  $1,90 \times 10^8$  rad. Das *meta*-vernetzte Harz zeigt eine etwas geringere Zunahme des Feuchtigkeitsgehalts (1,5% für 8%; 0,8% für 4%), was für eine stabilere Vernetzung spricht. Die Ergebnisse werden anhand der auftretenden Reaktionen, nämlich Desulfonierung, Hydroxylierung und Spaltung von Vernetzungstellen diskutiert.

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