JOURNAL OF APPLIED POLYMER SCIENCE VOL. 9, PP. 2655–2659 (1965)

Furfural-Based Ion-Exchange Resins. Part I. Preparation and Properties of a Cation Exchanger from Furfural–Styrene Reaction Product

B. D. DASARE and N. KRISHNASWAMY, *National Chemical Laboratory Poona, India*

Synopsis

The preparation and properties of a cation-exchange resin with polyfunctional groups from the reaction product of styrene and furfural is described.

Furfural has been shown to react with various materials, yielding base and cation-exchange resins.[1] Reports have also appeared of cation exchangers prepared by reaction of furfural with acid halides,[2] lignin,[3,4] and poly(vinyl alcohol) and its derivatives.[5]

Conventional ion-exchange resins based on styrene–divinylbenzene copolymer are well known.[6] Furfural reaction product with styrene and polymers,[7] copolymers of styrene with furan or monoalkyl furan,[8] and butadiene–styrene–furfural copolymers[9] have yielded products suitable as coating compositions. Styrene and aldehydes are listed as types of monomers responding to cationic polymerization.[10] Hence it was of interest to study the polymerization of styrene in presence of furfural and zinc chloride and investigate the possibility of utilizing the reaction product for further treatment to introduce ionogenic groups. Preliminary results indicated that without the addition of furfural to the reaction mixture of styrene and zinc chloride, it was not possible to obtain a thermoset product after curing. With increased amount of furfural added in the system, it was possible to obtain a thermoset product after curing.

EXPERIMENTAL

Preparation of Polymer

Styrene and furfural (both distilled) were reacted in the presence of zinc chloride till a gel was obtained. Tables I and II give the various details.

Sulfonation of Polymer

The polymer obtained in each case was crushed to definite mesh size and sulfonated under conditions set down in Tables III–V. The exchange capacities determined by standard methods are also tabulated.

pH Titration Curve

The standard procedure was adopted to characterize the resin. The resin was first extracted with benzene and later washed with water, regenerated, air-dried, and taken for the study.

NMR Spectra

A sample of the resin was studied in the Varian A60 NMR spectrometer according to the procedure of DeVilliers and Parrish.[11]

RESULTS

Styrene and furfural in the molar ratio of 1:1 were refluxed in the presence of different concentration of zinc chloride (based on the weight of styrene), and the time taken for obtaining a gel is given in Table I. The resulting gel was kept in an oven maintained at 100°C. for a period of about 6 hr. The nature of the polymer obtained is also indicated in Table I.

TABLE I

No.	Catalyst, %	Average gelling time, hr.	Nature of cured polymer
1	1.0	No gelling up to 20	Dark brown thermoplastic
2	2.0	15	" " "
3	3.0	8–11	Dark brown thermoset
4	6.0	2.5–3	" " "

Keeping the catalyst concentration at 3.0% (based on the weight of styrene) furfural was taken in different proportions for refluxing with styrene, and as above, the gelling time was noted; the nature of polymer after curing under conditions mentioned above is also indicated in Table II.

TABLE II

No.	Molar ratio styrene/furfural	Average gelling time, hr.	Nature of polymer
1	1.0:0.05	No gelling up to 20	Dark brown thermoplastic
2	1.0:0.5	6–8	" " "
3	1.0:1.0	8–11	Dark brown thermoset
4	1.0:1.5	5–6	" " "
5	1.0:2.0	4–5	" " "
6	1.0:3.0	3–4	" " "

The polymers obtained with different ratios of styrene and furfural after curing at 100–110°C. for a period of 6 hr. were subjected to sulfonation for 2 hr. at 100°C. with the use of concentrated sulfuric acid at an acid to polymer ratio of 10:1. The exchange capacity of the resin obtained is given in Table III.

TABLE III

No.	Molar ratio styrene/furfural	Nature of resin	Average capacity, meq./g.	
			Salt breaking	Total
1	1.0:0.5	Thermoplastic	3.0–3.4	3.8–4.0
2	1.0:1.0	Thermoset	2.7–3.1	4.0–4.2
3	1.0:1.5	Thermoset	2.6–2.8	3.6–3.9
4	1.0:2.0	Thermoset	2.0–2.5	3.0–3.5

For all further experiments, styrene and furfural were refluxed in the ratio of 1:1, and the gel obtained after curing at 100–110°C. for 6 hr. was taken for sulfonation employing a ratio of polymer to acid as 1:10. The temperature of sulfonation and period of sulfonation were studied and the results are presented in the tables. Table IV gives the capacity of the resin obtained after sulfonation for 6 hr. at different temperatures indicated.

Results obtained after sulfonation for different periods of time at controlled temperatures are presented in Table V.

TABLE IV

No.	Sulfonation temperature, °C.	Average capacity, meq./g.	
		Salt breaking	Total
1	25	Nil	Nil
2	40	2.2–2.7	2.9–3.4
3	50	2.5–2.9	3.2–3.5
4	75	2.6–3.0	3.6
5	100	2.8–3.1	4.0–4.2

TABLE V

No.	Sulfonation temperature, °C.	Period of sulfonation, hr.	Average capacity, meq./g.	
			Salt breaking	Total
1	100	2	2.8–3.1	4.0–4.2
2	100	4	2.8–3.1	4.0–4.2
3	100	6	2.8–3.1	4.0–4.2
4	75	2	2.4–2.8	3.4
5	75	4	2.4–2.8	3.4
6	75	6	2.6–3.0	3.6
7	50	2	2.1	2.6
8	50	4	2.1–2.6	2.9–3.2
9	50	6	2.5–2.9	3.2–3.5
10	50	8	2.5–2.9	3.2–3.6
11	40	2	2.0	2.6
12	40	4	2.1–2.2	2.9–3.0
13	40	6	2.2–2.7	2.9–3.4
14	40	8	2.4–2.7	3.0–3.5
15	25	2, 4, and 6	Nil	Nil

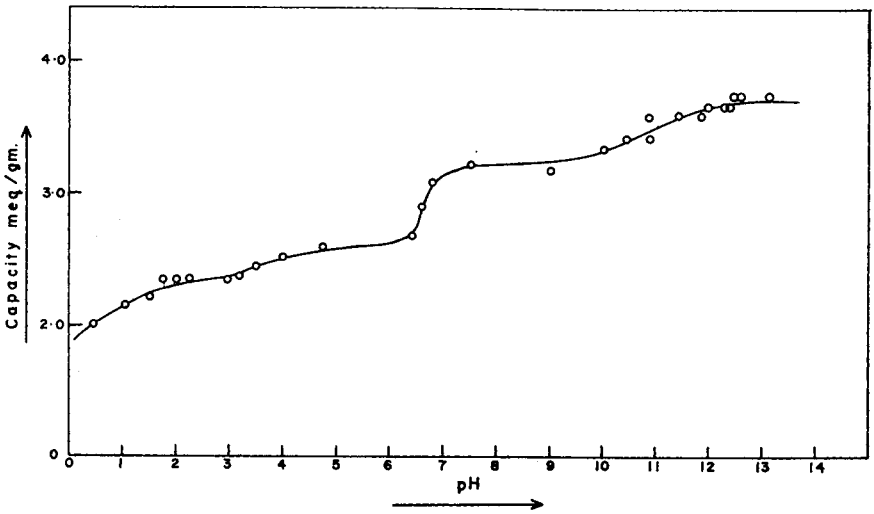

Fig. 1. pH titration curve of sulfonated styrene–furfural resin.

This shows that at 100°C. there is no variation in capacity on changing the period of sulfonation from 2 to 6 hr. At lower temperatures (up to 40°C.), total capacity increases with period of sulfonation. No reaction was observed at 25°C.

These data, in conjunction with the pH titration curve (Fig. 1) for a resin (prepared with styrene to furfural in 1:1 molar ratio and sulfonating at 100°C. for 2 hr.), show that a cation-exchange resin with polyfunctional properties is obtained. NMR spectra revealed the presence of a resin with a homogeneous structure. The carboxyl group activity in the resin is attributed to the action of sulfuric acid on the aldehyde group in furfural, and this could be reduced to the minimum by controlling the conditions of sulfonation. Khundkar et al.[4] have also provided evidence for carboxyl group activity in the furfural resins studied by them. Recently Helfferich and Luten[12] have reported the preparation of an ion-exchange resin with carboxyl and sulfonic groups which is useful as an oxygen transfer resin after further treatment. Since the sulfonated product from the styrene–furfural reaction exhibits both sulfonic and carboxyl activity it is being investigated for the same purpose along with column characteristic studies of the normal resin.

References

1. Dunlop, A. P., and F. N. Peters, *The Furans*, Reinhold, New York, 1953, p. 796.
2. Dudley, J. R., U. S. Pat. 2,420,419 (May 13, 1947).
3. Mahmood, A. J., M. Z. Rahman, and M. H. Khundkar, *Proc. Pak. Sci. Conf.*, **12**, c6 (1960).
4. Khundkar, M. H., and A. J. Mahmood, *Pak. J. Sci. Ind. Res.*, **5**, 147 (1962).
5. Kuriyama, S., and C. Yamashita, *Kogyo Kagaku Zasshi*, **63**, 1660 (1960).
6. Helfferich, F., *Ion-Exchange*, McGraw-Hill, New York, 1962.
7. Caplan, S., and W. F. Schaufelberger, U. S. Pat. 2,338,231 (Jan. 4, 1944).

8. Cairns, T. L., A. W. Larcher, and B. C. McKusick, U. S. Pat. 2,479,306 (August 16, 1949).
9. Harvey, M. T., and P. L. Rosamilia, U. S. Pat. 2,976,264 (March 21, 1961).
10. Ham, G., Ed., *Copolymerization* (*High Polymers*, Vol. XVIII), Interscience, New York, 1964, pp. 286–87.
11. DeVilliers, J. P., and J. R. Parrish, *J. Polymer Sci.*, **2**, 1331 (1964)
12. Helfferich, F., and D. B. Luten, Jr., *J. Appl. Polymer Sci.*, **8**, 2899 (1964).

Résumé

On décrit la préparation et les propriétés d'une résine échangeuse de cations possédant des groupes polyfonctionnels. Cette résine est le produit de réaction du styrène et du furfural.

Zusammenfassung

Darstellung und Eigenschaften eines Kationenaustauscherharzes mit polyfunktionellen Gruppen aus dem Reaktionsprodukt von Styrol und Furfural wurde beschrieben.

Received February 8, 1965