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Rates of Sulfonation of Bead Copolymers of Styrene Cross - Linked with Mixtures of m- and p-Divinylbenzene

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Rates of Sulfonation of Bead Copolymers of Styrene Cross-Linked with Mixtures of m- and p-Divinylbenzene

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Summary

The rate of sulfonation of bead copolymers of styrene cross-linked with 8 mole % divinylbenzene (mixed isomers) is remarkably sensitive to the isomeric (para/meta) composition of the mixture of divinylbenzenes. The rate is enhanced by a factor of 4 for compositions containing 20–40% para isomer.

In previous reports [1, 2] we have described variations in the rates of sulfonation of bead copolymers of styrene cross-linked with pure para-, pure meta-, a pure 2:1 mixture of meta-, and para-, and commercial (11 or 12 components) divinylbenzene. The data indicate an enhanced rate of sulfonation for the 2:1 mixture. To delineate the precise structure/reactivity relation inherent in this situation, we have studied the rate of sulfonation of series of bead copolymers prepared from styrene and 8 mole % divinylbenzene in which the meta/para ratio of the two isomers was varied over the entire range.

The data now available for the rates of sulfonation of this series of bead copolymers are summarized in Fig. 1, in which the initial slope of the rate curve (in meq/g/hr) is plotted against the mole fraction of p-DVB. For compositions containing 20–40% p-DVB, in the 8% of divinylbenzene used as cross-linking agent, the rate of sulfonation is enhanced by a factor of up to 4. Except for the copolymer beads cross-linked with pure m-DVB, for which the rate

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of sulfonation is very low (ca. 0.1), a variety of compositions, outside the 20–40% range, show rates of 0.5–1.5. For compositions containing 20–40% p-DVB (in the 8% of DVB) the values are 2.75–3.90 meq/g/hr. The rate for the 30:70 (para/meta) composition is estimated to be 3.90 meq/g/hr.

It is concluded that the primary gel network structure is different in these copolymers and that the structure formed from the mixture of 30% of p-divinylbenzene (70% meta) mixture is characteristically significant in determining a maximum for the rate of sulfonation. Presumably the interstices of the network in these copolymers are of the optimum size to allow access of the sulfonating species to the reacting benzenoid rings.

EXPERIMENTAL

The methods used for the separation [3] and characterization of the DVB isomers, the bead copolymerizations [4], and sulfonation

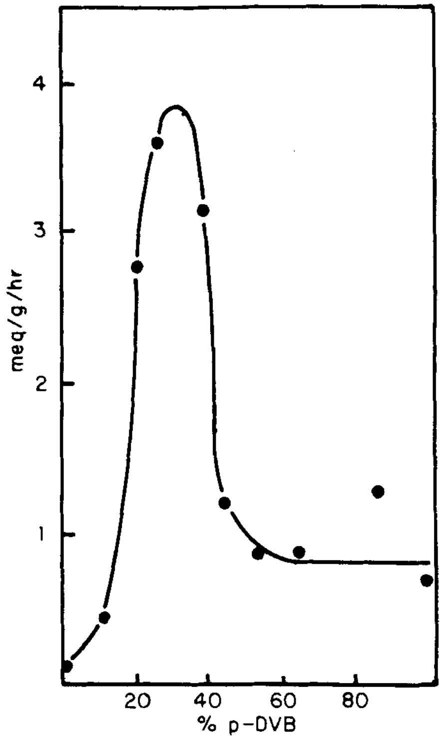

FIG. 1. Rates of sulfonation in meq/g/hr of polystyrene cross-linked with 8% of varying mixture of m- and p-divinylbenzene.

rate measurements [1, 2] have all been described in detail in previous publications. The isomeric monomers were 99.9+% pure. Thirty mesh beads prepared at 80°C with carboxymethylcellulose suspending agent and 0.1 wt. % benzoyl peroxide initiator were used. Sulfonations were run at 80°C with 98% sulfuric acid on beads swollen in ethylene dichloride. Titrations were made on aliquot samples of the beads by titration after adding the washed beads to 100 ml of 0.02 N potassium chloride. The relative rates are recorded as slopes of the initial (linear) portion of the sulfonation rate curves, in meq/g of dry resin/hr. The data are given in Fig. 1.

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REFERENCES

[1] R. H. Wiley and T. K. Venkatachalam, *J. Polymer Sci.*, **4**, 1892 (1966).
[2] R. H. Wiley and T. K. Venkatachalam, *J. Polymer Sci.*, **A3**, 1063 (1965).
[3] R. H. Wiley and R. M. Dyer, *J. Polymer Sci.*, **A2**, 3153 (1964).
[4] R. H. Wiley, J. K. Allen, S. P. Chang, K. Musselman, and T. K. Venkatachalam, *J. Phys. Chem.*, **68**, 1776 (1964).

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Zusammenfassung

Die Sulfonierungsgeschwindigkeit von Perlcopolymeren aus Styrol, das mit 8 Mol% Divinylbenzol (Isomerengemisch) verzweigt ist, ist in erstaunlich empfindlicher Weise von der Isomerenzusammensetzung (para/meta) des Divinylbenzolgemisches abhängig. Die Geschwindigkeit vergrössert sich um den Faktor vier für Zusammensetzungen mit 20–40% des para Isomeren.

Résumé

La vitesse de sulfonation des copolymères en perle du syrène, reticulés avec 8 pour cent de divinylbenzène (mélange d'isomères), est sensible d'une maniére rémarquable à la composition isomérique (para/méta) du mélange de divinylbenzènes). La vitesse est augmentée par un facteur de quatre pour une composition containant 20–40% de l'isomère para.