Synthesis

Block Copolymers by Combinations of Cationic and Radical Routes
3. A New Method for the Preparation of Macroporous Beads of Poly(Styrene-co-Divinylbenzen)

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SUMMARY
A new method is described for the production of macroporous beads by copolymerization of styrene and divinylbenzene initiated by azo linked polytetrahydrofuran, which was obtained by silver salt-diacid chloride technique. Swelling properties of the beads in various solvents were studied.

INTRODUCTION
Recently, we have presented a new conceptual approach to prepare block copolymers by combinations of cationic and radical routes. (YAĞCI, 1985 a) The method involves a two-stage procedure first the synthesis of a prepolymer \( (M_1)_n \), namely polytetrahydrofuran \( (p-THF) \) containing one azo linkage in the main chain,

\[
\begin{align*}
\text{Cl} - C - CH_2 - CH_2 - C - N = N - C - CH_2 - CH_2 - C - Cl \\
\text{CN} & & \text{CN}
\end{align*}
\]

\( (I) \)

\[
\begin{align*}
2\text{AgBF}_4 & \rightarrow \text{AgCl} \\
\text{THF} & \rightarrow
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & & \text{CH}_3 \\
\text{pTHF} - C - CH_2 - CH_2 - C - N = N - C - CH_2 - CH_2 - C - p\text{THF} & \rightarrow & \text{pTHF} - C - CH_2 - CH_2 - C - \text{pTHF}_n \\
\text{CN} & & \text{CN} & & \text{CN}
\end{align*}
\]

\( (II) \)

and, secondly decomposition of this azo linkage in the presence of vinyl monomer, \( M_2 \).

\[
\begin{align*}
\text{M}_2, & \rightarrow \text{N}_2 \\
\text{pTHF} - C - CH_2 - CH_2 - C - \text{pTHF}_n & \rightarrow \text{etc.}
\end{align*}
\]

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A different sequence of the same procedure may also be employed (YACCI, 1985 b). Common feature of the both methods is the overall structure of the block copolymers depends on the mode of termination by disproportionation and/or by addition of the vinyl monomer.

Porous beads by copolymerisation of styrene (st) and divinylbenzen (DVB) have attracted interest in recent years and found applications in many fields including ion exchange, gel permeation chromatography and catalyst support. In these applications, porosity is generally achieved by inert additives that are present in the monomer mixture.

We describe here the use of azo linked poly THF as an initiator for copolymerization of st and DVB. This procedure has allowed us to prepare macroporous beads without any additives and show further the general value of the combined system for block copolymer synthesis.

EXPERIMENTAL

Materials:

THF and st were purified by the conventional drying and distillation procedures. DVB, used as supplied, was a mixture containing 55% DVB isomers and 45 ethyl vinylbenzenes. 4,4'-azo bis-cyano pentanoic acid (ACPA), AgBF₄(Fluka) and the solvents were used as supplied.

Preparation of azo-linked p·THF

For this purpose, silver salt assisted oxo-carbenium polymerization of THF was carried out as described earlier (YACCI, 1985 a). High concentrations of diacid chloride and AgBF₄ were deliberately chosen so as to obtain low molecular weight polyTHF. Number average molecular weight of polyTHF was estimated from measurements of solution viscosity in benzen at 30°C with the aid of the relationship (KURATA et al. 1965).

\[ [\eta] = 1.31 \times 10^{-3} M_n^{0.6} \]

Preparation of poly(st-co-DVB)beads:

Functional polyTHF was reprecipitated from THF into distilled water at least two times in order to remove unreacted ACPA before used as an initiator. Poly(st-co-DVB) beads were prepared by suspension polymerization of a mixture of st and DVB (AKAR et al. 1983). St and DVB mixture containing some azo-linked polyTHF was added to a stirred solution of gelatine in water at 80°C over 10 min. Polymerization was continued until the beads became hard; then the beads were filtered off and dried.

RESULTS AND DISCUSSION

There is, to date, no report on the use of macroinitiators for the preparation of poly(st-co-DVB) beads. However, poly-styrene has been used as a polymeric additive in the monomer