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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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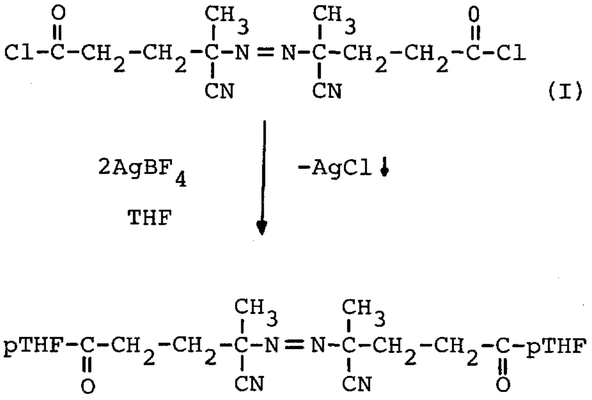
SUMMARY

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,



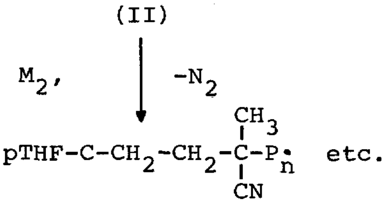
$$Cl-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl \qquad \text{(I)}$$

$$\Big\downarrow \; 2AgBF_4,\ THF \quad -AgCl\downarrow$$

$$pTHF-\underset{O}{\underset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\underset{O}{\underset{\|}{C}}-pTHF$$

(II)

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



$$\text{(II)} \xrightarrow[M_2,]{-N_2} pTHF-C-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-P_n^{\bullet} \quad \text{etc.}$$

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A different sequence of the same procedure may also be employed (YAĞCI, 1985 b). Common feature of the both methods is the overal 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 permation chromatography and catalyst support. In these applications, porousity 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 distilation procedures. DVB, used as supplied, was a mixture containing 55% DVB isomers and %45 ethyl vinylbenzenes. 4,4'-azo bis-cyano pentanoic acid (ACPA), $AgBF_4$ (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 (YAĞCI, 1985 a). High concentrations of diacid chloride and $AgBF_4$ were deliberately chosen so as to obtain low molecular weight poly THF. Number avarage molecular weiht of polyTHF was estimated from measurments of solution viscosity in benzen at 30°C with the aid of the relationship. (KURATA et al.1965).

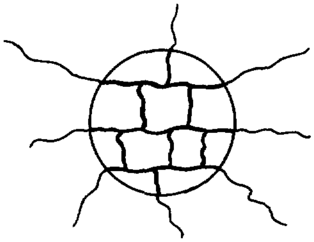
$$[\eta] = 1.31.10^{-3}\, M_n^{0.6}$$

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° 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, polystyrene has been used as a polymeric additive in the monomer mixture to produce macroporous beads. The molecular weight and the concentration of polystyrene are important variables to produce desired porousity (SEIDL et al. 1967). Similary, the essential feature of our method is the usage of preformed poly THF, which also has initiation ability. In a typical preparative reaction, suspension copolymerization of st and DVB (5/1, w/w) containing poly THF initiator (M_n = 9600) with 0.1 initiator/monomer ratio produced opaque beads after 2,5 hours. On extraction with benzen-chloroform mixture (1/1) these beads lose 10% of their initial weight and turn to semi-opaque appearance. The extracted material was found to be polyTHF of intrinsic viscosity only slightly lower than that of the initial poly THF. This could have been due to the combination of primary radicals of this type. As might be expected, when the initiator molecule is larger, as for azo-linked poly THF; initiation efficiency is considerably decreased. The increased size of the primary radicals reduce the rate of diffusion, thus increasing the chance of recombination. This is complementary way to produce macropores in an addition to utilising poly THF in the monomer mixture. In order to see the effect of poly THF segment introduced to the beads, they were put into toluen and examined with an optical microscope. Figure 1 shows swelling properties of the beads in comparison with beads having the same and lower DVB content. It is clear that the macroporous beads produced in this study lie in between the two beads that are compared. This suggests that poly THF segments stay out of the crosslinked domain as schematicly shown below.



Penetration of the solvent into crosslinked region and the subsequent swelling must be therefore provided by these free segments. This idea was further substanciated with swelling property of the beads in various solvents (Table I)

Due to the penetration of toluen and THF, these beads are completly swollen whereas for the beads with the same DVB content the swelling is insignificant.

CONCLUSIONS

It is clear that the method is suitable to prepare beads which have good swelling properties, eventhough they have high DVB content. The good swelling properties grant range of application of crosslinked beads. Further studies are now in progress to use polymeric initiators other than poly THF.

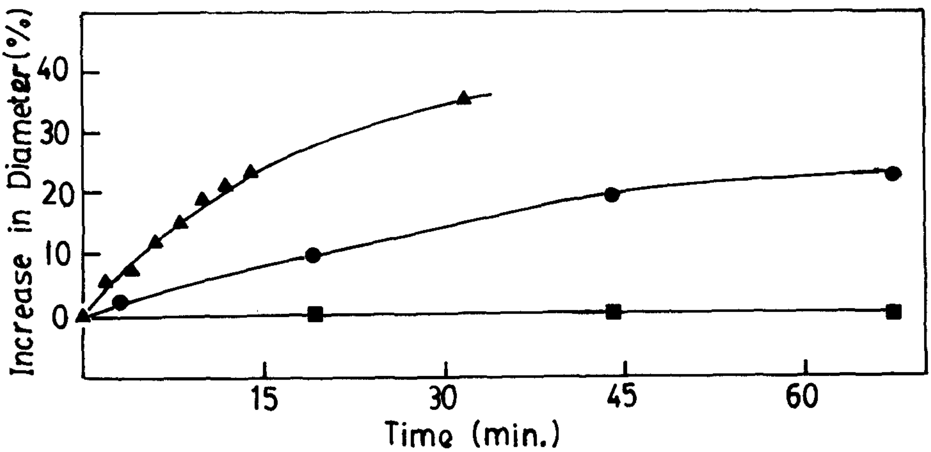


Fig.1. Swelling Properties of beads in tlouen ; Initiator:Dibenzoyl peroxide. DVB content: ▲:1,5% , ■:10% initiator: poly THF DVB content :●10%.

Table I

Swelling Properties of Macroporous beads[a] in Various solvents in 24 hours

Solvent	Increase in Diametre (%)
Toluen	30
Toluen	1[b]
THF	25
Ethanol	4

[a] Initiator : (II)

[b] Beads were produced in the same conditions except initiator was dibenzoyl peroxide

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