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Suspension Crosslinking of Polystyrene with Friedel-Crafts Catalysts

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Summary

A new experimental technique was developed for the production of crosslinked polystyrene (PS) particles in a suspension crosslinking reaction. The suspending medium being used was silicone oil saturated by 1,2-dichloroethane (DCE),without any suspension stabilizer. Antimony pentachloride, 1,4-dimethyl-2,5-dichloromethyl benzene and DCE were used as a catalyst, crosslinking agent, and polystyrene solvent, respectively. The products were colorless transparent spherical particles of a very high purity and they could be produced in short reaction times.

Introduction

Polymerization and crosslinking of PS by divinylbenzene (DVB) is a common technique for the production of polymer gels suitable for chromatographic analysis and/or for ion-exchange resins upon appropriate chemical modification.

For the purpose of achieving PS gels of superior purity, homogeneity, thermal and chemical resistance and uniform pore size distribution considerable research has been carried out recently on the use of mono- and difunctional derivatives of benzene, p-xylene and related aromatic compounds as crosslinking agents for PS (1-12). Crosslinking agents chosen for this approach have included 2,5-dimethyl benzyl chloride (1,2), 2,3,5,6-tetramethyl benzyl chloride (3) and other mono- and difunctional agents (4-9). The work of Peppas N.A. and his coworkers (10-12) has shown that 1,4-dimethyl-2,5-dichloromethyl benzene is the crosslinking agent of choice due to its ability to form regular bridges between the

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PS chains.

However, the major problem with these materials was that they were produced in solution polymerization, leading after crosslinking and crushing to irregularly shaped crosslinked products.

Design of the Crosslinking System

Here we report preliminary data on a new experimental technique for the production of crosslinked PS particles in a suspension crosslinking reaction at low temperatures. The main innovation of the new technique is that a Friedel-Crafts reaction can still be carried out with the selection of an appropriate suspending medium.

Suspension crosslinking reaction of dichloroethane-dissolved PS were carried out using $SbCl_5$ as Friedel-Craft catalyst and 1,4-dimethyl-2,5-dichloromethyl benzene as the crosslinking agent. Water was eliminated as a suspending medium, due to its known property of inactivating most Friedel-Crafts catalysts at low catalyst concentrations. However, Peppas and Barar (13) recently reported successful Friedel-Crafts suspension crosslinking reactions with water as the suspending medium at very high catalyst concentrations.

The suspending agent selected was silicone oil which had the following advantages : it did not deactivate or react with the catalyst ; it did not react with the evolved HCl ; it was not hygroscopic and it self-stabilized the PS solution suspension. DCE was used as the solvent for PS, since it is only partially miscible with silicone oil, whereas toluene, methyl ethylketone, butyl acetate and tetrahydrofuran do not satisfy this requirement. 1,4-dioxane, which is also partially miscible with silicone oil, was not used because of its miscibility with water.

Experimental Part

The PS used was supplied by Dow-Chemicals Hellas (Lavrion,Greece) and it had $\bar{M}n$=117,500, $\bar{M}w$=265,000, polydispersity index of 2.26 and softening point Ts=101.5^{o}C.

In a typical experiment 120 ml of a PS solution (16.78% by weight) in DCE (Merck, synthetic grade) were used and catalyst $SbCl_5$ was added at concentrations of 0.0025 - 0.0042 moles/lt (Merck, synthetic grade, in ampoules of 10 grs). To this system an appropriate amount of the crosslinking agent was dissolved to obtain molar ratios S of polystyrene repeating units to the crosslinking agent ranging from 4 : 1 to 128 : 1. The crosslinking agent was prepared as reported before (2).

The solution was dispersed in 300 ml of a silicone oil (Grade 47V 350, Rhodorsil Silicones, Rhone-Poulenc) and DCE solution at a volume ratio of 3 : 2. Reaction temperatures of 30-70°C and times of 2-8 hours were used and the system was continuously kept in suspension at 500 rpm.

The crosslinked PS was received by filtration, rinsed with petroleum ether, purified in boiling methyl ethylketone under vertical condenser for 30 minutes, twice, and it was dried in a vacuum-oven at 80°C for 24 hours.

The final material was crosslinked since it swelled in common PS solvents, such as chloroform and toluene at 25°C, without measurable weight loss.

Yields were determined as the percentage of the weight of the dry product to the sum of the weights of PS and crosslinking agent.

Infrared (IR) absorption spectra were obtained in a Perkin-Elmer IR Spectrophotometer, Type 283, from thin films of the material (thickness of about 100 microns), prepared under the same conditions as the particles, but without the suspending medium.

Particle size distribution was obtained by microphotographs at magnifications X 100 and X 250.

Results and Discussion

Table I shows the effect of reaction temperature on the yield of the final crosslinked PS, for 4 hours reaction time, molar ratio S, as defined earlier, 4 : 1 and catalyst concentration 0.0033 moles/lt.

Temperature (°C)	Yield (%)
30	67.3
50	74.3
70	78.5

Table I. Effect of the reaction temperature on the yield of the reaction.

Table II presents the effect of catalyst concentration, for 4 hours reaction time, molar ratio S 4 : 1 and temperature 50°C, while Table III shoes data on the effect of molar ratio S, for 4 hours reaction time, temperature 50°C, and catalyst concentration 0.0033 moles/lt, on the yield of the final crosslinked PS.

Catalyst (moles/lt)	Yield (%)
0.0025	69.1
0.0033	74.3
0.0042	77.3

Table II. Effect of catalyst concentration on the yield of the reaction.

Molar ratio S	Yield (%)
4 : 1	74.3
8 : 1	85.6
16 : 1	94.7
64 : 1	97.0
128 : 1	97.4

Table III. Effect of molar ratio S on the yield of the reaction.

A typical grain analysis of the dry products, as determined from microphotographs is given in Table IV.

Microns	(%)
+250	4.5
200-250	34.7
150-200	38.9
100-150	10.4
50-100	5.6
- 50	5.9

Table IV. Typical particle size distribution.

The IR absorption spectra obtained were almost identical for PS and crosslinked PS, except for the region extending from 450 to 280 cm^{-1} where some distinct differences were observed. In this region a number of weak bands with a maximum at 370 cm^{-1} appeared in pure PS, due probably to skeletal vibrations (14), and it was gradually diminished going from PS to highly crosslinked products.

This could be explained by limitations in skeletal vibrations induced by crosslinking effect. The relative intensities at 370 cm^{-1} for films prepared at 50^{o}C, 4 hours reaction time and 0.0033 moles/lt catalyst concentration are presented in Table V.

Molar ratio S	Relative intensities (370cm^{-1})
PS	100
128 : 1	60
64 : 1	40
32 : 1	10
16 : 1	$<$10

Table V. Relative intensities of IR absorption at 370 cm^{-1} wavenumber.

Data on swelling analysis and the determination of molecular weight $\bar{M}c$ will be reported in a future publication.

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