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Friedel-Crafts Crosslinking Methods for Polystyrene Modification

5. Sulfonated Crosslinked Polystyrene Particles

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Summary

A new method of preparation of sulfonated, crosslinked polystyrene particles is described. Particles were formed by Friedel-Crafts suspension crosslinking of polystyrene dissolved in nitrobenzene. The crosslinking agent was 1,4-dichloromethyl-2,5-dimethyl benzene. Sulfonation was achieved in the swollen state and the particles received were analyzed in terms of molecular structure and degree of swelling.

Isoporous Friedel-Crafts Crosslinked Polystyrene

In recent studies (REGAS and PAPADOYANNIS, 1980, PEPPAS and BARAR, 1980, 1982, BARAR et al., submitted) it has been reported that spherical particles of crosslinked polystyrene can be produced by Friedel-Crafts crosslinking of linear polystyrene in suspension reactions. Two general methods have been discussed. The method of REGAS and PAPADOYANNIS (1980) employs a 3:2 vol/vol mixture of silicone oil and 1,2 dichloroethane as suspending medium. The dispersed phase contains polystyrene dissolved in 1,2-dichloroethane and the Friedel-Crafts catalyst is $SbC\ell_5$. The method of PEPPAS and BARAR (1982) employs water with a small amount of poly(vinyl alcohol) as the suspending medium. The dispersed phase contains polystyrene dissolved in nitrobenzene and the catalyst is $ZnC\ell_2$ at high concentration (70 wt%) in water. Both techniques utilize 1,4-dichloromethyl-2,5 dimethylbenzene (DCMDMB) as the crosslinking agent, due to its ability to create linear bridges between the polystyrene chains (PEPPAS and VALKANAS, 1977).

Isoporous polystyrene networks were first produced by Friedel-Crafts crosslinking in bulk or solution (DAVANKOV et al., 1973 a, b, 1974, TSYURUPA et al. 1974, PEPPAS and VALKANAS 1976, PEPPAS et al., 1976, PEPPAS et al., 1981, BUSSING and PEPPAS, 1980). These materials show unusual physical properties, such as homogeneous porous structure, ability to swell in non-solvents of linear polystyrene and high surface area to weight ratio. However, particles of crosslinked polystyrene have been produced only by crushing samples in a mill, sieving them and

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analyzing them for chromatographic applications (TSYURUPA and DAVANKOV, 1980, DAVANKOV and TSYURUPA, 1980).

It was not until recently that the problem of Friedel-Crafts catalyst inactivation by water was solved so that crosslinked, spherical particles could be produced in suspension crosslinking (BARAR _et al_., submitted a,b). By judicious balance of catalyst and suspending agent concentration in the aqueous phase it was possible to sustain the crosslinking reaction by diffusion of $ZnC\ell_2$ from the aqueous phase to the organic phase (dissolved polystyrene) droplets.

Ion-exchange resins from Friedel-Crafts crosslinked particles of polystyrene have been discussed in recent studies by TSYURUPA _et al_. (1974) and MARTSINKEVICH _et al_. (1978). Here we present novel techniques of sulfonation of these particles and analysis of their physical behavior.

Preparation of Crosslinked Polystyrene Particles

Briefly, the method of preparation of the polystyrene particles (BARAR _et al_., submitted, a) consists of dissolving 3.57 g of polystyrene (Polysciences Corp., Warrington, PA, $\bar{M}_n$ = 116,000, $\bar{M}_w$ = 261,000) in 25 cm^3 of reagent grade nitrobenzene and adding 1,4-dichloromethyl-2,5 dimethyl benzene (DCMDMB) to this solution in a 1000 cm^3 reactor. Different amounts of crosslinking agent were employed so that the nominal crosslinking ratio, X, could be adjusted to 0.0625, 0.125, 0.25, 0.33, 0.50 or 0.75 moles DCMDMB per PS repeating unit.

The suspending medium was prepared by combing 600 cm^3 of 70 wt% aqueous solution of $ZnC\ell_2$ with 6 cm^3 of concentrated $HC\ell$ to adjust the pH at 0.10. Poly(vinyl alcohol) was added at a level of 5×10^{-4} g/cm^3 of solution.

Suspension crosslinking occured at 60°C for 4 hours under agitation rate of 1300 rpm. The spherical particles produced were washed with water and acetone, dried, and reswollen in chloroform, tetrahydrofuran or toluene depending on the specific application.

Sulfonation

Sulfonations were carried out with several polystyrene samples crosslinked at ratios of X = 0.25 and 0.50. In a typical reaction, 0.1-0.5 g crosslinked polystyrene particles were swollen in 20 cm^3 nitrobenzene at 30°C for 24 hours. The system was heated to 80°C and concentrated H_2SO_4 was added every 15 minutes in 1 cm^3 aliquots. About 0.2 cm^3 of acetic anhydride were added to prevent crosslinking by formation of sulfone-type chains which could increase the crosslinking density and alter the macromolecular structure of the original networks (CERFONTAIN, 1974).

Upon completion of the reaction, the sulfonated particles were washed with acetone and deionized water, and swollen in water at 30°C. The degree of sulfonation was determined by titration with a 0.085 N aqueous solution of NaOH in the presence of phenolphthalein.

Results and Discussion

Crosslinked particles prepared by the aforementioned Friedel-Crafts reaction were analyzed in terms of equilibrium swelling studies in toluene to determine their degree of crosslinking, ρ_x, and number average molecular weight between crosslinks, $\overline{M}_c$. The expressions of PEPPAS and MERRILL (1976) were used.

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{\upsilon/V_1[\ell n(1-\upsilon_{2,s}) + \upsilon_{2,s} + X\,\upsilon_{2,s}^{2}]}{\upsilon_{2,r}\left[\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)\right]} \qquad (1)$$

$$\rho_x = \frac{1}{\bar{\upsilon}\,\overline{M}_c} \qquad (2)$$

Here $\bar{\upsilon}$ is the specific volume of polystyrene (=0.95 cm^3/g), V_1 is the molar volume of toluene (=106.1 $cm^3/mole$), $\overline{M}_n$ = 116,000, and $\upsilon_{2,r}$ and $\upsilon_{2,s}$ are the volume fractions of polystyrene in the particles after reaction but before swelling and after swelling, respectively. The value of $\upsilon_{2,r}$ was constant at $\upsilon_{2,r} = 0.1197$ for all samples, whereas values of $\upsilon_{2,s}$ for different samples are presented in Table 1. The Flory interaction parameter, χ, was determined from osmotic pressure data (SHICK _et al._, 1950) as a function of $\upsilon_{2,s}$

TABLE 1

Equilibrium Swelling Behavior of Polystyrene Particles in Toluene

Nominal Crosslinking Ratio X(moles/mole)	Equilibrium Volume Fraction $\upsilon_{2,s}$	Interaction Parameter χ	$\overline{M}_c$ (daltons)	ρ_x (moles/cm^3)
0.0625	0.062±0.002	0.216	5,900	1.8×10^{-4}
0.125	0.081±0.003	0.211	3,900	2.7×10^{-4}
0.250	0.094±0.007	0.210	2,500	4.2×10^{-4}
0.330	0.125±0.001	0.210	1,700	6.1×10^{-4}
0.50	0.138±0.001	0.210	1,100	9.5×10^{-4}
0.75	0.149±0.003	0.210	900	11.7×10^{-4}

The values of the number average molecular weight, $\overline{M}_c$, and degree of crosslinking, ρ_x, are also presented in Table 1. Crosslinking increases as the crosslinking agent (DEMDMB) added to the system increases. However, this dependence is not linear showing that some of the DCMDMB has polycondensed to form larger bridging chains between the polystyrene chains. By calculating the theoretical $\overline{M}_{c,t}$ from the values of X using equation (3) it is possible to determine the actual number of polystyrene repeating units and the degree of polycondensation of DCMDMB as shown in Table 2.

$$M_{c,t} = 2M_r/X \qquad (3)$$

Here M_r is the molecular weight of the polystyrene repeating unit.

TABLE 2

Molecular Structure of Polystyrene Networks

Nominal Crosslinking Ratio X(moles/mole)	Experimental $\overline{M}_c$	Theoretical $\overline{M}_{c,t}$	Number of PS Repeating Units	Number of DCMDCB Units
0.0625	5,900	3330	28.4	1.8
0.125	3,900	1660	16.4	2.0
0.25	2,500	830	12.0	3.0
0.333	1,700	620	6.7	2.2
0.50	1,100	410	5.3	2.6
0.75	900	280	3.4	3.2

Typical values of the degree of sulfonation and equilibrium volume fraction of polystyrene in the sulfonated, crosslinked particles are presented in Table 3. Clearly the present technique may produce moderately sulfonated particles without alteration of the network structure. Thermal analysis of dried, sulfonated particles using differential scanning calorimetry gave values of Tg which were very close to the value of the non-sulfonated networks, suggesting that no further crosslinking of the original network structure had occured during sulfonation.

TABLE 3

Characteristics of Sulfonated, Polystyrene Particles *

Ratio of Reactants (cm^3H_2SO_4/g PS)	Reaction Time (min)	Degree of Sulfonation (%)	Water Degree of Swelling	Glass Transition Tg(°C)
9.62	60	1.0	1.24	96
13.20	100	2.9	1.76	96
13.44	30	6.5	2.18	96.5
16.22	60	9.3	4.15	96
52.41	60	43.0	12.42	94
60.79	90	48.7	13.60	97

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* Initial crosslinking ratio X = 0.25, $\overline{M}_c$ = 2,500, Tg = 96°C

In conclusion, the new method can produce sulfonated polystyrene particles without the undesirable crazing observed during sulfonation of glassy polystyrene beads and with controlled molecular structures

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