

Structure of Friedel-Crafts Crosslinked Polystyrene and Sulfonated Resins Thereof

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Summary

A new method of crosslinking of polystyrene using difunctional chloromethylated crosslinking agents is reported. The solution crosslinking took place in dichloroethane with SnCl_4 as a catalyst at 80°C and with molar ratios of polystyrene to crosslinking agent ranging from 1:2 to 12:1. The crosslinked networks prepared by this method had thermal transitions considerably affected by the degree of crosslinking. Ion-exchange resins were prepared by sulfonation of these networks. Water swelling ratios as high as 16.2 were measured leading to indications about the physical structure of these networks.

Crosslinking of Polystyrene

Crosslinked polystyrene structures can be prepared either by copolymerization of styrene and another monomer containing two or more reactive groups, or by polymerization of styrene followed by a crosslinking reaction in which another monomer or crosslinking agent is reacted with the polystyrene chain to form a network structure. The process of crosslinking restricts the segmental mobility and related diffusive properties in a manner similar to the effect of a decrease in molecular weight of the primary chains. Copolymerization of styrene with divinyl benzene (DVB) is the most widely used crosslinking process. While the rigidity of DVB crosslinks leads to higher T_g and T_m values, it also produces some structural disadvantages. The DVB crosslinks not only have an adverse effect on the mechanical properties of polystyrene, but also they produce a completely random, uncontrolled three-dimensional structure.

In the last ten years extensive independent re-

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search from the groups of Grassie and Peppas has led to new methods of crosslinking of polystyrene and its copolymers using Friedel-Crafts type reactions. Crosslinking agents chosen for this approach have been 2,5-dimethyl benzyl chloride (PEPPAS and VALKANAS 1974 a,b), 2,3,5,6-tetramethyl benzyl chloride (HAAS *et al.* 1955), and various other monofunctional and difunctional agents (GRASSIE *et al.* 1976a,b, GRASSIE and GILKS 1973a, b, GRASSIE and MELDRUM 1968, 1971, TRUSHIN and TYURIKOV 1974, GRASSIE *et al.* 1970). Past research of our group has proven that a series of crosslinking agents including 1,4-dimethyl-2,5-dichloromethylbenzene and oligomethylbenzylenes lead to crosslinked polystyrene with structural regularity of the network, and linear chains (bridges) between two polystyrene chains. (PEPPAS and VALKANAS 1976a,b, BUSSING and PEPPAS 1978).

Various reported crosslinking techniques using these agents include a two-stage polymerization-crosslinking process of styrene with Friedel Crafts catalysts such as SnCl_4 in dichloroethane at 25-60°C (BUSSING and PEPPAS 1978); and a direct crosslinking of polystyrene in acetic acid, butyl acetate, nitroethane or methylethyl ketone using catalysts such as H_2SO_4 and HClO_4 (PEPPAS and VALKANAS 1976b, 1977). Recently suspension crosslinking techniques for the production of crosslinked polystyrene particles have been also reported; these techniques use Friedel-Crafts catalysts in suspensions in water or silicone oils (REGAS and PAPADOYANNIS 1980, PEPPAS and BARAR 1980).

Not only do Friedel-Crafts crosslinked polymers have improved thermal properties, they also show improved properties for use as ion-exchange resins (DAVANKOV *et al.* 1973a, b, 1974a,b). Normally, polystyrene ion-exchange resins are obtained by copolymerization with DVB followed by sulfonation or amination. However, Friedel-Crafts crosslinking leads to a statistical distribution of crosslinks, increased swelling capacity and higher porosity. In this work we report novel techniques for the preparation of these crosslinked polystyrene structures and their ion-exchange resins.

Preparation and Characterization of Crosslinked Polystyrene

Polystyrene with $\bar{M}_w = 118,000$, dispersity index of 2.07 and $T_g = 89^\circ\text{C}$ was crosslinked in a dichloroethane (DCE) solution at temperatures between 50°C and 80°C using 1,4-dimethyl-2,5-dichloromethylbenzene (monomer I) as a crosslinking agent (for the preparation of I see PEPPAS and VALKANAS 1974b) and SnCl_4 as a catalyst. The molar ratio of styrene repeating units to monomer I varied between 1:2 and 12:1, and the concentration of polystyrene was 3.50 moles/liter of solution. The catalyst was dissolved to DCE and added

to the system at a final concentration of 0.2 moles/liter. The kinetics of the reaction were obtained by titrating the HCl evolved and entrapped during the reaction. The products were precipitated from the solution with methanol, reprecipitated after dissolving in dioxane and dried under vacuum at 50°C.

Change of the molecular weight during the reaction was followed viscometrically, by dissolving samples in toluene at 25°C for which the values of the constants of the Mark-Howink equation are $K = 44 \times 10^{-3}$ ml/gr and $a = 0.65$.

Ultraviolet (UV) spectra were obtained on 0.05% solutions of several polymer samples. As analyzed before (PEPPAS and VALKANAS 1977) the absorption band at 2780 Å is characteristic of linear grafting and crosslinking and can give quantitative results about the crosslinking reaction.

Thermal characterization of the polymer samples was performed with a differential scanning calorimeter (Perkin Elmer DSC 1-B) and thermomechanical analyzer (Perkin Elmer TMS 2) 10°C/min.

Experimental results on the production of cross-linked polystyrene are shown in Table 1, for a range of polystyrene to crosslinking agent ratio varying from 1:2 to 12:1. As shown in this table, T_g can increase up to 132°C, while T_m up to 347°C. This is a significant improvement over previously reported values (PEPPAS and VALKANAS 1977, GRASSIE and GILKS 1973b), increasing the glass transition temperature by upto 43°C above the base material. The same Table shows that the optimum ratio of polystyrene to crosslinking agent is 4:1. Above this ratio the crosslinking agent is not sufficient to lead to satisfactory crosslinking.

TABLE 1

Crosslinking of Polystyrene with Monomer I
at 80°C for 3 hours

Series	Molar Ratio of PS:I	Yield (%)	T_g (°C)	T_{pm} (°C)	T_m (°C)
K-1	1:2	47.3	97	277	305
K-2	2:1	62.5	103	276	308
K-3	4:1	87.3	132	-	347
K-4	8:1	94.7	121	306	326
K-5	12:1	96.5	97	284	306

Table 2 presents the structural analysis of the samples obtained by a crosslinking reaction of polystyrene at a molar ratio of 4:1. A gelation point was observed at 255 minutes, but the reaction continued due to the unreacted crosslinking agent in the gel. The average molecular weight between crosslinks \bar{M}_c was determined by thermodynamic swelling tests at 30°C in cyclohexane. For this swelling agent values for the

Flory-interaction parameter χ exist in the literature (HERT and STRAZIELLE 1975), while for the calculation of \bar{M}_c a previously reported equation was used (PEPPAS and MERRILL 1976).

TABLE 2
Crosslinking of Polystyrene with Monomer I
(ratio 4:1) at 80°C

Series	Time(hrs)	\bar{M}_c	T_g (°C)	T_{pm} (°C)	T_m (°C)
L-1	1	*	107	258	290
L-2	2	*	114	256	287
L-3	3	*	132	-	347
L-4	4	*	133	-	-
L-5	5	11,170	134	308	-
L-6	6	8,210	136	313	339
L-7	7	4,150	140	-	-

*Slightly grafted polystyrene, before the gelation point (255 minutes).

A gradual increase of the glass transition temperature T_g was observed from the initial base value of 89°C to 140°C for a highly crosslinked polystyrene of $\bar{M}_c = 4,150$ obtained after 7 hours under the reaction conditions. As the reaction proceeded grafting was observed, as evident from the shift of the 2780 Å shoulder of the UV spectrum up to the gelation point. Similar behavior was exhibited by the premelting transition T_{pm} . The existence of a melting point T_m in these crosslinked polymers has been attributed to long linear bridges of the crystallizable polybenzylens formed by the crosslinking agent I, as explained elsewhere (PEPPAS and VALKANAS 1977).

Three series of fully crosslinked polystyrene gels were obtained. The average values of \bar{M}_c were determined as 11,170, 8,210 and 4,150. Within the range of crosslinking densities studied, the glass transition T_g increased. However, these results of swelling behavior of this type of Friedel-Crafts crosslinked polystyrene are in contradiction to the results of DAVANKOV et al. (1974a,b) who observed an abnormal swelling behavior not explained by Flory's thermodynamic theories.

These three series of crosslinked gels (L-5,6,7) and other samples were further sulfonated to obtain ionic resins with possible applications as ion-exchange resins for liquid chromatography and other separation techniques. The sulfonation technique was a modification of previously reported methods (KATO 1960). In a typical sulfonation a crosslinked polystyrene sample of 0.2 gr was swollen in hexane and H_2SO_4 where 0.02 gr of Ag_2SO_4 were added. The system was heated at 80°C

for 4 hours and the resulting sulfonated network was repeatedly washed and dialyzed to remove the unreacted H_2SO_4 . The sample was swollen in distilled water at $30^\circ C$ upto thermodynamic equilibrium. Subsequently it was dried under vacuum at $72^\circ C$ for 3 days. Using the weights of the sample in the swollen state and after drying, the swelling ratio was determined. The sample was then titrated using a standardized basic solution to determine the degree of sulfonation. Table 3 includes some of the swelling characteristics of these gels. A high weight swelling ratio in water was observed even for gels with low degree of sulfonation.

TABLE 3

Swelling Behavior of Sulfonated Friedel-Crafts Polystyrene Gels in Water at $30^\circ C$

Series	\bar{M}_c	Degree of Sulfonation (%)	Weight Swelling Ratio Q
L-5	11,170	62	8.7
	11,170	95	16.2
L-6	8,210	67	7.9
	8,210	93	13.5
L-7	4,150	54	6.8
	4,150	87	11.1

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