Chemical Modification of Polystyrene. VII. Optimization of Reaction Conditions for the Synthesis of Polystyrene Pyromellitic Dianhydride Condensate

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Synopsis

Cross-linked, isoporous polystyrene was prepared by crosslinking of polystyrene with pyromellitic dianhydride using Friedel-Crafts acylation reaction. The catalyst and solvent used were anhydrous aluminium chloride and nitrobenzene, respectively. reaction temperatures varied from 40 to 100°C and reaction times were between 30 min to 40 h. The optimum reaction condition for the production of the cross-linked polystyrene was established.

INTRODUCTION

The present work is a continuation of the previously published[1,2] work of the author in which the syntheses of polystyrene pyromellitic dianhydride (PSPMDA) condensate has been reported and the corresponding strong cation exchange resin–sulfonated polystyrene pyromellitic dianhydride (PSPMDAS). This paper highlights a systematic study to optimize the reaction conditions for PSPMDA and also the rationalization of data.

Conventional cross-linked polystyrene gel and ion-exchange resins are produced by copolymerization—crosslinking of styrene and divinylbenzene. These resins are characterized by inhomogeneous pore structure due to different reaction rates of the comonomers. Tsyurupa et al.[3,4] have shown that in the case of cross-linking after polymerization process, the cross-linking agent is evenly distributed throughout the volume of the polymer. As the concentration of the polymer solution is high relative to the cross-linking agent, the cross-linked bridges formed as a result of the reaction. The cross-linked polymer should have the same statistical distribution in gel as in the initial polymer solution with respect to spatial arrangement. The cross-linked products formed by this method are termed isoporous. The inhomogeneous pore structure in the conventional resin is allegedly responsible for their low osmotic ability and their insufficient permeability to large organic ions. This is also an undesirable feature for gel permeation chromatography, because wide pore size distribution affects separation processes.

Davankov and Tsyurupa[5] have shown that polymers prepared by Friedel-Crafts alkylation of polystyrene exhibit structural and swelling properties not demonstrated by cross-linked PSDVB compolymer. These unusual properties include homogeneous pore structure, alleged ability to swell in nonsolvents.

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An increased internal surface area of the isoporous polymer facilitates the attachment of more ion-exchange groups.

Biswas and Chatterjee[1,6,7] have reported the syntheses of a series of novel polymers from polystyrene by Friedel-Crafts acylation reaction using aromatic and alicyclic mono anhydrides such as phthalic anhydride, trimellitic anhydride, cis-1,2,3,6-tetrahydrophthalic anhydride, and with one aromatic difunctional anhydride—pyromellitic dianhydride. In addition to the other advantages as stated by Davankov and Tsyurupa, PSPMDA acts as a weak ion-exchange resin (due to presence of —COOH group) and is totally insoluble in all the organic solvents and inorganic acids and alkalis. These may further be converted to strong sulfonic acid resins.[2,8] Compared to other polystyrene-based anhydride-modified sulfonic acid resins as well as conventional poly-styrene-based sulfonic acid resin, PSPMDAS exhibits attractive thermal, ion exchange[9,10] and electrical properties[11] due to quinonic crosslinking. All these factors urge elaborate study to establish optimum production of operating conditions necessary for commercial exploitation.

EXPERIMENTAL

Materials

For the synthesis of PSPMDA condensate, chemicals used are: Polystyrene ($\overline{DP}$ = 480) of Poly Chem., India, Ltd., Pyromellitic dianhydride of Fluka AG, Buches, Switzerland; Anhydrous aluminium chloride, sublimed for synthesis (E. Merck, India); and a middle fraction distillate of nitrobenzene.

SYNTHESIS OF POLYSTYRENE PYROMELLITIC DIANHYDRIDE CONDENSATE

In the synthesis procedure[1] reported earlier, polystyrene in nitrobenzene solution was reacted with pyromellitic dianhydride in the presence of $AlCl_3$ as Friedel-Crafts catalyst to give polystyrene pyromellitic dianhydride con-densate. However, no attempt was made to optimize the reaction conditions.

In the present study the reaction condition was optimized by varying the following reaction parameters.

Effect of Reaction Temperature. The Friedel-Crafts acylation reaction was carried out at 40, 60, 70, 80, and 100°C for the fixed weight ratio of PS : PMDA : $AlCl_3$ as 1 : 2 : 1 and the corresponding minimum time for com-pletion of gel formation was noted.

Effect of Time. To ensure if the variation of time had any effect on the yield, the reactions were performed at 60, 70, and 80°C for maximum period of 24 h, otherwise under identical conditions.

Effect of Variation of $AlCl_3$ Concentration. To find the effect of $AlCl_3$ concentration on condensation, experiments were carried out at various con-centration levels keeping PS:PMDA ratio constant at 1 : 2 and temperatures at 60°C and 80°C.

Effect of Variation of Pyromellitic Dianhydride Concentration. The amount of pyromellitic dianhydride was varied keeping temperature constant at 60°C and 80°C and weight ratio of PS : $AlCl_3$ at 1 : 2 and 1 : 1.

RESULTS AND DISCUSSION

Figure 1 shows the effect of reaction temperature on minimum time of complete gel formation and the corresponding yield was noted in Table I. Interestingly, the minimum time of complete gel formation is exceedingly decreased from 4 h to 30 min with the rise of temperature from 40°C to 100°C. It is further observed that the minimum time of gel formation falls sharply up to 70°C, and beyond which the rate of fall is slow. However, the yield of reaction increases to some extent with temperature of reaction (Table I).

After 24 h of reaction at 60, 70, and 80°C, the yield was not notably improved (Table II).

At 100°C the reaction rate was so fast that it would be difficult to control the subsequent operation of pearl making. Therefore, for further studies maximum temperature variation was up to 80°C. Synthesis of condensate was not possible when weight ratio of PS and $AlCl_3$ was 1 : 0.25 at 80°C. However, with the increase of PS : $AlCl_3$ ratio from 1 : 1 to 1 : 2.5, the minimum time for complete gel formation decreases from 2 h to 30 min (Fig. 2) at 80°C. This suggests that $AlCl_3$ has a pronounced effect on the time of complete gel formation. Therefore, it is expected that at low temperatures like 60°C, if $AlCl_3$ content is increased in the reactants, the time of reaction will decrease.
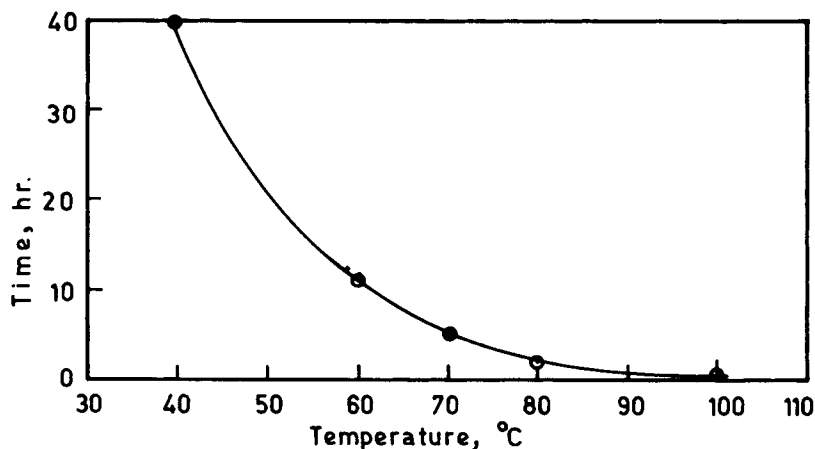

Fig. 1.   Effect of variation of temperature on minimum time for complete gel formation.

TABLE I
Effect of Reaction Temperature on Yield

Temperature (°C)	40	60	70	80	100
Yield (g)	1.04	1.29	1.23	1.23	1.38

TABLE II
Effect of Maximum Reaction Time of 24 h on Yield at Different Temperatures

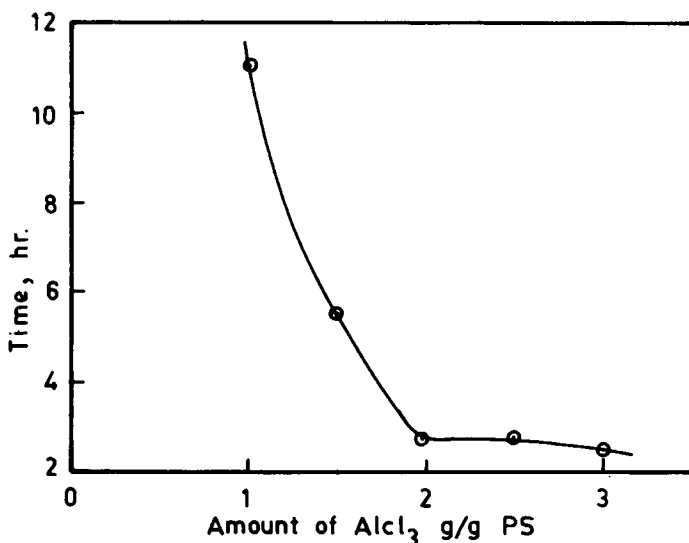| Temperature (°C)	60	70	80
Yield (g)	1.03	1.08	1.09

Fig. 2. Effect of variation of $AlCl_3$ concentration on minimum time for complete gel formation at 80°C.

Also, reaction time reduced from 11 h to 5 h 30 min to 2 h 45 min when weight of $AlCl_3$ was increased from 1 g to 1.5 g to 2 g per gram of PS. With further increase of catalyst in the reactants, the decrease in complete gel formation time was negligible. This may be seen from Figure 3. Interestingly, however, the yield of reaction reaches a maximum value of 2.22 g (Table IV) when 1.5 g of $AlCl_3$ was added under the similar operating conditions. Decrease in yield was observed with further addition of $AlCl_3$ at 60°C. The same trend (Table III) was observed at 80°C. The fall in reaction time is very sharp at 60°C up to addition of 2 g of $AlCl_3$ (Fig. 3), beyond which the curve becomes asymptotic, whereas at 80°C the decrease in reaction time is continuous.
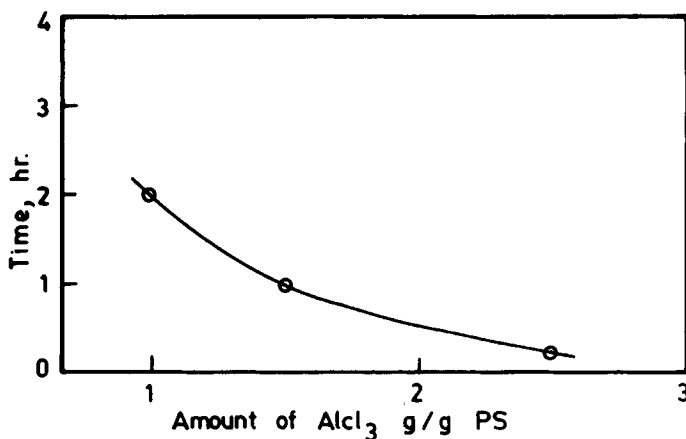

Fig. 3. Effect of variation of $AlCl_3$ concentration on minimum time for complete gel formation at 60°C.

TABLE III
Effect of Variation of $AlCl_3$ Concentration on Yield at 80°C

Weight of $AlCl_3$ (g/g of PS)	0.25	1.00	1.50	2.50
Yield (g)	No reaction	1.23	1.50	1.56

TABLE IV
Effect of Variation of $AlCl_3$ Concentration on Yield at 60°C

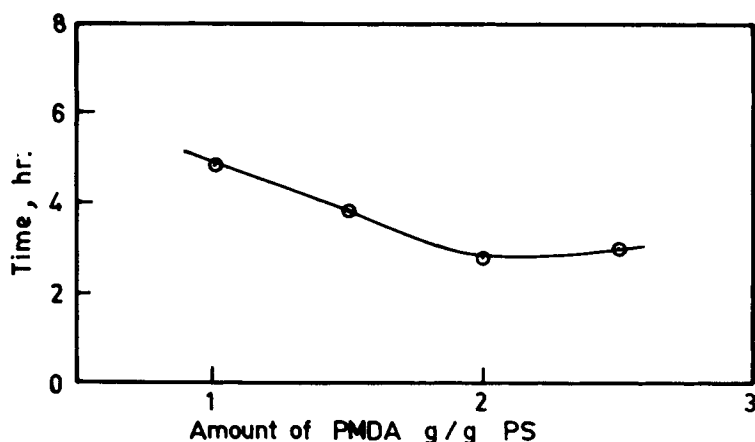| Weight of $AlCl_3$ (g/g of PS)	1.00	1.50	2.00	2.5	3.00
Yield (g)	1.29	2.22	1.86	1.89	1.47

Fig. 4. Effect of variation of PMDA concentration on minimum time for complete gel formation at 60°C.

The above analysis suggests that to study the effect of PMDA concentration on reaction time and yield at 60°C, the weight ratio of PS : $AlCl_3$ can be kept constant at 1 : 2. From Figure 4 it is observed that with the increase of PMDA in the reaction up to certain values (PS : $AlCl_3$: PMDA as 1 : 1.5 : 2.5) complete gel formation time is reduced, thereafter, addition of excess PMDA has a retarding effect. On the other hand at 80°C, as shown in Figure 5, addition of PMDA has little effect on the reduction of complete gel formation time. The yield is also too low (Table VI) compared to that at 60°C (Table V).

Hence the reaction temperature of 60°C and weight ratio of PS : PMDA : $AlCl_3$ as 1 : 2 : 2 is the best reaction condition for the synthesis of PSPMDA.

Regarding the volume of solvent, it is found that isoporosity is dependent on concentration of polystyrene in the initial solution.[12,13] Isoporous materials are only obtained for dilution of 1 g/10 cc. For concentration of polystyrene greater than 1 g/5 cc or below 1 g/20 cc, there was wide pore size distribution (between 20 and 100 Å).[12] Hence, in the present method, a concentration of 1 g/10 cc has been used, thus ensuring narrow pore size distribution.
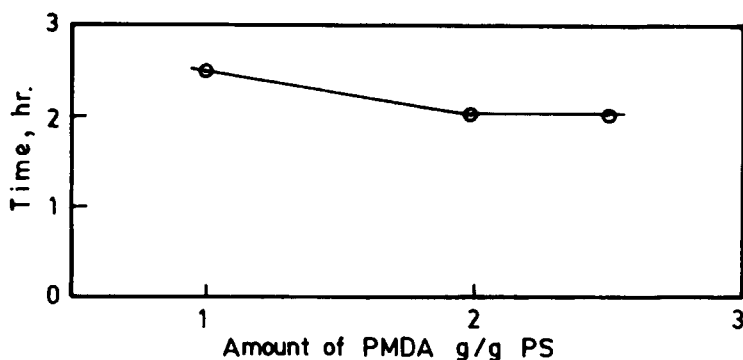
Fig. 5. Effect of variation of PMDA concentration on minimum time for complete gel formation at 80°C.

TABLE V
Effect of variation of PMDA Concentration on Yield at 60°C

Weight of PMDA (g/g of PS)	1.00	1.50	2.00	2.50
Yield (g)	1.73	2.65	1.86	2.22

TABLE VI
Effect of Variation of PMDA Concentration on Yield at 80°C

Weight of PMDA (g/g of PS)	1.00	2.00	2.50
Yield (g)	1.22	1.23	1.23

When gel formation of separate macromolecular coils in space proceeds, a new polymer having cross-linking bridges in between the polystyrene chain forms.[2]

From the above-described experimental data it appears, that at higher temperature, concentration of aluminium chloride to some extent and concentration of pyromellitic dianhydride to a limiting value facilitates the crosslinking, which is reflected in reduction of time for complete gel formation. However, excess of anhydride beyond certain amount hinders the reaction.

Like the conventional cross-linking process, a small part of PMDA molecules involves at early stages.[5] The remaining molecules of pyromellitic dianhydride react at first by only one of their functional groups and wait for favorable conformation of the neighboring polystyrene chain. Ultimately, the other group will react to give least unstrained structure. Unlike the case of Davankov and Tsyurupa,[5] solvent is not the reactant in the proposed reaction. Hence macrosyneresis will not stop even when the network becomes sufficiently rigid. The sulfonation of PSPMDA results in a polyquinonic structure in between the polythene chain[2] which possesses the most rigid crosslinks, hence a highly limited conformational mobility.

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