

Letter to the Editor

Comment on "Electrophilic Substitution of Polystyrene with Aromatic Anhydrides" *

Recently we have had occasion to carry out a number of experiments very similar to those reported by Biswas and Chatterjee and wish to point out an important omission in their paper. We have acylated linear polystyrene (MW ~100,000) using both phthalic and succinic anhydrides in nitrobenzene, and AlCl_3 and SnCl_4 as the Lewis acid component. All reactions followed the same basic pattern. If the temperature was controlled carefully and not allowed to rise above room temperature a soluble product resulted with no evidence of any acylation having occurred. On the other hand, if the reaction temperature was allowed to rise to ~70–100°C, an insoluble product was formed displaying an aromatic carbonyl stretch in its infrared spectrum. The latter products readily swelled in an appropriate solvent, e.g., methylene chloride, but did not dissolve, and were clearly crosslinked. We have no evidence concerning the nature of the crosslinking process but it is undoubtedly an important side reaction and the structure II reported in Scheme I by the above authors is an oversimplification. Their product from phthalic anhydride acylations was clearly also crosslinked, since they were able to extract these with benzene and methanol without dissolution.

Unfortunately, in our own work we require linear soluble polymers so this route is not appropriate and we have discarded it for the time being. However, this side reaction is also important in the work of Biswas and Chatterjee, since they report an increase in the thermal stability of polystyrene modified in this way. Their stabilities were defined according to TG analyses and a significant reduction in weight loss on crosslinking any linear polymer would be expected (and indeed is recognized by these authors in the case of polystyrene modified using pyromellitic dianhydride). We believe therefore that their conclusion regarding an increase in stability arising simply on substitution of the polystyrene is a misleading one, and great care should be taken by readers in interpreting the results reported in this paper.

* M. Biswas and C. Chatterjee, *J. Appl. Polym. Sci.* **27**, 3851 (1982).

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