

Some Observations on Morphology of Anhydride-Modified Polystyrene

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SYNOPSIS

Friedel–Crafts acylation reaction between polystyrene and phthalic anhydride in the presence of AlCl_3 has been performed in two different solvents, 1,2-dichloroethane and nitrobenzene. The morphology of the condensate prepared in 1,2-dichloroethane has revealed the participation of 1,2-dichloroethane, i.e., a competitive Friedel–Crafts alkylation reaction.

INTRODUCTION

The systematic study of the chemical modification of polystyrene with aromatic and alicyclic anhydrides^{1–3} further suggests the observation of the morphology of the polymers to understand the effect of solvents.

However, conventional styrene–divinylbenzene copolymers have been modified to make microporous or macroreticular ion exchange resin by solvent modification of styrene–divinylbenzene copolymers. In this process the diluent used in the monomer mixture is extracted after polymerization, leaving holes (pore) in the structure.⁴ Polymers, solvents, or nonsolvents of polystyrene or a mixture of them^{5,6} have been used as diluents, resulting to different pore sizes. In practice, the situation is considerably more complex with nonsolvating than with solvating ones. Porous ion exchange resins with improved ion exchange rate, capacity and high regeneration efficiency are prepared.^{7–11} All those efforts could not overcome the possibility of formation characteristic of inhomogeneous pore structure in the micro level due to different reaction rates of the comonomers. This characteristic of the conventional resin is allegedly responsible for their low osmotic ability and their insufficient permeability to large organic ions, which is an undesirable feature for gel permeation chromatography. Davankov and Tsyurupa¹² have

shown that in the case of crosslinking after polymerization process, the crosslinking agent is evenly distributed throughout the high concentrated polymer solution. A crosslinking of some statistical distribution is feasible. The crosslinked products are termed macronet isoporous polymers.

This work highlights the morphology of the chemically modified polystyrene by phthalic anhydride in a (1) nonsolvent for modified polymer, i.e., nitrobenzene medium and (2) in 1,2-dichloroethane medium, which is a solvent as well as a reactant for the reaction.

EXPERIMENTAL

Materials

The following were used for the synthesis of polystyrene–phthalic anhydride condensate: polystyrene (DP = 480) of Poly Chem., India, Ltd.; phthalic anhydride from BDH was purified by sublimation and finally recovered as white needles; anhydrous aluminium chloride, sublimed for synthesis (E. Merck, India); and a middle fraction distillate of nitrobenzene and 1,2-dichloroethane.

Synthesis

Polystyrene–phthalic anhydride condensate was synthesized using the procedure of Biswas and Chatterjee.¹ The reaction was repeated in 1,2-dichloroethane medium under otherwise identical conditions.

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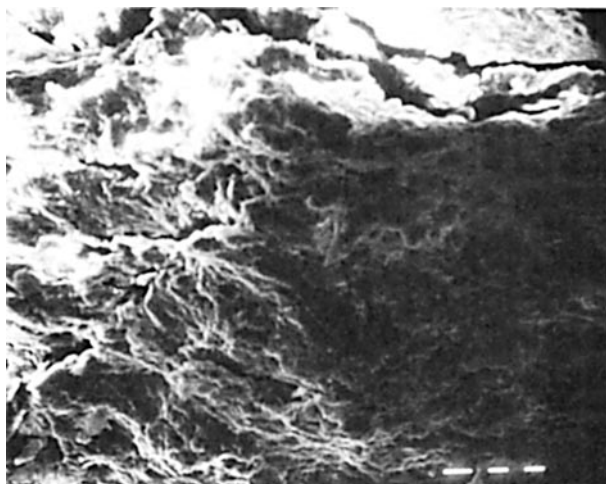


Figure 1 Scanning electron micrograph of surface of polystyrene-phthalic anhydride condensate prepared from nitrobenzene at low magnification. 310 \times .

SCANNING ELECTRON MICROGRAPH

Polystyrene-phthalic anhydride condensate prepared in nitrobenzene and 1,2-dichloroethane media were processed for observation under scanning electron microscope (SEM). Test pieces of about $2 \times 1 \times 1$ cm size were swelled in benzene in order to expell the remaining solvent. A sharp cut of about 2 mm depth made by knife was at the midpoint along the length of the swelled sample, and the test piece was pulled in tension till its rupture. The sample was dried in vacuum, at 40 $^{\circ}$ C to a constant weight. The

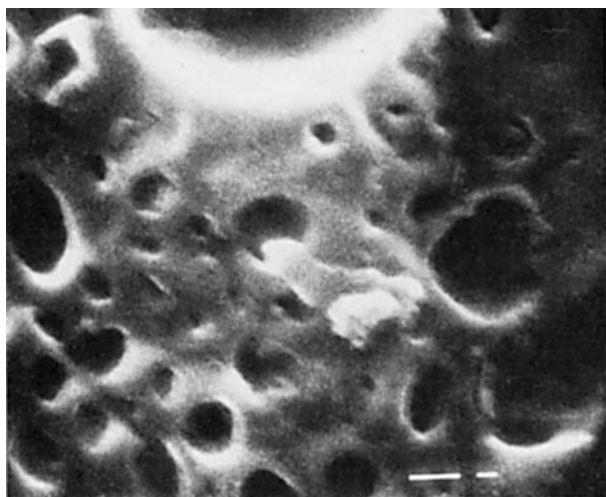


Figure 2 Scanning electron micrograph of surface of polystyrene-phthalic anhydride condensate prepared from nitrobenzene at higher magnification. 5800 \times .

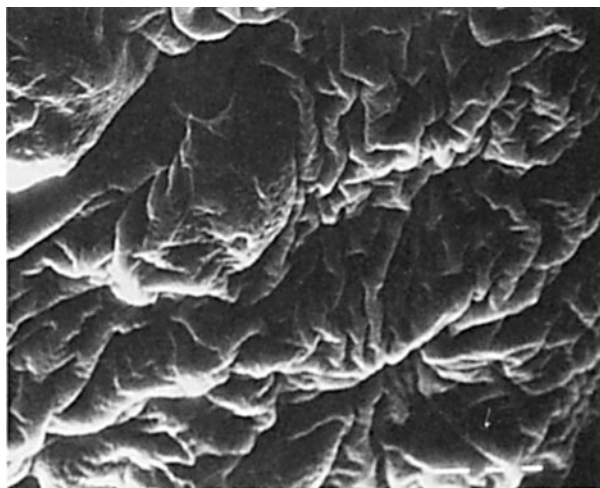


Figure 3 Scanning electron micrograph of surface of polystyrene-phthalic anhydride condensate prepared from 1,2-dichloroethane. 470 \times .

fracture surface of the sample was sputter-coated with gold, and SEM observations were made using ISI-60 model.

RESULTS AND DISCUSSION

Scanning electron micrographs of the condensates synthesized in nitrobenzene and in 1,2-dichloroethane medium were observed in high and low magnification to understand the morphology of the products, which are presented in Figures 1, 2, 3, and 4.

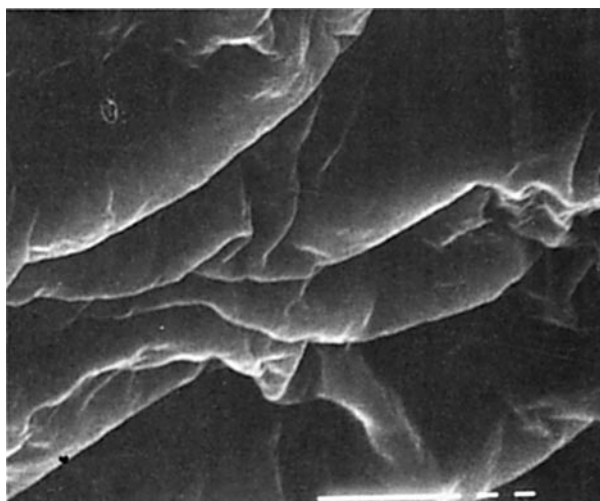


Figure 4 Scanning electron micrograph of surface of polystyrene-phthalic anhydride condensate prepared from 1,2-dichloroethane at higher magnification. 4710 \times .

All the samples show ductile fracture. At higher magnification, polystyrene-phthalic anhydride synthesized in nitrobenzene shows large number of holes (Fig. 2), which are created by the removal of nitrobenzene due to the solvent action of benzene. On the other hand Figure 4 shows that such holes are absent in condensate synthesized in 1,2-dichloroethane medium; rather it shows a corrugated surface because of high substitution on the benzene ring of polystyrene due to competitive Friedel-Crafts acylation and alkylation reactions that was not possible when nitrobenzene was used as solvent.

REFERENCES

1. M. Biswas and S. Chatterjee, *J. Appl. Polym. Sci.*, **27**, 3851 (1982).
2. M. Biswas and S. Chatterjee, *Angew. Macromol. Chem.*, **113**, 11 (1983).
3. M. Biswas and S. Chatterjee, *Eur. Polym. J.*, **19**, 317 (1983).
4. J. Seidl, *Adv. Polym. Sci.*, **5**, 113 (1967).
5. A. A. Tagar, *Vyskomol. Soedin.*, **A13**, 2370 (1971).
6. W. L. Sederel, *J. Appl. Polym. Sci.*, **17**, 2835 (1973).
7. I. M. Abrams, U. S. Pat. 3,122,514 (1964).
8. I. M. Abrams, *Ind. Eng. Chem.*, **48**, 1469 (1956).
9. S. P. A. Resindion, Ital. Pat. 653,389 (1963).
10. S. P. A. Resindion, Brit. Pat. 1,082,635 (1967).
11. L. Roubinesk and A. G. Wilson, S. African Pat., 6,604,866 (1968).
12. V. A. Davankov and M. P. Tsyurupa, *Angew. Macromol. Chem.*, **91**, 127 (1980).

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