

Porous Polymer Carbons. III. Surface Structure of Precursor Polymers

It has been shown previously¹ that porous polymer beads may be obtained by the suspension polymerization of vinylidene chloride and ethylene glycol dimethacrylate. The products are found to possess a surface structure which is quite distinct in morphology to the agglomerated microglobules of the interior. Inasmuch as the skin is formed in copolymerizations only, its formation is explained as follows. Because of the disparate reactivities of the two monomers, first-formed copolymer is rich in dimethacrylate units, contains unreacted double bonds, is relatively hydrophilic, and precipitates in a swollen form at the droplet/water interface; subsequent reaction converts it to a densely crosslinked layer of low porosity.

If this explanation is correct, it should be possible to prevent skin formation by one or other of the following changes in formulation. First, if the diluent in the polymerizing droplet were more hydrophilic than the initially formed polymer, the tendency to deposit at the interface would be removed. Secondly, if the crosslinking monomer were consumed at the same rate as the vinylidene chloride, there would be no compositional difference between the first-formed polymer located at the interface and the rest of the product. We report below some experiments made in the context of the above suggestions.

The suspension polymerizations were made as before,¹ except that reaction was extended to three to four days to ensure complete monomer conversion. Improved micrographs in scanning electron-microscopic examination were obtained by bedding the polymer beads to the aluminum stud with high-conductivity paint, which much reduced the propensity to become charged under the electron beam. The coding of samples is as previously described,¹ except that a letter is inserted to designate the crosslinker employed.

The different appearance of polymer beads synthesized with and without ethylene glycol dimethacrylate may be seen from Figures 1a and 1b. The puckered, continuous skin on the fractured copolymer bead is clearly evident in Figure 1a, whereas Figure 1b illustrates that, for the homopolymer, the interior morphology (upper part of micrograph) is similar to that in the "lace work" outer surface. An attempt was made to replace the normal diluent (a 3:1 mixture of toluene and carbon tetrachloride) by the more hydrophilic 1-pentanol. However, it proved difficult to obtain stable dispersions, and the resulting polymers were powders rather than beads.

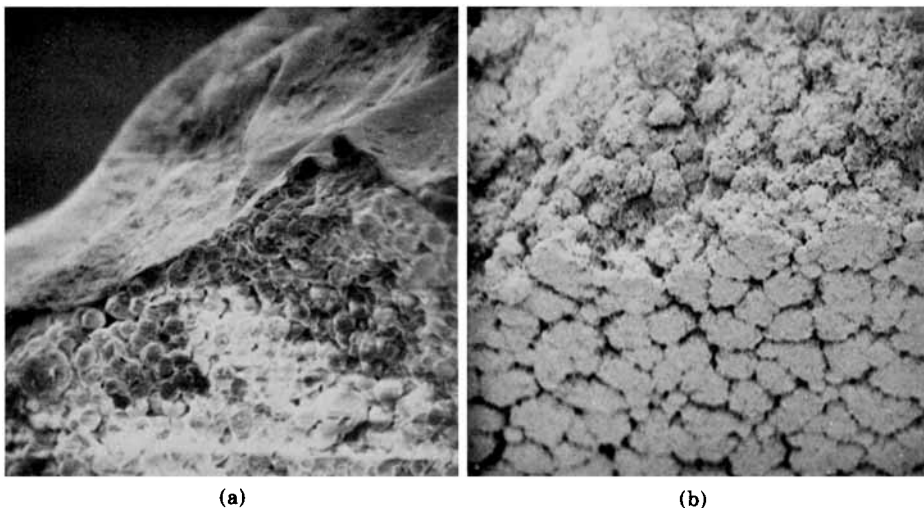


FIG. 1. Scanning electron microscopy of polymer beads made with dimethacrylate crosslinker; edge of cut in bead: (a) D/.167M/.500 ($\times 1,560$); (b) D/.00/.351 ($\times 780$) (homopolymer).

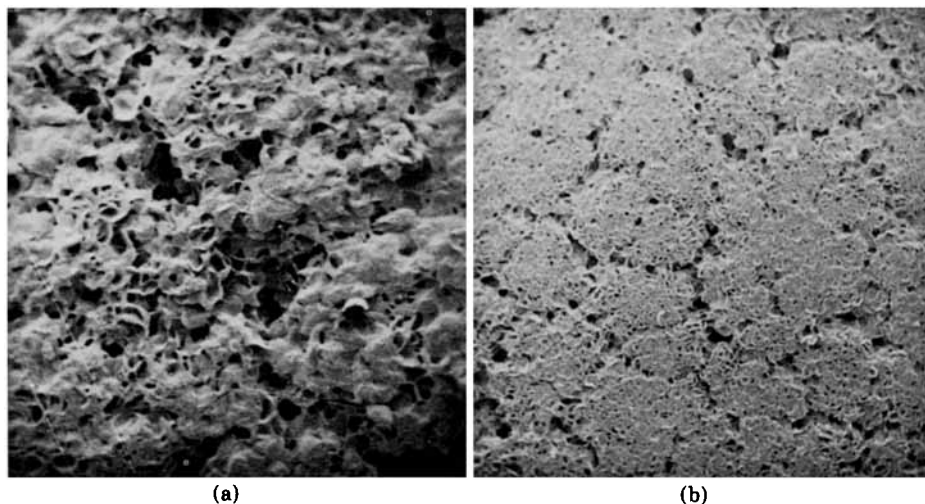


Fig. 2. Scanning electron microscopy of polymer beads made with diacrylate crosslinker; outer surface of bead: (a) D/.250A/.500 ($\times 1,500$); (b) D/.026A/.500 ($\times 720$).

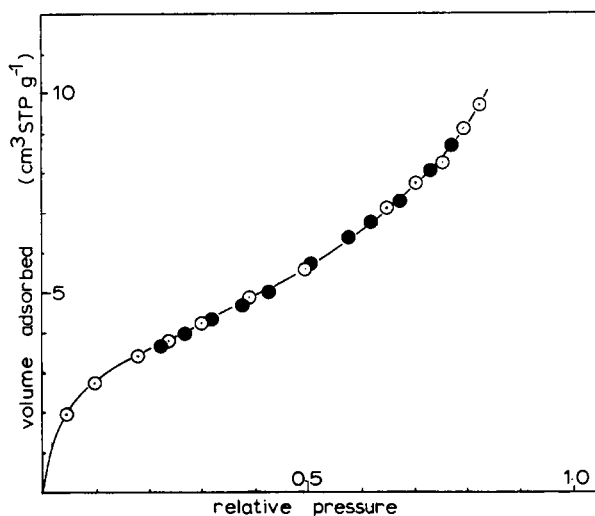


Fig. 3. Adsorption isotherm of D/.250A/.500 (N_2 , $77^\circ K$). Open circles, adsorption; filled circles, desorption.

Two formulations yielded products which contained beads as well as powdery polymers. In the first, the methylcellulose suspension stabilizer was replaced by a proprietary product (Promulsin, Watford Chemical Co.); in the second, the diluent was a 4:1 mixture of carbon tetrachloride and 1-pentanol. In both cases, however, examination in the scanning electron microscope revealed that the beads retained the characteristic skin structure; it may be that the diluent mix is not sufficiently hydrophilic to prevent skin formation.

The alternative approach was to replace ethylene glycol dimethacrylate as the crosslinking comonomer by the corresponding acrylate. No copolymerization data on ethylene glycol diacrylate, and hence no Q, e values, are given in the *Polymer Handbook*.² The monomer reactivity ratios for analogous compounds are, however, suggestive. With vinylidene chloride as monomer 1, the following values have been reported: Methyl acrylate, $r_1 = 1.0$, $r_2 = 1.0$ ³ and $r_1 = 0.99$, $r_2 = 0.84$ ⁴; methyl methacrylate, $r_1 = 0.24$, $r_2 = 2.53$.⁵ The calculated values (from

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the Q, e parameters listed in ref. 2) for vinylidene chloride with ethylene glycol dimethacrylate are $r_1 = 0.24$, $r_2 = 4.1$. There is, therefore, strong circumstantial evidence to suppose that the copolymerization of vinylidene chloride with ethylene glycol diacrylate would give a nearly random copolymer with little drift in composition with conversion. This conclusion is in accord with the opinion expressed by Wessling and Edwards.⁶

Four preparations were made with ethylene glycol diacrylate; the volume fraction of this crosslinker (of total monomers) ranged from 0.025 to 0.250. Scanning electron microscopy revealed that in all preparations the skin structure was absent, the open surface morphology being indistinguishable from the interior. Two examples are shown in Figure 2. The percentage porosity of one sample (D/.250A/.500) was found by comparison of the apparent densities in mercury and in helium; the high value of 72% is not altered by grinding the beads. The corresponding sample made with the dimethacrylate crosslinker¹ has a porosity of 64%. The surface area (N_2 , BET) of 14.5 m²/g is also unchanged on fracturing the beads and is noticeably higher than that found with copolymers made with the dimethacrylate.¹ Whole dimethacrylate copolymer beads exhibit low-pressure hysteresis of the nitrogen desorption branch,¹ which is removed on grinding. The isotherm for whole beads of D/.250A/.500 is, however, reversible (Fig. 3).

References

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G. J. HOWARD
S. SZYNAKA*

Department of Polymer and Fibre Science
University of Manchester Institute of Science and Technology
Manchester 1, England

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*Present address: Searle Laboratories, High Wycombe, England.