

Reactive Polymers. XXXIII.* The Influence of the Suspension Stabilizer on the Morphology of a Suspension Polymer

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Synopsis

Sorbents based on glycidyl methacrylate were used in an investigation of the effect of the type of the suspension stabilizer and of its concentration on the shape, size, and morphology of beads consisting of submicroscopic particles (globules). Of many stabilizers used, only poly(vinyl pyrrolidone) and poly(vinyl alcohol) led to the formation of regular spherical beads with a surface shell. As expected, beads obtained using a stabilizer producing higher interfacial tension poly(vinyl pyrrolidone)-K 90 were much larger. A similar effect may be reached by lowering the concentration of poly(vinyl alcohol), if this lowering is accompanied by a rise in the interfacial tension. Despite this, however, the surface shell was not compact in this relatively narrow range of interfacial tensions.

INTRODUCTION

In our previous paper¹ we examined the effect of the composition of the dispersed phase in the suspension polymerization of glycidyl methacrylate and ethylene dimethacrylate (GMA-EDMA) on the morphology and some properties of the arising macroporous product. Changes in the composition of the dispersed phase caused changes in the interfacial tension. The investigation of the effect of interfacial tension at the boundary between the continuous and dispersed phases before the start of suspension polymerization on the morphology of the polymer bead is, however, better carried out by changing the interfacial tension from the bulk of the aqueous phase, because changes in the composition of the dispersed phase lead further to changes in the polymer structure and in some of its other properties.

The possibility of affecting the bead size or their distribution width and the structure of the suspension polymer by choosing a suspension stabilizer with the lowest possible interfacial tension is not a novel one. There exist papers dealing, in particular, with the morphology of suspension poly(vinyl chloride) (PVC).^{2,3} The polymerization of vinyl chloride resembles the copolymerization GMA-EDMA in that in both cases we have a precipitation polymerization. With PVC we have separation of the polymer from the monomer; in the other system the copolymer is separated from an inert mixture. The difference consists of the fact that in pores of the arising PVC there is still also the unreacted monomer, which reacts later, while the reactive polymer based on GMA-EDMA has in its pores a liquid inert mixture, the volume of which stays unchanged.

* For Part XXXII see Ref. 1.

It is known that high values of the interfacial tension between the continuous and dispersed phases lead to a compact structure of beads. The porosity of PVC formed with the addition of various water-soluble suspension stabilizers possessing comparable viscosity increases with the decreasing interfacial tension at the boundary of the continuous and dispersed phases.²

In another paper,³ Wolf and Kramer described an intentionally produced influence on the bead size distribution and on the properties of PVC by changing the structure of the interfacial area between the dispersing agent and the monomer. The change was achieved either by additions soluble in the monomer (e.g., alcohols ranging from butanol to octadecanol), or else by the addition of

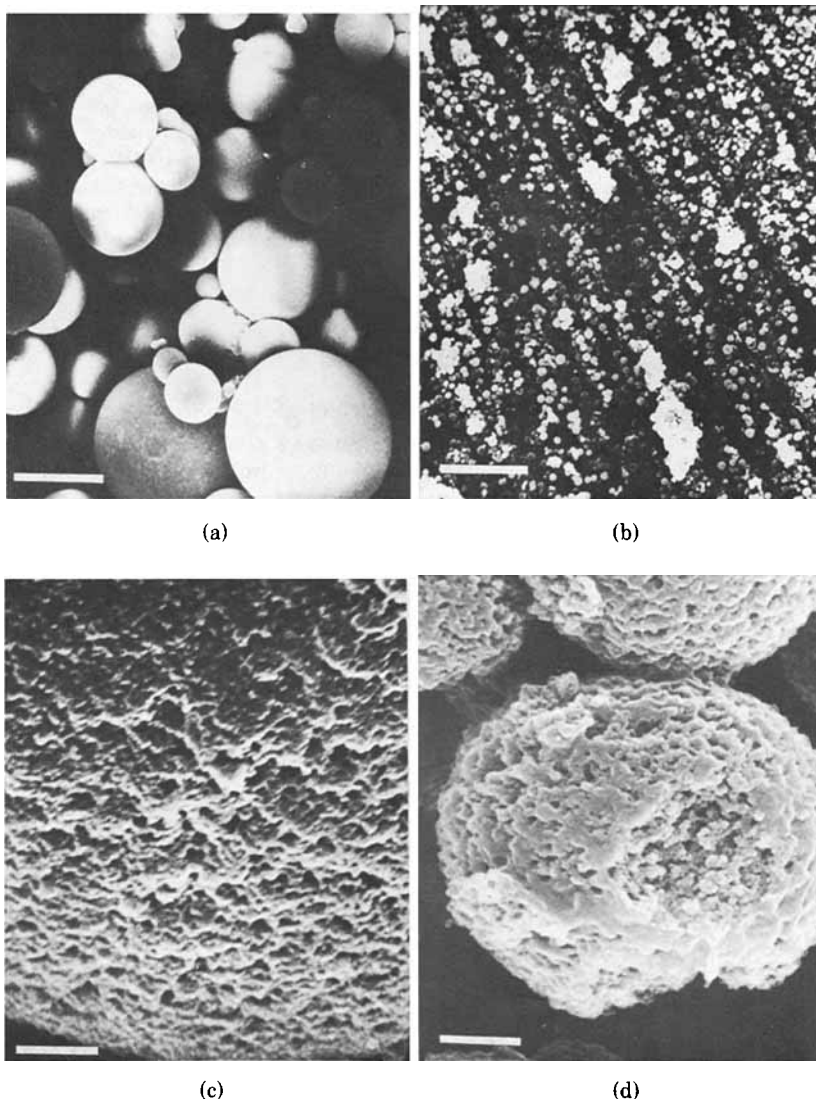


Fig. 1. Effect of the suspension stabilizer on the size and morphology of the polymer bead: poly(vinyl pyrrolidone)-K 90 [(a), (c)], poly(vinyl alcohol) [(b), (d)]. Concentration of stabilizers in water—2 wt %. Bead in (d) has its top part cut off. The intercept corresponds to 100 μm [(a), (b)], 2 μm [(c), (d)].

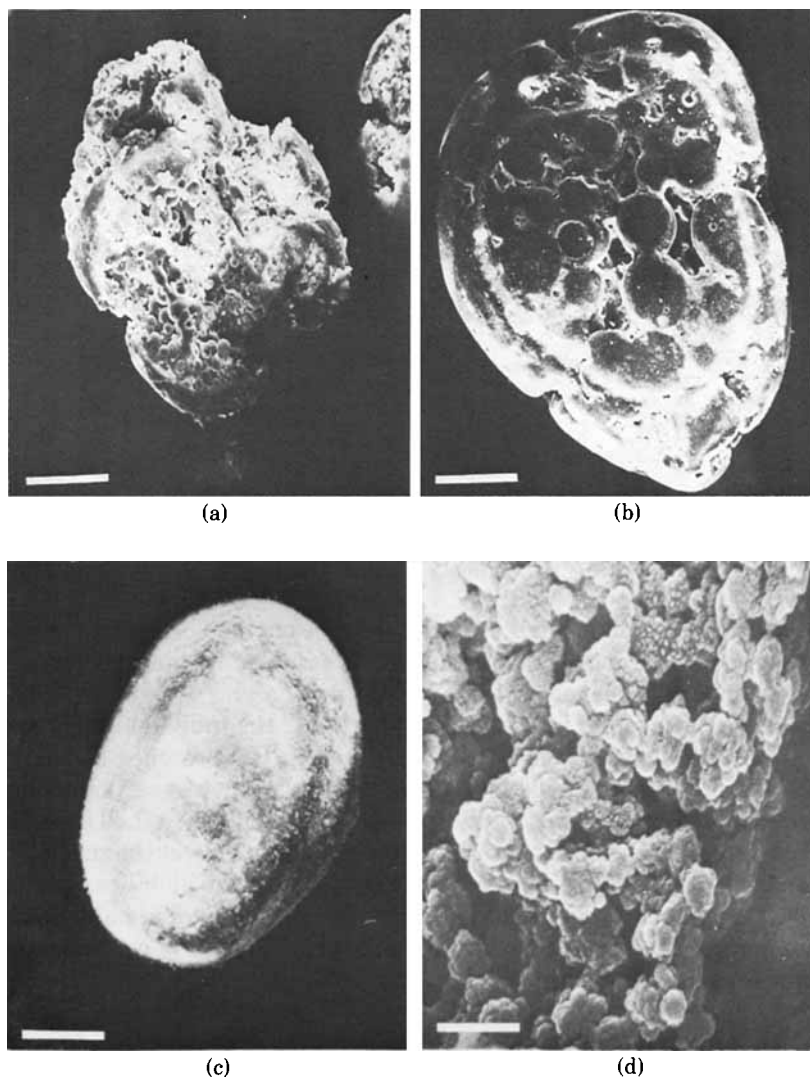


Fig. 2. Nonspherical polymer beads prepared by using surface active compounds possessing poor stabilizing efficiency: sodium caseinate [(a), (d)], poly(vinyl pyrrolidone)-K 30 [(b), (e)], Slovnik PV-370/B [(c), (f)]. The intercept corresponds to $200\ \mu\text{m}$ [(a), (b), (c)]; $2\ \mu\text{m}$ [(d), (e), (f)].

poly(ethylene oxide) or poly(propylene oxide), both of which are soluble in water. The additions of both substances raise the porosity or the fraction of large pores. Optimal results with respect to the stabilizing efficiency were observed with Povimal (sodium salt of the hydrolyzed copolymer styrene-maleic anhydride) modified with 0.1% divinyl benzene; this compound is still soluble in water, and its shell, consists of the crosslinked polymer adsorbed on the surface of the monomeric drop, exhibits the same strength (while being much thinner) as the thicker layer of uncrosslinked Povimal. The product contains an increased fraction of large pores.

Hence, it is obvious that the bead size of the suspension polymer and its porosity are affected by the interfacial tension characteristic of the given suspension stabilizer. With increasing interfacial tension the bead size also increases.⁴ Our

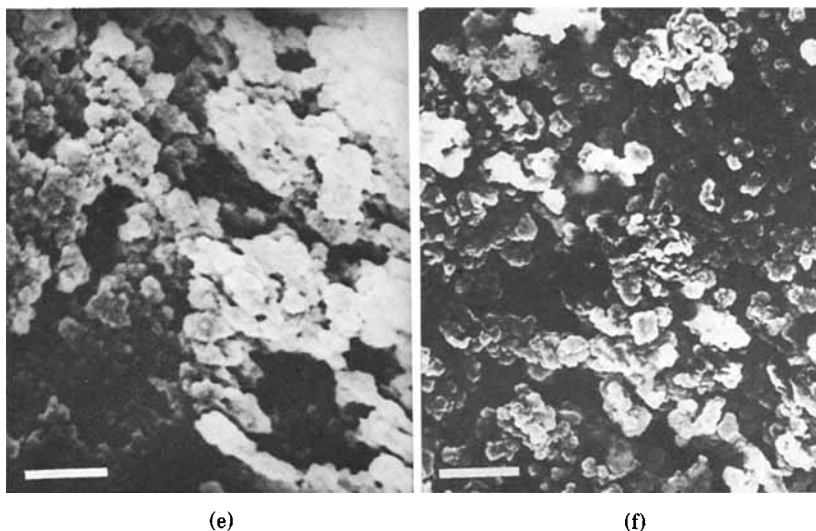


Fig. 2 (Continued from previous page.)

aim was to examine these qualitative dependences in the GMA-EDMA system, where the porogenic role of the precipitant is assumed by inert components—cyclohexanol and dodecanol—instead of the monomer.

It has also been found in an earlier paper⁵ that the individual beads of the suspension copolymer GMA-EDMA prepared in the presence of poly(vinyl pyrrolidone)-K 90 exhibit a distinct surface shell in their cross section, consisting of more compactly arranged globules. The formation of such a shell is attributed to radial forces, arising due to interfacial tension, which affect the surface of the polymerizing bead and compress the surface layer of the globules. It may be expected that, by reducing interfacial tension by using a suitable stabilizer, beads without surface shell could also be obtained, which may be of considerable importance for some applications.

EXPERIMENTAL

At a constant composition of the organic phase [volume ratios monomeric:inert mixture 2:3; GMA:EDMA 7:3; dodecanol : cyclohexanol 1:9, 2,2'-azobisisobutyronitrile in monomers 1 wt %] and under the same conditions of sus-

TABLE I
Characterization of the Polymers

Stabilizer	Stabilizer concentration, wt %	Interfacial tension of dispersed and continuous phases $\text{mN}\cdot\text{m}^{-1}$	Mean bead diameter, μm
Poly(vinyl pyrrolidone)-K 90	2	41	110
Poly(vinyl alcohol)	2	17.5	7
Poly(vinyl alcohol)	0.2	24	787 ^a
Poly(vinyl alcohol)	0.007	75	1523 ^a

^a Determined microscopically.

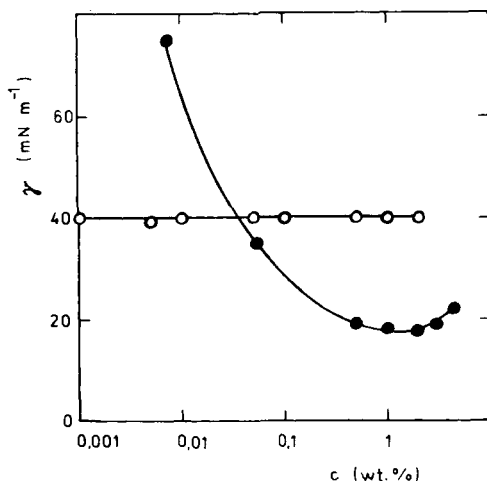


Fig. 3. Dependence of the interfacial tension (γ) of the continuous and dispersed phases on the concentration of suspension stabilizer (c); stabilizers: (○) poly(vinyl pyrrolidone)-K 90 (●) poly(vinyl alcohol). Composition of the monomeric mixture: volume ratio monomeric : inert mixture 2:3; glycidyl methacrylate : ethylene dimethacrylate 7:3; dodecanol : cyclohexanol 1:9; measured at 25°C.

pension polymerization described elsewhere,⁶ we investigated the effect of the following suspension stabilizers: poly(vinyl alcohol) (PVAL),⁷ sodium caseinate (produced by CHZWP Nováky, Czechoslovakia), poly(vinyl pyrrolidone) (PVPyrr)-K 90 ($M_w \sim 360,000$) and K 30 ($M_w \sim 40,000$; Fluka A.G., Swiss), Slovanik PV-370/B (copolymer of ethylene oxide and propylene oxide at the molar ratio 1:900) (CHZWP Nováky, Czechoslovakia).

The determination of interfacial tension as well as a scanning electron mi-

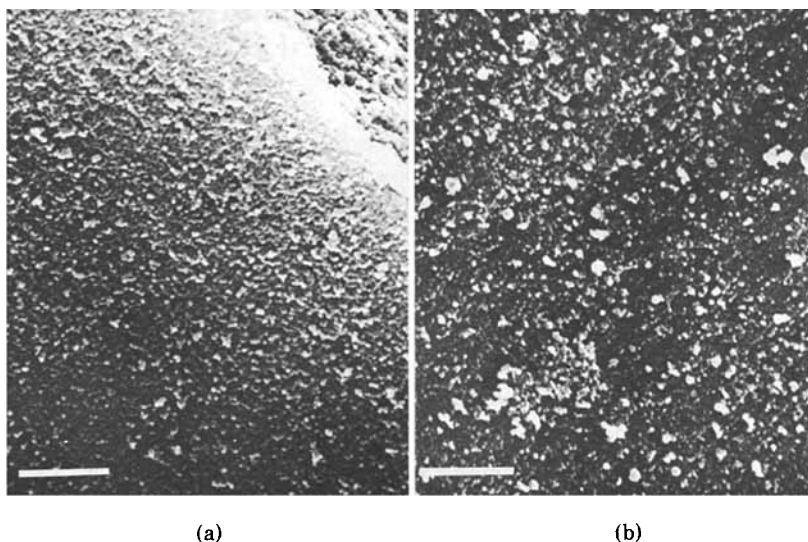


Fig. 4. Effect of the poly(vinyl alcohol) concentration on the polymer bead morphology; 0.007 wt %, $\gamma = 75 \text{ mN}\cdot\text{m}^{-1}$ (a); 0.2 wt %, $\gamma = 24 \text{ mN}\cdot\text{m}^{-1}$ (b); (a) shows the cross section of the bead. The intercept corresponds to 4 μm .

croscope technique have been described in the previous paper.¹ The mean bead diameter up to 800 μm was determined with a Coulter Counter TA II; otherwise, it was measured microscopically.

RESULTS AND DISCUSSION

The stabilizing ability of suspension stabilizers depends not only on the decrease in the interfacial tension, but also on the mechanical properties of the protective film. When reducing the interfacial tension by means of surface active compounds, one should consider their chemical nature. The larger the hydrophobic part of the molecule, the higher the surface activity of the compound (or the larger the decrease in the interfacial tension caused by it).⁸

Also among stabilizers used in this paper, two cases must be distinguished. Figure 1 shows cases of a good stabilizing effect, reflected in the spherical character of the beads or in the formation of a continuous layer (shell) of polymeric submicroscopic particles around the bead surface, and differing from the case of nonspherical beads [Figs. 2(a)–(c)]. In addition to the nonspherical character and the absence of shell, Figures 2(a) and (b) demonstrate a pronounced heterogeneity of the beads, formed by the agglomeration of unstable suspension during the polymerization. The fine globular structure of these units [Figs. 2(d)–(f)] resembles that shown in Figures 1(c) and (d), though it is more heterogeneous.

Such a poor stabilizing effect can be observed, e.g., with sodium caseinate, Slovanik PV-370/B and with the relatively low-molecular-weight PVPyrr-K 30. Owing to the large size of the beads (up to 1–2 mm), they cannot be measured with a Coulter Counter.

On the contrary, by using suspension stabilizers suited for the preparation of spherical beads (i.e., PVPyrr-K 90 with molecular weight higher by an order of magnitude than that of type K 30 and PVAL), the stabilizer producing a lower interfacial tension allows us to prepare beads smaller by an order of magnitude (Table I) than that of a higher interfacial tension (Fig. 1). Both samples have, however, a roughly identical porous shell with distinct surface pores, because interfacial tension is low and differs only little. This finding fits in with the view that a noncompact shell is formed at a low interfacial tension.

The difference in the interfacial tension values of PVPyrr-K 90 and PVAL is also documented in Figure 3, which offers a comparison between the concentration dependences of the interfacial tensions of both stabilizers. While in the case of PVPyrr-K 90 interfacial tension is concentration-independent within the given range, it markedly increases for PVAL with decreasing concentration. At these concentrations interfacial tension is high, and larger beads are formed than at a higher concentration of PVAL (Table I). The surface morphology of both sorbents, which differed during the preparation in the concentration of PVAL, but not too much in their interfacial tension, is again without major differences (Fig. 4).

Hence, shell compactness is less sensitive to interfacial tension than bead size. Hence, by choosing the suspension stabilizer or by changing its concentration, bead size may be varied to a large extent, but, in this range of relatively low interfacial tensions, no changes in the surface layer morphology can be perceived.

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