Color Bands in Methacrylic Acid Polymerization

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White and pink alternating bands have been found to be formed in the polymerization of methacrylic acid in methanol in the presence of benzoyl peroxide and N, N-dimethylaniline in a glass tube. The band structure depends on the initial concentrations of methanol and benzoyl peroxide.

Autowaves can occur when a chemical reaction is coupled with diffusion. This phenomenon is a ubiquitous feature of chemical, biological and physical excitable media. Such waves have been observed in self-replicating RNA variants, the BZ (Belousov-Zhabotinskii) reaction and some other systems.[1-6] Agladze and Krinsky have reported flower patterns in a growing active chemical medium.[7] Oosawa *et al.*[8] have reported refraction, reflection and frequency change of chemical waves propagating in a nonuniform BZ medium. Traveling wave front has been observed in the methacrylic acid (MA) polymerization reaction.[9-11] In this letter, we report our new finding of the formation of stationary bands, composed of alternating white and pink layers, in the polymerization reaction of MA in methanol in a glass tube with benzoyl peroxide (BP) as an initiator and N, N-dimethylaniline (DMA) as a promoter.

MA, BP (from CDH), methanol, DMA and ethanol (from Merck) were used as received. Methanol was added to the freshly prepared solution of BP in MA in a test tube (i.d. 13 mmϕ) to obtain homogeneous solution with the depth of 60 mm. The reaction was started by adding a critical amount of DMA with a micro pipette to the top of the solution. A white solid polymer nucleates at the top of the solution to form a sharp wave front. This moves downward with a uniform velocity leaving behind white and pink stationary bands. At lower [methanol], the pink parts become colorless and transparent. The movement of front was followed with a cathetometer as a function of time.

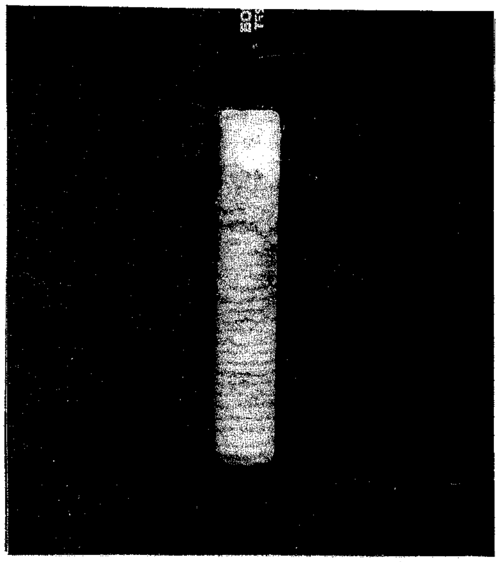

Figure 1. Photograph of stationary white and pink bands. [MA] = 9.52 M, [methanol] = 3.49 M, [BP] = 0.017 M. 0.29 mg of DMA was added to a tube of 13 mmϕ at 30 ± 0.5 °C.

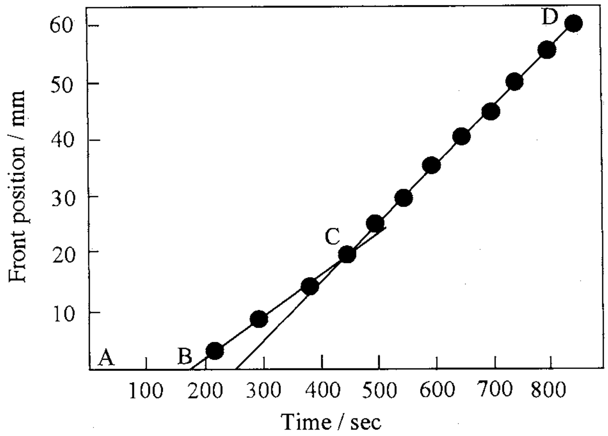

Figure 2. Plot of the front position against time. Experimental conditions are the same as those in Figure 1.

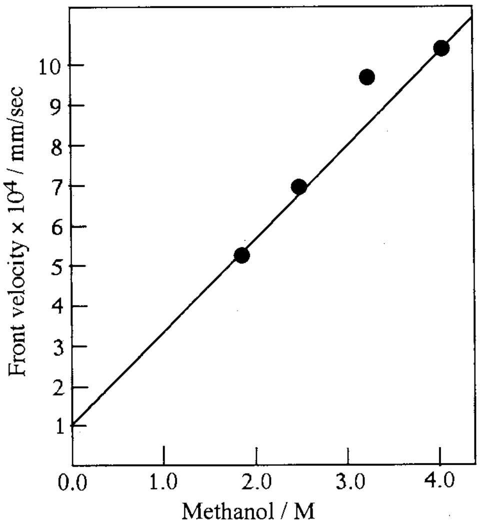

Figure 3. Dependence of the front velocity on [methanol]. Experimental conditions are the same as those for Figure 1 except for [MA] = 10.2 M.

A typical photograph of the band structure is shown in Figure 1. The position of front is shown in Figure 2 as a function of time. On adding 2.9×10^{-4} g of DMA to the top of the homogeneous colorless solution of [MA] = 9.52 M, [methanol] = 3.49 M and [BP] = 0.017 M, a white polymer starts to nucleate at the top of the solution and covers the surface with 1 mm thickness within a few minutes (AB in Figure 2). Then this column moves downward to form a wave front (region BC in Figure 2, corresponding to the onset time of the wave front). The sharp front moves downward with uniform velocity leaving behind a stationary band structure with alternating white and pink bands (region CD). This has been observed in the concentration range of [methanol] = 2.0 - 4.4 M and [BP] = 0.017 - 0.068 M.

Band structure depends on the methanol concentration. A typical plot of the front velocity against [methanol] is shown in Figure 3, which shows the front velocity to increase on increasing [methanol]. It is further observed that the band spacing increases on increasing [methanol]. Similar bands have been observed when methanol is replaced with ethanol, but with an increased time of initiation and a decreased front velocity.

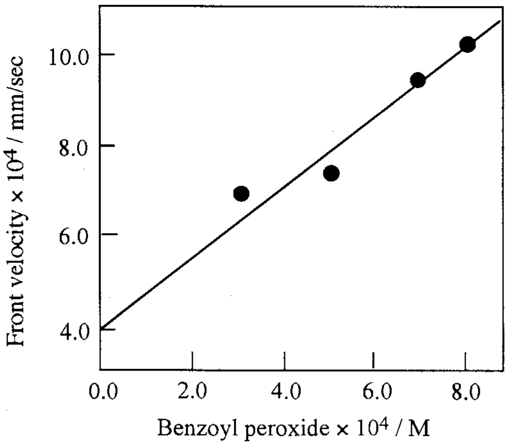

Figure 4. Dependence of the front velocity on [BP]. Experimental conditions are the same as those for Figure 3 except for [methanol] = 2.03 M.

Bands are also sensitive to [BP], as shown in Figure 4. On increasing [BP], the front velocity increases and the band spacing decreases, the induction time is shortened, and the resultant front becomes diffuse after a 10 - 15 mm movement. At lower [BP], period AB in Figure 2 increases. The front formed has weak driving force to move and stops after 10 - 15 mm movement.

The band formation also depends upon the tube diameter but is independent of the depth of solution. In a smaller diameter tube, higher [BP] is required to form bands. On increasing the tube diameter, the front velocity increases. At a critical tube diameter, a slightly higher [BP] results in the polymer to cover the upper part of the solution to inhibit the front to propagate, whereas front is not formed at all for a slightly lower [BP]. Figures 2 - 4 show that the front propagates with constant velocity and the velocity is linearly dependent on [methanol] and [BP].

Further research is under way in our laboratory to replace methanol with higher alcohols and MA with other acrylic acids to establish the phenomenon and to propose a detailed mechanism. This research has been supported by AICTE, New Delhi.

References and Notes

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