

The Mechanism of Frontal Polymerization of Methyl Methacrylate

INTRODUCTION

A new phenomenon of frontal polymerization was described in Ref. 1. A polymer begins to form near the interface soon after solid poly(methyl methacrylate) (PMMA) is in contact with methyl methacrylate (MMA). The interface, which can be easily seen because of the difference in refractive indices of PMMA and MMA (and existence of the gradient of the concentration) (Fig. 1), moves upwards and after a few days the whole monomer turns into solid polymer (at 20°C). The mechanism of this process was unclear. Previous authors suggested as a mechanism the common propagation of polymer chains initiated by radicals that have been captured in the glass-like PMMA. In this note, a different mechanism of frontal polymerization is given, which also explains some new observations made by us.

RESULTS AND DISCUSSION

There is a considerable amount of initiator in the solid polymer. PMMA and the initiator (dicyclohexilperoxidicarbonate) begin to dissolve soon after contact of PMMA and MMA. Hence the polymerization of MMA begins at the swollen surface layer which is like a special microreactor. Heat released after 10–20 min leads to convection in the monomer.² This produces a homogeneous

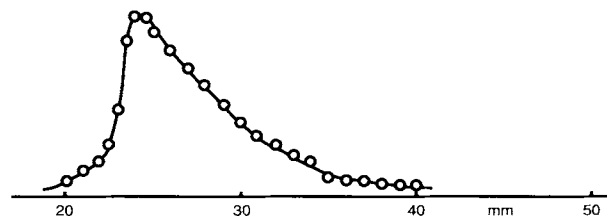


Figure 1 Typical picture for the deviation of a light ray in frontal polymerization. The relative deviation of light ray vs. length of ampoule. The relative deviation is proportional to the gradient of the PMMA concentration.

distribution of the initiator in the volume of MMA. As a result, slow polymerization begins throughout the monomer. But in the swollen polymer the rate of polymerization is considerably higher due to the Trommsdorf effect. It is this which is the actual reason for the frontal polymerization.

Contrary to Ref. 1, frontal polymerization would not occur if the original PMMA had been made by photopolymerization despite the fact that this polymer has a considerable amount of captured radicals. In this case only slow swelling of PMMA took place (Fig. 2). But even in this case frontal polymerization may be brought about by shining UV or visible light on an ampoule (Fig. 3).

Apparently dicyclohexilperoxidicarbonate is less compatible with a solution of PMMA in MMA than with pure MMA. Therefore, during the frontal polymerization the initiator collects in the top part of the ampoule. This increases the rate of polymerization at the end of the process. The concentration of the initiator in the top part of ampoule was directly confirmed by autoradiography with a ³H-marked initiator.

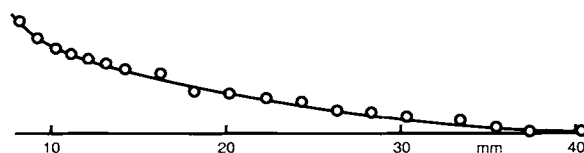


Figure 2 The relative deviation of light ray for the sample produced by photopolymerization.

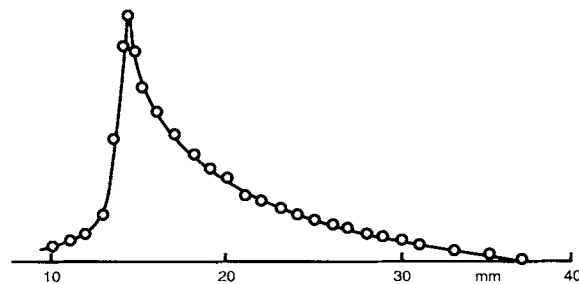


Figure 3 The relative deviation of light ray for the sample produced by photopolymerization after 3 h in sunlight.

References

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