

# Photochemical Rupture of Microcapsules: A Model System

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## Synopsis

Polyamide microcapsules containing solutions of azo-bis-isobutyronitrile (AIBN) were prepared and characterized as regards diameter and wall thickness. Under UV irradiation the AIBN eliminates nitrogen, and this, under suitable conditions, leads to rupture of the capsules. The influence of capsular diameter and wall thickness of the crosslinking agent silane, of AIBN concentration, and of light intensity on the photoelimination and rupture were studied by determining rates of nitrogen release and by microscopic examination. The results are interpreted in terms of release of nitrogen in the core followed by diffusion of nitrogen or of core solution through the walls, or rupture of the microcapsules. The application to controlled photochemical release of contents is considered.

## INTRODUCTION

The aim of this work was to develop a microcapsular system (MC) which can be induced to release its contents, in a controlled manner, by exposure to light. To this end we investigated the feasibility of incorporating into the solution which eventually forms the core of the capsule a material that photochemically eliminates gaseous products. It was our expectation that exposure of the MC thus obtained to suitable light would lead to the photoelimination of the gases, buildup of pressure within the capsule, and eventual rupture of the MC wall with release of the contents. An earlier report<sup>1</sup> indicates that such expectations are reasonable; however, for effective, efficient, and controlled release, we need information concerning the requisite properties of the MC-photoeliminator system.

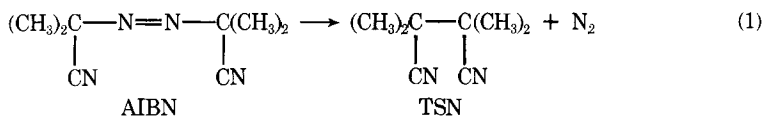
In order to achieve our aim, we must ensure that the system undergoes as little noncontrolled release as possible. Thus, the capsules must be stable on storage, which requires mechanical strength and stability in contact with the solvent, and their contents must not diffuse out over appreciable times. For efficient photofracture, the microcapsules should have suitable mechanical properties, which remain to be investigated; they should not absorb an appreciable part of the active light; and they should be stable in contact with the photoeliminator. This last material, for its part, would advantageously strongly absorb light of a convenient wavelength and should be soluble in the core solvent, give gaseous products with high quantum yield, and be stable under reasonable storage conditions. Further, the products of the photoelimination reaction should not absorb appreciably the exciting light.

On the basis of the above criteria, we selected the following as model components of the system:

- (1) The microcapsules were of [partially (?) crosslinked] polyamide, prepared

by interfacial polycondensation<sup>2,3</sup> of terephthaloyl dichloride in benzene/xylene with diethylenetriamine (DETA) in water.<sup>4</sup> This polymer is strong,<sup>5</sup> has low permeability to nitrogen,<sup>6</sup> is transparent to near-UV light, and is chemically stable to the photoeliminator we used. It is readily further crosslinked by coupling agents such as silane and has proved convenient to handle.<sup>7</sup> Guidelines are available<sup>8</sup> concerning selection of the parameters of the polymeric wall material, of the solute, of the capsules, and of the environment so as to minimize the permeability of the wall to solute molecules.

(2) As photoeliminator we used azo-bis-isobutyronitrile (AIBN). This material is readily available and easily purified, but care is necessary because of possible toxicity of products. AIBN has been extensively studied<sup>9</sup>; it is soluble in a wide variety of solvents, but not in water. Further, its solubility properties suggest that the rate of its permeation through the polyamide shell should be low. It has an absorption maximum, admittedly weak, at 345 nm, a convenient wavelength. AIBN decomposes both thermally and photochemically, the principal reaction leading to nitrogen and tetramethyl succinodinitrile (TSN):



These products essentially do not absorb light in the range of 310–390 nm. (Other products formed do absorb some light at  $\lambda < 325$  nm.) The fact that the gas formed is nitrogen is an advantage since this gas permeates polyamide films more slowly than do other common photoeliminated gases (e.g.,  $\text{CO}_2$ ).<sup>10</sup> The quantum yield of photoelimination from AIBN in solution is of the order of 0.45. In the dark, the decomposition of this compound in benzene and xylene is slow at 25°C and negligibly so at 0°C.

(3) The solvent (internal phase) needs to have good solvating power for AIBN and terephthaloyl chloride, needs to be immiscible with water and should yield good-quality films<sup>8</sup> (mechanical strength, permeability). Benzene/xylene (2:1 v/v) was used in most experiments.

In what follows it should be noted that if it is assumed that one monomer is fully consumed and that all polymer produced goes into forming the capsule walls, the wall thickness should increase linearly with the diameter of the capsule.

## EXPERIMENTAL

### Materials

AIBN (Fluka, Switzerland, Purum) was twice crystallized from ethanol (mp 101°C). Terephthaloyl chloride (Eastman) was twice crystallized from *n*-hexane (mp 83°C). Diethylenetriamine (Merck, Zur Synthese), silane (Dow Corning, Z6020), and poly(vinyl alcohol) (BDH, MW 30,000) were used as such. Solvents were analytical grade: xylene (Frutarom) and benzene, acetone, and ethanol (Merck).

### Equipment and Methods

The stirrer motor used in microcapsule preparation was a Multifix-Constant MC model 1000 (Alfred Schwinherr). Particle size was determined with a Quantimet Image Analyzing System, model 720 (Cambridge Instruments). Absorption spectra were measured with an SP-1800 spectrophotometer (Pye-Unicam). The Ultrasonic Cell Disruptor, used for disrupting MC and exposing their contents, was a model 130 (Branson). Scanning electron microscopy was performed with a Superinism model 2 (I.S.I.); capsules before testing were gold coated (Spotter Unit, Polaron) for 5 min.

Gas evolution was followed in a conventional manometer in which the volume of the dead space was very small compared to those of the (doubly jacketed) reaction cell and of the measuring tubes. The reaction cell was thermostatted; most photochemical experiments were carried out at 15°C. Testing of the system with known amounts of AIBN showed its accuracy to be >99%.

The thickness of the capsule walls,  $h$ , was determined by use of one of two expressions. The first, owing to Nang et al.,<sup>11</sup> is

$$h = \frac{\bar{r}(1-p)d_1}{3[pd_2 + (1-p)d_1]} \quad (2)$$

The alternative is

$$h = r_1 \left[ \left( \frac{d_1}{d_2} \cdot \frac{1-p}{p} + 1 \right)^{1/3} - 1 \right] \quad (3)$$

In these expressions  $r_1$  and  $\bar{r}$  are, respectively, the inner and mean radii of the capsules;  $p$  is the ratio of the weight of the core material to that of the full capsule; and  $d_1$  and  $d_2$  are, respectively, the densities of the solution and of the capsule walls. The latter is determined from  $d_1$  and the overall density of the full capsule,  $d_3$ :

$$d_2 = \frac{d_1(1-p)}{(d_1/d_3) - p} \quad (4)$$

For some fractions the value of the wall thickness thus obtained was checked and confirmed by SEM measurements.

### Preparation of Capsules

An 0.4% aqueous solution (280 ml) of poly(vinyl alcohol) was emulsified with 105 ml benzene/xylene containing terephthaloyl chloride, with or without AIBN. To this was added an aqueous solution of diethylenetriamine with or without silane, and mixing was continued for 1 hr. The capsules were separated by decantation and repeatedly washed with distilled water until the wash liquid was neutral. To obtain dry, free-flowing powders, the capsules were rapidly washed with acetone in a stream of air. There was loss of AIBN in this drying step. Table I gives details of the preparations of various batches.

It was found that the speed and time of mixing during emulsification were critical in determining the distribution of diameters in a given batch. Batches were fractionated by standard sieves, and the mean diameter and wall thickness were determined for each fraction (Table II).

The results establish the expected, approximately linear relationship between

TABLE I  
 Systems Used in Preparation of Various Batches of Capsules

Batch no.	Equivalents triamine equivalents dichloride	T, °C	AIBN, % w/w	Silane	Volume internal phase, ml
21 (B) <sup>a</sup>	26	20	0	+ <sup>b</sup>	105
21	26	20	4.0	+	105
25 <sup>c</sup>	26	20	4.0	+	210
32 <sup>d</sup>	26	20	4.0	+	105
33(B)	26	20	0	—	105
33	26	20	4.0	—	105
30(B)	30	15	0	+	105
31	30	15	4.0	+	105
28	30	15	2.0	+	105

<sup>a</sup> (B) indicates blank (i.e., no AIBN). Monomer concentrations constant throughout except for batch 32.

<sup>b</sup> + Indicates that silane was added (1.4 ml in the usual case, 2.8 ml in the double-volume preparation).

<sup>c</sup> Double volume, but monomer concentrations as for other batches.

<sup>d</sup> Monomer concentrations half of other batches.

wall thickness and capsular diameter. Note that batch 21, with silane, has, for a given diameter, thicker walls than batch 33, without silane. Note also the thin walls of batch 25; for this double-volume preparation there was IR evidence for residual monomer dichloride in the capsule core material.

The distributions of capsular diameters in two fractions can be visualized from photomicrographs shown in Figures 1(1) and 1(2). We see that the capsules as prepared are spherical, completely filled, and transparent to visible light.

 TABLE II  
 Characterization of Capsules from Various Batches

Batch no.	Diameter (2r), $\mu\text{m}$		Density $d_2$ , <sup>a</sup> g/ml, $\pm 5\%$	$p$ (core/capsule), wt %	Wall thickness, $\mu\text{m}$ , $\pm 10\%$
	Sieve	Quantimet			
25	500–800	750	1.03	98.12	1.33–2.13
25	420–500	455		98.15	1.10–1.31
25	297–420	355		98.13	0.78–1.11
25 <sup>b</sup>	210–297	360		97.93	0.61–0.87
21	500–800	720	0.99	97.14	2.10–3.38
21	420–500	410		97.45	1.58–1.88
21	297–420	355		97.11	1.26–1.70
21	210–297	245		97.11	0.91–1.30
28	297–420			97.98	— <sup>c</sup>
31	297–420			97.50	— <sup>c</sup>
33	500–800		0.96	98.63	1.04–1.66
33	420–500			98.63	0.87–1.04
33	297–420			98.63	0.60–0.85
33	210–297			98.82	0.42–0.59

<sup>a</sup> The density  $d_3$  of the whole capsules was  $0.878 \pm 0.001$  g/ml for the silane-containing capsules and  $0.876 \pm 0.001$  g/ml for the others. The values given for the densities  $d_2$  of the capsule walls are averages of the results of two or three measurements.

<sup>b</sup> The cause of the discrepancy between the Sieve and Quantimet results is not clear.

<sup>c</sup> Not determined.

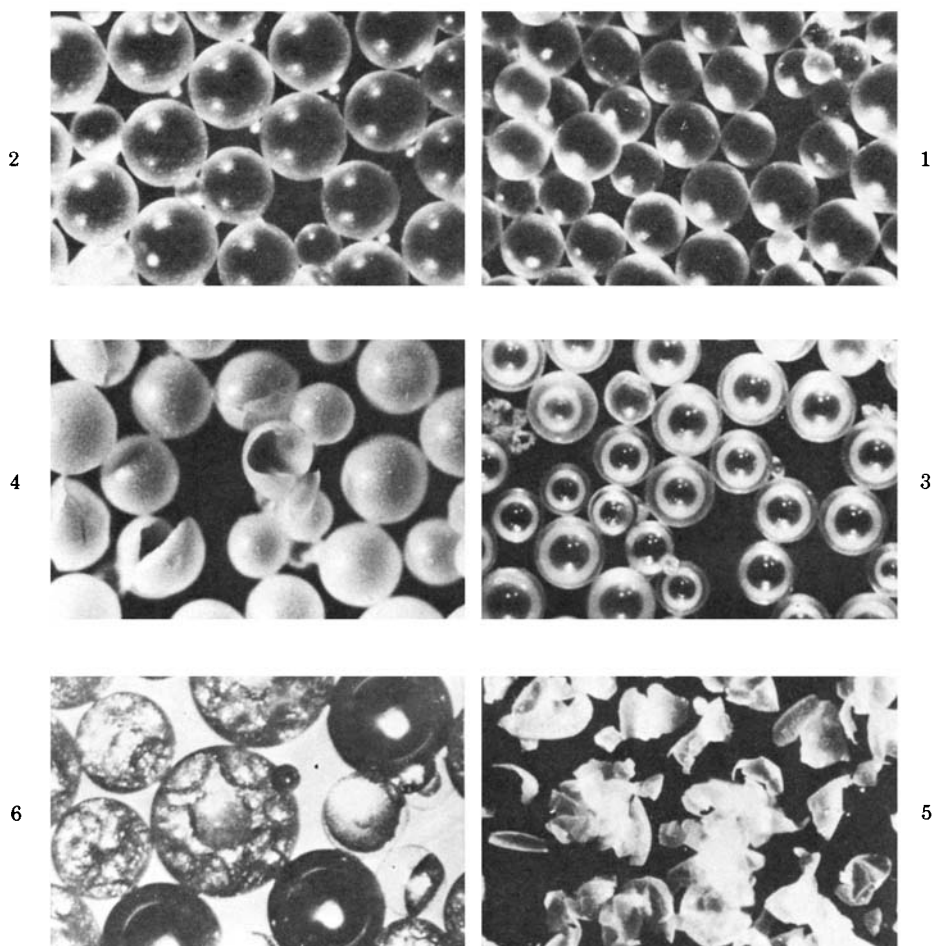


Fig. 1. Capsules under the microscope. (1)–(6), Optical microscope; (7)–(9), scanning electron microscope: (1) after preparation, spherical and dry, 420–500  $\mu\text{m}$ ; (2) after preparation, spherical and dry, 297–420  $\mu\text{m}$ ; (3) after irradiation, with gas bubbles, 297–420  $\mu\text{m}$ ; (4) after irradiation, some ruptured, some whole and empty, 420–500  $\mu\text{m}$ ; (5) after sonification; (6) during irradiation in water; (7) wall ( $\times 12,000$ ); (8) empty, with holes ( $\times 240$ ); (9) empty, with holes ( $\times 1200$ ).

## RESULTS AND DISCUSSIONS

### Thermal Stability of Microcapsules

In order to obtain information on thermal stability, weighed samples of the microcapsules were introduced into an oven at 100°C. The samples were removed from time to time, reweighed, and reintroduced into the oven. Results were obtained as residual fraction of internal phase versus time. In this way two fractions each of blank batches 21(B) and 33(B) were compared. The former batch, containing silane, gradually and slowly loses content; after 40 days, about 85% of the internal phase remains. The latter batch, without silane, behaves initially like the former; however, after about 25 days, there is an acceleratory loss of content, with very little remaining after 40 days. Capsules of 420–500  $\mu\text{m}$  react more rapidly than those of 300–400  $\mu\text{m}$ . In batch 33, containing AIBN, there is an earlier (ca. eight-day) acceleratory loss of content; thus, these mi-

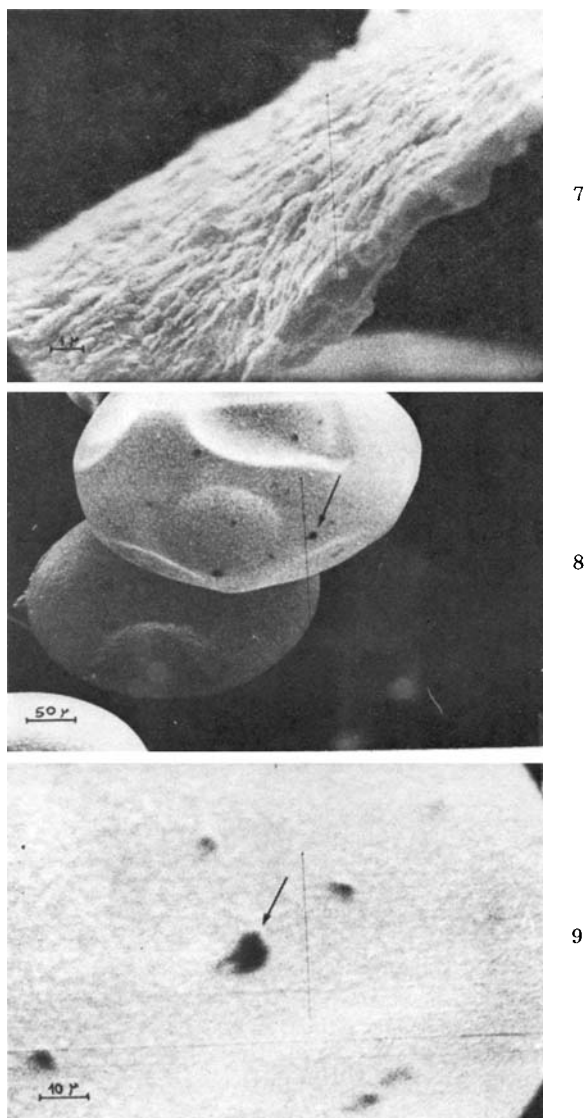


Fig. 1. (Continued from previous page.)

crocapsules are essentially empty within 20 days, the effect again being marked for the larger capsules. Fractions of diameter 300–420  $\mu\text{m}$  of silane-containing batches 30(B), 28, and 31 were compared; these have nominal AIBN concentrations of 0, 2, and 4%, respectively. While the first two behave much like 21(B) (see above) over a period of 28 days, the third rapidly empties, with a half-life of the order of two days.

The decomposition of AIBN is essentially instantaneous (half-life of the order of 1 min) under these conditions. Thus, these experiments test the stability of the microcapsule to the internal pressure owing to the vapor pressure of solvent and pressure of nitrogen, which rapidly developed. The loss of nitrogen from the MC would hardly be observable in these experiments.

Further experiments showed that even at 50°C loss of nitrogen from the capsules is rapid. A sample of batch 25, fraction 420–500  $\mu\text{m}$ , was introduced into the manometric system, with the sample cell at this last temperature. Nitrogen evolution started immediately; it followed first-order kinetics with a rate constant of  $2.64 \times 10^{-5} \text{ sec}^{-1}$ , which is the same as that for a solution of AIBN in benzene at this temperature.<sup>13-17</sup> The sample after one month in the system was cooled to 15°C and irradiated with UV light. There was no further nitrogen evolution.

These results indicate that at 50°C and above, the capsule walls provide no barrier to nitrogen loss. This loss is by diffusion since the walls remain intact over long periods, as shown by the retention of solution.

On the other hand, at 15°C the thermal decomposition and loss of nitrogen were slow compared to those achieved under irradiation, and generally no background correction was necessary in the photochemical runs. Further, the dry capsules can be stored in the refrigerator for a year or more without deterioration.

## Photochemical Experiments

### *General*

Standard conditions were used throughout, unless otherwise noted. A known weight of MC, usually 0.7 to 1.0 g, was suspended in 5 ml xylene (refractive index 1.433; cf. the polyamide, 1.51). This suspension was introduced into the reaction cell thermostatted at 15°C and magnetically stirred at a known rate. The system was allowed to equilibrate. Blank capsules (no AIBN) were stable (no weight loss) under these conditions. In the dark, there was some diffusion of AIBN from the capsules; however, this was inappreciable (9% in 105 min) during the time of a photochemical run.

The suspension was now irradiated, through the Pyrex walls of the cell, by light from a medium-pressure mercury lamp. For high-intensity irradiations, the full lamp output was used; for low intensities, the light was passed through Corning Glass Filters Nos. 9863 + 5850. In the latter case, the intensity of active light was found to be of the order of  $5 \times 10^{-8} \text{ einstein/sec}$  (from the rate of decomposition of nonencapsulated AIBN).

Results were obtained as "percentage of nitrogen released" versus "time of irradiation" and for all runs were compared to the results for AIBN in solution (nonencapsulated). In all cases, the evolution on long irradiation tended asymptotically to 100%, based on the weight of AIBN used. In the case of nonencapsulated AIBN, the evolution started at zero time with a finite rate; for most AIBN-containing microcapsules there was, however, an induction period, showing that the polymer provides a barrier to release. Figure 2 shows a typical case and defines the "induction time"  $T_\theta$  and the "half-reaction time"  $T_{1/2}$ .

If the weight of the capsules before irradiation is  $W$  and that at the end of irradiation is  $W'$ , then the percentage rupture was obtained from

$$\begin{aligned} \% \text{ rupture} &= \frac{\text{weight loss}}{\text{original weight}} \\ &= \frac{W - W'}{W} \end{aligned} \quad (5)$$

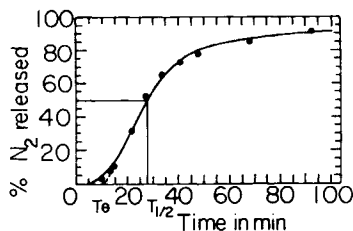


Fig. 2. Photochemical release of nitrogen from AIBN-containing MC (% vs. time). Batch 21, mixed fractions, sizes 210–800  $\mu\text{m}$ .

In most cases, samples of the MC before and after irradiation were examined under the optical microscope. After irradiation, four types of capsules were recognized:

(1) Whole spheres, full of solution, and appearing similar to the starting capsules [Figs. 1(1) and 1(2)]. Spectroscopic examination of their contents showed them to contain TSN [eq. (1)], but no AIBN. Thus, the evolved nitrogen has escaped.

(2) Whole capsules containing bubbles of nitrogen [Fig. 1(3)].

(3) Ruptured capsules [Fig. 1(4)].

(4) Capsules which are empty but still spherical and apparently whole (recognized by opacity) [Fig. 1(4)].

Different batches and reaction conditions led to different distributions between these four types.

It is clear that the percentage rupture as defined by eq. (5) measures essentially loss of *solution*, by any mechanism, and thus types 3 and 4 and to some extent type 2. On the other hand, there is nitrogen loss from capsules of type 1 which is not accompanied by release of solution, and which is an inefficient process from the point of view of our overall aim.

#### *Influences of Capsular Diameter, Wall Thickness, and AIBN Concentration*

In Figure 3 are shown the results for the various fractions of batch 21 in benzene/xylene under high-intensity irradiation. While it is difficult to be precise about the behavior of  $T_0$ , it is clear that  $T_{1/2}$  increases markedly with decreasing capsular diameter. The  $T_{1/2}$  values for curves 2, 3, 4, and 5 are, respectively, 14, 16, 21, and 43 min. At the same time the percentage rupture decreases: the values are 91, 87, 62, and 18%, respectively. It should be noted that because of the drying with acetone, the AIBN concentrations for curves 4 and 5 were lower

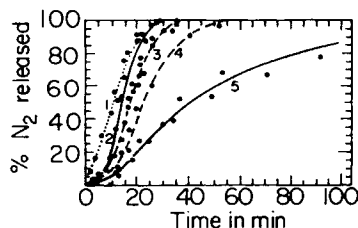


Fig. 3. Photochemical release of nitrogen from AIBN solution and from various fractions of AIBN-MC (% vs. time). Batch 21, 0.71 g MC per 5 ml benzene/xylene. (1) AIBN solution; others AIBN-MC: (2) 500–800; (3) 420–500; (4) 297–420; (5) 210–297  $\mu\text{m}$ .

than those for curves 2 and 3 (the AIBN is more effectively "washed out" when the surface area is higher). However, we consider the dominant influence to be the size effect, for reasons which will be clear later. It thus seems that percentage rupture increases and  $T_{1/2}$  decreases with increasing capsular diameter, and therefore with increased wall thickness.

Microscopic examination of these irradiated capsules showed that for the fractions of large diameter (high rupture), these were mainly of types 3 and 4, referred to above, with a little of type 2. On the other hand, the small capsules (210–297  $\mu\text{m}$ ) were mainly of type 4, with a little of type 1. This suggests that in small particles diffusion of nitrogen or solution from the capsules is important; the former cuts down on the efficiencies of the various forms of rupture.

The fractions of batch 25 show variations in the same sense. Here, however, the differences in AIBN concentrations were smaller, and the  $T_{1/2}$  values are less spread out ( $T_{1/2} \sim 26$ –36 min). The percentage rupture is uniformly higher (95–70%) than in batch 21. (These and all later experiments refer to xylene as suspension medium.)

Clearly, it is not easy to differentiate between the influences of capsular diameter and of AIBN concentration. The following experiments aimed at trying to clarify this point.

The 297–420  $\mu\text{m}$  fractions of batches 25 and 32 were compared. Since the latter was prepared from half-concentrations of monomers, its wall thickness must be appreciably less than that of the former. At the same time, the AIBN concentrations (determined for disrupted capsules) were very similar (for the former  $3.6 \times 10^{-2}$  g/g capsules, the latter  $3.4 \times 10^{-2}$  g/g capsules). The  $T_{1/2}$  values were, respectively, 18 and 26 min, and the corresponding percentages rupture 81 and 41. Thus, there is definite influence of the wall thickness, in the same sense as above. Capsules of batch 32 after irradiation were found to be mainly of type 1, with some type 4 and little type 2. Here, diffusion seems to be the dominant mechanism.

The influence of the concentration of the photoeliminator was studied by comparing the behavior of a fraction of batch 31, of a given diameter and of high AIBN concentration, with that of a fraction of batch 28, of the same diameter and of low AIBN concentration. These two batches were polymerized under the same conditions and are assumed to have the same wall thickness. The  $T_{1/2}$  values were 28 and 140 min for batches 31 and 28, respectively. The corresponding percentages rupture were 73 and 14. The gas evolution curve is S-shaped for the former, but not for the latter (Fig. 4).

The tentative picture emerging from all the above results is as follows: Both AIBN concentration and capsular wall thickness affect the rate of nitrogen ev-

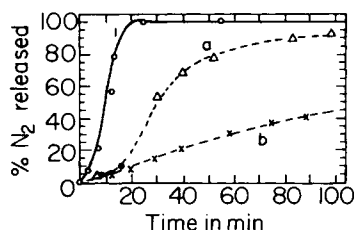


Fig. 4. Influence of AIBN concentration on nitrogen release as a function of exposure time: (1) AIBN solution,  $4.1 \times 10^{-2}$  g/g; (a) batch 31,  $4.1 \times 10^{-2}$  g/g MC; (b) batch 28,  $2.3 \times 10^{-2}$  g/g MC.

olution and the extent of rupture. Desirable properties are a low value of  $T_{1/2}$  and high percentage rupture; these are achieved with high-diameter, thick-walled capsules at high AIBN concentration. With thin-walled capsules and low AIBN concentration, diffusion tends to become important. Further, these results suggest that not only is the amount of nitrogen released a determining factor but also is the *rate* of its release.

Another tentative suggestion may be derived by consideration of Figure 4. It is seen that curve (b) for batch 28 appears very much like an extension of the induction portion of curve (a) for batch 31. In other words, it may well be that the same mechanism is operative in the induction period for batch 31 as throughout for batch 28. But the latter is primarily diffusion of gas and solvent. Thus, it seems that the induction period generally found for the microcapsules is associated with diffusion of core contents into the wall, which then becomes susceptible to rupture.

### *Influence of Intensity of Light*

The 297–420  $\mu\text{m}$  fraction of batch 25 was used for a detailed study of the influence of light intensity. This intensity was varied by interposing wire mesh filters, each of 35% transmittivity. For each run the results were compared to those for AIBN solution (nonencapsulated) at the same intensity. Figure 5 shows some of the results. The results are summarized in Table III. Similar results were obtained with the nonsilane microcapsules of batch 33.

Microscopic examination shows little difference between the two batches. The outstanding feature is that with decreasing light intensity there is a decrease in the number of ruptured cells, with a corresponding increase in the number of capsules containing gas bubbles (type 2) and of those whole but empty (type 4).

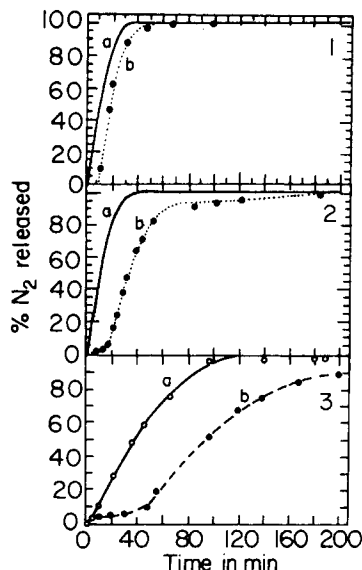


Fig. 5. Influence of light intensity  $I$  on nitrogen release as function of photoexposure time. Batch 25, fraction 297–420  $\mu\text{m}$ : (a) AIBN solution; (b) AIBN-MC; (1)  $I = I_0$ ; (2)  $I = 0.35I_0$ ; (3)  $I = 0.12I_0$ .

TABLE III  
Influence of Light Intensity on Nitrogen Evolution from Microcapsules<sup>a</sup>

Fig. no.	Light intensity	AIBN $T_{1/2}$ , <sup>b</sup> min	$T_{1/2} - T_{1/2}^{\text{AIBN}}$ , <sup>b</sup> min	Rupture, %
5.1	$I_0$	8	11	78
5.2	$0.35I_0$	15	19	71
5.3	$0.12I_0$	38	56	53

<sup>a</sup> Batch 25, fraction 297–420  $\mu\text{m}$ , in xylene, AIBN concentration  $3.6 \times 10^{-2}$  g/g capsules.

<sup>b</sup>  $T_{1/2}^{\text{AIBN}}$  is the value of  $T_{1/2}$  for AIBN solution (nonencapsulated).

We note in Figure 5 that in all cases there are obtained S-shaped curves; however, it is conceivable that at still lower intensities the induction period would merge into the curve for the overall process. The rates during the acceleratory periods are very similar to those for the decompositions of the AIBN solution; the curves are displaced with respect to one another in time because of the induction period. In fact, the length of this period,  $T_\theta$ , varies more or less linearly with  $T_{1/2}$  of AIBN; this suggests that a certain critical pressure of nitrogen must be built up before the capsules start rupturing.

The results with the microscope indicate that there is some coupling between formations of type 2 and type 4 capsules; possibly, the pressure of the gas bubbles formed induces either rupture or "forced" diffusion of the solvent. In fact, microscopic examination *during* irradiation of capsules of batch 25 during low-intensity irradiation shows that gas bubbles first form in the capsules, and the latter then empty.

Some experiments were performed using light filtered through the Corning glass filter combination; fractions of batch 25 (with silane) and of batch 33 (without silane) were compared. The results are complex and have not been fully analyzed; the induction periods are shorter and the acceleratory rates higher for batch 33. However, there is an inversion in the size dependence: the 420–500  $\mu\text{m}$  fractions, in both batches, have higher percentages of ruptures and lower values of  $T_{1/2}$  than do the fractions of smaller and larger capsules.

These last experiments led us to examine some capsules, irradiated under these conditions, in the scanning electron microscope. At very high magnifications the surface features of capsules with and without silane seem similar [Fig. 1(7)]. However, at lower magnifications, the walls of capsules of batch 25 were found to contain holes of size of the order of 1–5  $\mu\text{m}$  [Figs. 1(8) and 1(9)]. Such holes have not been observed in capsules from batches containing no silane.

#### *Influence of the Suspending Medium*

Capsules of diameter 297–420  $\mu\text{m}$  of batch 25 were suspended either in water or xylene. Gas evolution in the former shows no induction period; however, because of the rapid acceleration in xylene, gas evolution from water continues for a longer time. In xylene, bubble formation in the capsule and emptying of the capsule were observed. However, in water another phenomenon was observed—formation of small gas bubbles at the outer surface of the capsule [Fig. 1(6)]. This is direct evidence for diffusion of nitrogen through the walls of whole capsules.

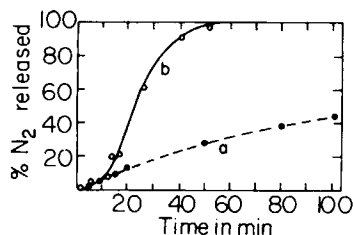


Fig. 6. Comparison of nitrogen release from AIBN-MC on continuous irradiation (b) and during and after short (14 min.) irradiation (a). Batch 25, fraction 297–420  $\mu\text{m}$ .

### *Effect of Short and Interrupted Irradiations*

The fraction 297–400  $\mu\text{m}$  of batch 21 was irradiated under the standard conditions for 14 min. During this time, about 9% of nitrogen was evolved. The light was then switched off, but we continued to monitor the amount of nitrogen evolved: *this continued to increase in the dark* and eventually reached 46%. This behavior is compared with that of a continuously irradiated fraction in Figure 6. The sample in the dark was then warmed from the standard temperature of 15–30°C, to free any further entrapped nitrogen. It was then recooled to 15°C, when the amount of gas evolved was found to be 74%. The percentage rupture in this experiment was low (34%).

During the initial irradiation (14 min), much of the AIBN in the core solution would have decomposed, but little nitrogen was evolved. Thus, the pressure in the capsule is high, and apparently there then follows a pressure-induced diffusion of gas and/or solution into the wall. The pressure here, however, seems to be insufficient to cause rupture. The source of the nitrogen evolved must be diffused nitrogen and possibly, to a smaller extent, nitrogen resulting from diffused AIBN.

An interesting experiment was performed on fraction 297–400  $\mu\text{m}$  of batch 25. This fraction was subjected to alternate light and dark periods, and the evolution of nitrogen was continuously monitored. As may be seen from Figure 7, the evolution curve is indistinguishable from that obtained under continuous irradiation. Here, apparently the internal gas pressure under the first and second irradiations was sufficiently high to bring some of the capsules to a rupturable state.

We can conclude also that the duration of the induction period, i.e., the onset of the acceleratory period and of rupture, is determined by the amount of release of nitrogen by the AIBN and by the rate of this process.

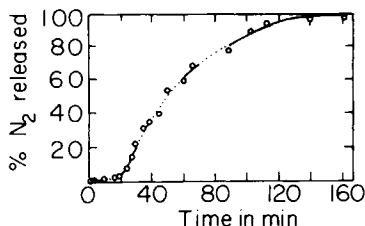
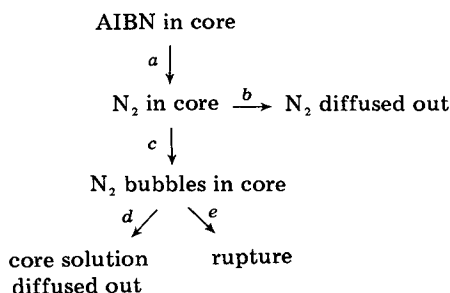


Fig. 7. Nitrogen release during alternate light (full curve) and dark (dotted curve) periods. Batch 25, fraction 297–420  $\mu\text{m}$ .

## CONCLUSIONS

We have reached the following tentative conclusions:

- (1) Large-diameter, thick-walled capsules are more efficiently ruptured than thin-walled ones.
- (2) This efficiency is higher in capsules treated with silane than in those not so treated. This may be due to the larger diameters and/or to the additional rigidity of the former.
- (3) AIBN concentration must be above a certain level to ensure rupture.
- (4) High light intensities are desirable from the point of view of rate, but not essential for rupture.
- (5) The overall process may be analyzed as follows:



Stage *a* is determined by light intensity and AIBN concentration. The partition between *b* and *c* must be determined by the properties of the wall and also, probably, by the rate of *a*. Finally, from the point of view of release of content, both *d* and *e* are effective processes.

(6) There is evidence for similar steps for nonsilane capsules in the dark at 100°C, the driving force presumably being supplied by the vapor pressure of the core solvent.

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