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An Accurate Method for Determining Inhibition Period of Vinyl Acetate Monomer

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The factors like ambient temperature, catalyst purity and heterogeneity of reaction system, have been taken into consideration while evolving a precise method for the determination of inhibition period of vinyl acetate monomer. The standard deviation and the accuracy in the new method are 2.17 sec and ±0.2% respectively.

Inhibition time, commonly known as activity time, inhibition period or polymerization time[1-3] is an important pointer for the quality of vinyl acetate monomer, specially when used in homo or copolymerization reactions. Five different emerical methods[1-3] for determining the inhibition period are available; three short methods (determination time 2-30 min) and two long methods (130-170 min). None of the three short methods, viz. (i) Celanese, (ii) Hoechst or (iii) USIS, tried by us was found to give accurate results. Our efforts in this direction have resulted in an accurate method which is described herein.

Vinyl acetate monomer (VAM) used was 99.9% pure by GC (using a chromosorb-101, SS 0.32×180 cm column at 135° and 20 ml of H_2/min as carrier gas on TCD) and had impurities like moisture (200 ppm), acetaldehyde (20 ppm), acetone (10 ppm), methyl acetate (15 ppm), ethyl acetate (126 ppm), benzene (267 ppm) and acetic acid (50 ppm).

Benzoyl peroxide of 89% purity (remaining 11% being water) was further purified by precipitation or crystallization[4] from chloroform and its purity further checked by a known method[5]. The experimental set-up used for determining the inhibition time is shown in Fig. 1.

Procedure

Benzoyl peroxide (50 mg) and VAM (10 g) which was prestored at 25° were accurately weighed in a special tube (Fig. 1) and covered tightly with suction-type adapter using spring on the hooks. The whole assembly was connected to the pressurizing system adjusted for 760 mm of Hg and dipped into a constant temperature water bath maintained at $68 \pm 0.2°$, in such a fashion that the tube dipped only upto 7.5 cm height in water. The time difference between the initial dipping of the tube in the bath and the starting of the first vigorous frothing at the upper surface of the liquid gave the inhibition period.

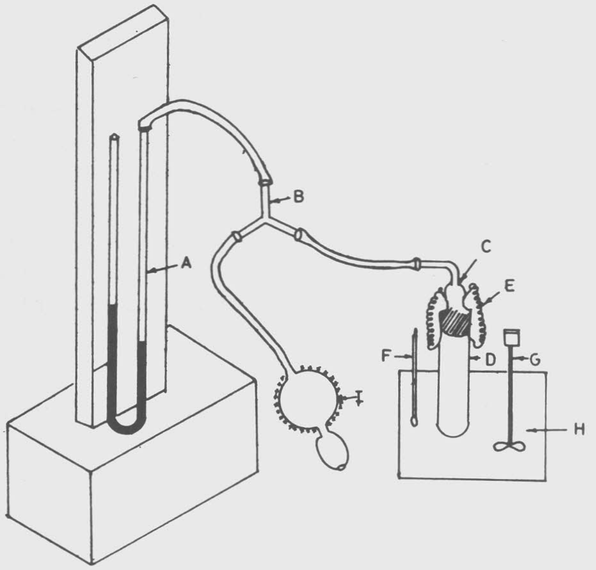

Fig. 1—Apparatus for determining inhibition period of VAM [A, manometer; B, Y-tube; C, B-24(male) suction adapter; D, special tube (200 × 25 mm) with B-24 (female) joint at its top; E, spring; F, thermometer; G, agitator; H, constant temperature water bath; and I, bladder with air pump]

The temperature profiles were determined by measuring actual reaction temperature at 1 min intervals in a slightly different set-up where in adapter (C) of Fig. 1 was replaced by a two-way adapter which was provided with an arrangement for the thermometer and also a tube, connected to pressurizing system. In Hoechst method the temperatures were measured at ambient pressure only.

The three short methods, viz Celanese, Hoechst and USIS are essentially based on bulk polymerization and differ from each other in (i) concentration of free radical initiator (benzoyl peroxide)[6] (Celanese 0.0078; Hoechst, 0.0206; and USIS, 0.0770 mol dm^{-3}), (ii) the reaction temperature (Celanese, 70°; Hoechst, 68°; and USIS, reflux temp.) and (iii) quantity or volume of vinyl acetate employed (Celanese and Hoechst, 10 ml; USIS, 20 g). Using VAM having the same composition (GC), the experiments for determining inhibition period by these methods and the modified method presently designed were repeated at least 5 times by each method following carefully and rigorously the methodologies. It is evident from the results that the literature methods are not very accurate and show considerable variation depending upon the method used. Also in these methods the following apparently minor but important factors which influence the inhibition period have not been taken into consideration:

(i) In Celanese and Hoechst methods, the effect of ambient temperature plays an important role as (a) the volume of VAM measured could vary from 20° or less in winter to 45° or more in summer leading to erroneous results and (b) it affects the time for the reaction mass to attain the desired reaction temperature or activation energy of 80-100 kJ/mol[7] and hence is likely to affect the inhibition period.

(ii) Since the particle size determines the dissolution time, it implies that with varying size of crystals (from 5 mm long needles to powder) in different runs for the same VAM the inhibition time would also be affected and further more the reaction system is not homogeneous (Hoechst method).

(iii) The USIS method though takes care of some of these factors, suffers from uncontrolled heat in-puts (directly heated by a burner) which also affects the frothing pattern.

To evolve a more accurate method it was considered worthwhile to investigate the effect of above factors on the inhibition period. Aliquots (10 ml each) were withdrawn at 20° and 40° and inhibition period determined using Hoechst method. The variation in inhibition period for the same sample of VAM due to measurement of volume at different temperatures is significant; the values at 20° and 40° are 13 min 12 sec and 12 min 12 sec respectively. The time required to attain the reaction temperature (i.e. 68°) has been found to be 2 min 41 sec and 2 min 17 sec respectively for VAM stored at 20° and 40°. The dissolution periods for big crystals and fine powder (in Hoechst assembly) were 38 and 5 sec at 68° respectively. At this juncture we also examined the effect of purity of benzoyl peroxide on the inhibition period and for this commercial samples were crystallized and also precipitated[8] and their purities checked[5]. The inhibition period of same VAM using commercial sample (83.4% pure) of benzoyl peroxide was 14 min 16 sec, for crystallized sample (92.7% pure) it was 13 min 50 sec and for precipitated sample (94.7% pure) was 13 min 28 sec. These results indicate that higher the initiator concentration lower is the inhibition period and vice versa. As is expected, benzoyl peroxide when dissolved prior to the experiment shows lower inhibition period (12 min 48 sec) as compared to that (13 min 15 sec) in the heterogenous system of Hoechst.

The temperature profile of reaction during the inhibition period determination is presented in Table 1. Though in Hoechst method the initiator appears to dissolve in first few seconds, the system is not uniform, as is clearly born out by the fact that the temperature at the bottom (i.e. at a point closest to higher initiator concentration) is higher by atleast 5° as compared to that in a homogeneous system (present method).

Table 1—Temperature Profiles during Inhibition Period

Time (min)	Temp °C		Time (min)	Temp °C	
	Hoechst method	Modified method		Hoechst method	Modified method
1	62.0	60.5	9	71.0	70.2
2	66.0	66.0	10	71.5	70.5
3	67.0	67.0	11	72.2	70.7
4	68.0	67.7	12	73.2	70.7
5	68.7	68.2	13	74.7	71.0
6	69.5	68.8	13′31″	77.0	71.1
7	70.0	69.2	15	—	71.5
8	70.5	69.8	15′50″	—	71.7

Table 2—Accuracy and Standard Deviations in Determining Institution Period of VAM by Various Methods

Method	Variation over 5 expts (sec)	Accuracy %(±)	Standard deviation
Celanese	39	0.90	17.74
Hoechst	60	3.13	30.49
USIS	15	2.91	6.09
Present method	6	0.204	2.17

In view of the reports[9] that VAM forms complex with oxygen which acts as a inhibitor during polymerization, we carried out the experiments in the presence and absence of oxygen. For this, a portion of VAM was carefully distilled under nitrogen. Inhibition periods of this sample of VAM under 1 atm N_2 pressure and that of VAM (stored normally) using 1 atm air pressure were found to be 13 min 32 sec and 13 min 30 sec respectively, thereby ruling out the possibility of O_2 affecting inhibition period.

In the present method the deficiencies in the known methods have been overcome. This will be evident from the fact that the frothing pattern in the present method is more regular compared to that of earlier methods[1-3].

The standard deviations and per cent accuracy for all the methods are given in Table 2; these are found to be 2.17 and ±0.204% for the present method. It must be pointed out that in the absence of any theoretical value $\bar{X}$ has been taken as x and percentage accuracy has accordingly been calculated.

References

1 *Standard Method of test for determining vinyl acetate activity by bulk polymerization—Method No. SMA-25-64* (Celanese Chemical Corporation of America, New York) 1964, pp. 1.

2 Kirtikar V Y, *Private Communication* (Hoechst Dyes, India).

3 *VAM* Vinyl acetate monomer handbook* (USI Chemical Corporation, USA) 1971, pp. 27.

4 Vogel A I, *Text book of practical organic chemistry*, (ELBS, London) 1978, pp. 283.

5 Gilman H & Blatt A H, *Organic syntheses, Coll. Vol. I* (John Wiley, New York) 1941 pp. 433.

6 Mathews G, *Vinyl and allied polymers*, Vol. II, (Plastic Institute, London) 1972, 21-24.

7 Ulbricht J, *Synthese Von Hochpolemeren* (Akademie Verlag, Berlin) 1978 pp. 80-81.

8 Sax N I, *Dangerous properties of industrial materials*, (Van Norstrand, New York) 1979 pp. 409.

9 Allen P W, *J polymer Sci*, **17** (1955) 156.