

EFFECT OF DODECYL MERCAPTAN ON THE BENZOYL PEROXIDE INITIATED POLYMERIZATION OF VINYL ACETATE

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The solution polymerisation of vinyl acetate in the presence of dodecyl mercaptan has been carried out at 100° using benzoyl peroxide as initiator and ethyl acetate as diluent. Dodecyl mercaptan decreases the polymerization of vinyl acetate and at low concentration shows no induction period. It acts as chain transfer agent. The value of chain transfer constant for DDM is determined as 4.2×10^2 . DDM may be used as molecular weight regulator.

Key words: Polymerization, Dodecyl mercaptan, Vinyl acetate, Chain transfer agent.

INTRODUCTION

Earlier work [1-4] on vinyl acetate polymerization in bulk and in solution showed significant effects of small amount of impurities and difficulties encountered in controlling the polymers on a large scale. Some impurities including molecular oxygen show inhibition or retardation effects on polymerization of commercial vinyl acetate when heated at temperatures below 120° [5]. The inhibition period due to oxygen was explained as a period of oxygen absorption during which peroxides form.

Poly vinyl acetate of different molecular weight is the starting material so that poly vinyl alcohols of required molecular weight could be prepared on an economical scale. Most of the mercaptans are frequently used as transfer agents when it is required to control the molecular weight of the polymer. Long chain mercaptans have the dual role of regulator and activator. Tertiary dodecyl mercaptans at low concentrations are less effective than *n*-dodecyl mercaptans [6-7]. Tertiary dodecyl mercaptan oxidizes more slowly than dodecyl mercaptan. It is very interesting to note here that dodecyl mercaptan (DDM) retards the polymerization of vinyl acetate whereas it is a good transfer agent for styrene monomer [8-9]. This paper deals with the benzoyl peroxides catalysed polymerization of vinyl acetate in the presence of dodecyl mercaptan using ethyl acetate as a diluent at 100°.

EXPERIMENTAL

Material. Vinyl acetate (E.Merck) was purified by distilling at 73°. Ethyl acetate and acetone were distilled before use. Dodecyl mercaptan (*n*-dodecanethiol) obtained from E.Merck was used as such. Benzoyl peroxide A.R grade was recrystallised twice in chloroform.

Procedure of polymerization. All polymerization reactions were carried out in sealed pyrex tubes. A weighed amount of vinyl acetate, ethyl acetate (equal to monomer) and dodecyl mercaptan were added in the reaction tube already containing 0.15 % benzoyl peroxide. The reaction tubes were sealed after flushing with nitrogen and heated at 100°. After the reaction time required the tubes were broken open. The resulting product was precipitated with distilled water. It was dried under vacuum. It was also noted that the yield was not reproducible when the monomer was polymerized in sealed tubes but the order of the yield remains unaltered. The viscosity of the dilute solutions of poly vinyl acetate prepared in acetone was measured at $30 \pm 0.1^\circ$ using an Ostwald type viscometer.

RESULTS AND DISCUSSION

Data regarding the effects of dodecyl mercaptans (DDM) on benzoyl peroxide catalysed polymerization of vinyl acetate using ethyl acetate as diluent at 100° are presented in Tables 1 and 2. These results indicate that DDM retarted the polymerization of vinyl acetate. The rate of polymerization of vinyl acetate decreases with increasing amount of DDM (Fig. 1). At 2.65 % concentration of DDM the conversion comes down from 95 % to 10.6 %. In Fig. 2, curves of percentage conversion against time show that DDM lowers the polymerization rate without an inhibition period (Table 2). The lowering down of rate of polymerization is due to conversion of DDM into disulfide. It reacts with chain radicals (which are produced by reacting vinyl acetate and benzoyl peroxide) and yield propagating radicals of lower reactivity. These less efficient propagating radicals do not trap or stop the kinetic chain but results in decrease in the rate of polymerization. The conversion of DDM into disulfide might be due to oxygen

Table 1. Retardation effect of dodecyl mercaptan on the benzoyl peroxide (0.15 %) catalyzed polymerization of vinyl acetate (10 g) using ethyl acetate (10 g) as a diluent at 100°.

Samples No.	Dodecyl mercaptan %	Time (min)	Yield %	[η] dl/g	\bar{M}_n	\bar{P}_n
1.	0.000	240	94.0	0.112	13277	154.38
2.	0.265	240	60.8	0.100	11238	130.6
3.	0.530	240	45.2	0.098	10910	126.86
4.	0.80	240	40.7	0.097	10746	125.00
5.	1.06	240	32.0	0.097	10746	125.00
6.	1.32	240	26.2	0.096	10584	123.07
7.	2.65	240	10.6	0.095	10422	121.12

Table 2. Effect of time on the benzoyl peroxide (0.15 %) catalyzed polymerization of vinyl acetate (5.0 g) in presence of dodecyl mercaptan (DDM) using ethyl acetate (5.0 g) as diluent at 100°.

S. No.	Time (min)	Yield (%)	
		Without DDM	With DDM 0.26
1.	5	17.64	5.00
2.	10	32.50	8.40
3.	15	40.80	18.10
4.	30	47.70	22.40
5.	60	64.20	32.00
6.	75	—	41.2
7.	90	83.2	—
8.	120	90.0	43.90

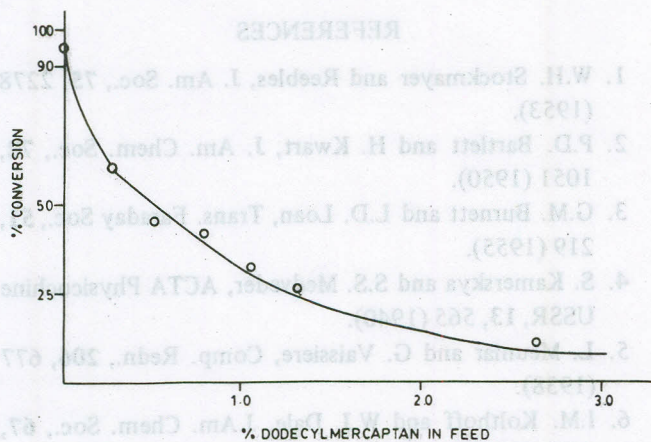


Fig. 1. Effect of varying amount of dodecyl mercaptan on the benzoyl peroxide initiated polymerization of vinyl acetate at 100°

dissolved in vinyl acetate and peroxide present in the system. The dissolved oxygen is partially used up in oxidising DDM into disulfide and partially in converting vinyl acetate into acetaldehyde and free acid since purified vinyl acetate is very sensitive towards oxygen. The decrease in the rate of polymerization at different concentrations of DDM, keeping the concentration of diluent and benzoyl peroxide at a constant for all experiments shows that the

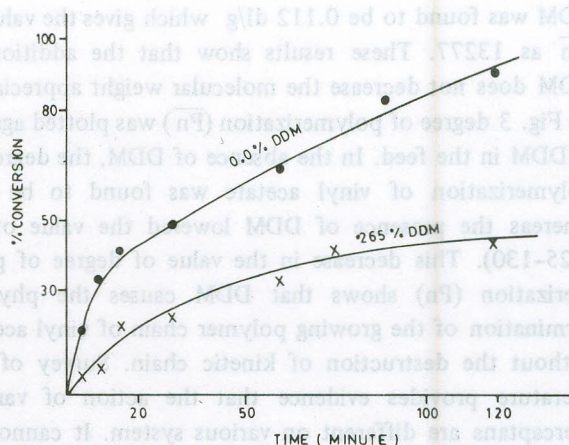


Fig. 2. Retardation in the benzoyl peroxide initiated polymerization of vinyl acetate at 100°

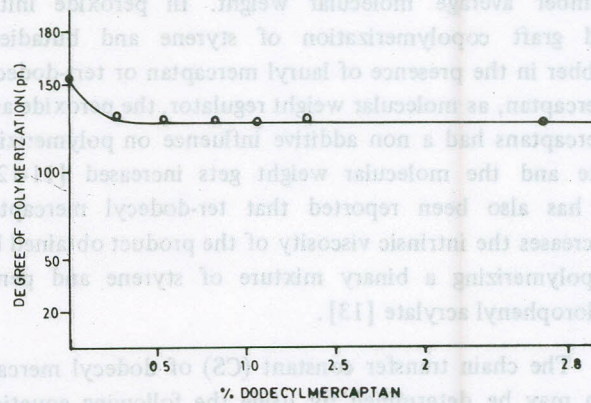


Fig. 3. Effect of dodecyl mercaptan on the degree of polymerization in benzoyl peroxide initiated polymerization of vinyl acetate at 100°.

disulfide is the main reason of decreasing the rate of polymerization. Similar results are obtained in the peroxide initiated copolymerization of styrene and butadiene in the presence of lauryl mercaptans and tert dodecyl mercaptan. These mercaptans decrease the rate of copolymerization of styrene and butadiene [10].

The number average molecular weight (\bar{M}_n) of polyvinyl acetate samples was determined by viscometry using the following intrinsic viscosity [η] molecular weight relationship [10].

$$[\eta] = 1.76 \times 10^{-4} \bar{M}_n^{0.68}$$

Intrinsic viscosity was obtained by plotting η_{sp}/C against C . Here η_{sp} is the specific viscosity and C is the concentration of solution prepared in acetone. The intrinsic viscosity of poly vinyl acetate samples prepared in the presence of DDM ranges from 0.097 to 0.100 dl/g. The number average molecular weight calculated from these values are obtained as 10422-11238 and summarized in Table 1. The intrinsic viscosity of poly vinyl acetate prepared in the absence of DDM was found to be 0.112 dl/g which gives the value of \bar{M}_n as 13277. These results show that the addition of DDM does not decrease the molecular weight appreciably. In Fig. 3 degree of polymerization (\bar{P}_n) was plotted against % DDM in the feed. In the absence of DDM, the degree of polymerization of vinyl acetate was found to be 154 whereas the presence of DDM lowered the value of \bar{P}_n (125-130). This decrease in the value of degree of polymerization (\bar{P}_n) shows that DDM causes the physical termination of the growing polymer chain of vinyl acetate without the destruction of kinetic chain. Survey of the literature provides evidence that the action of various mercaptans are different on various system. It cannot be generalised that mercaptans lower the molecular weight of the product. They may both increase or decrease the number average molecular weight. In peroxide initiated graft copolymerization of styrene and butadiene rubber in the presence of lauryl mercaptan or tert-dodecyl mercaptan, as molecular weight regulator, the peroxide and mercaptans had a non additive influence on polymerizing rate and the molecular weight gets increased [11-12]. It has also been reported that ter-dodecyl mercaptan decreases the intrinsic viscosity of the product obtained by copolymerizing a binary mixture of styrene and penta chlorophenyl acrylate [13].

The chain transfer constant (CS) of dodecyl mercaptan may be determined by using the following equation [14].

$$\frac{1}{\bar{P}_n} = \frac{(K_1 K_3)^{1/2} [I]^{1/2}}{K_2 [M]^{1/2}} + \frac{K_4}{K_2} + \frac{K_5}{K_2} \frac{[S]}{[M]}$$

where K_1 , K_2 , K_3 , K_4 and K_5 are the rate constants for initiation propagation, termination monomer, transfer, and solvent transfer respectively. K_4/K_2 and K_5/K_2 are monomer transfer (CM) constant and chain transfer constant (CS) respectively. The first term of above equation may be neglected since the concentration of solvent and catalyst are constant for all preparations. The slope of the plot $1/\bar{P}_n$ vs $[S]/[M]$ (Fig. 4) gives the value of CS whereas the intercept is the measure of CM. Thus the chain transfer constant

obtained from this plot is 4.2×10^{-3} whereas the value of CM obtained from the intercept of the plot is 7.6×10^{-3} .

From these results, this may be concluded that DDM reacts with initiating radicals formed by the decomposition of benzoyl peroxide in the presence of ethyl acetate and produce weak active centres resulting in less efficient propagating radicals. These less efficient propagating radicals not only decrease the rate of polymerization of

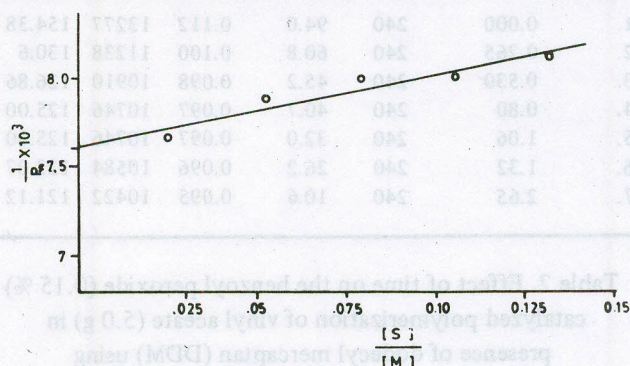


Fig. 4. A plot $1/\bar{P}_n \times 10^3$ vs $[S]/[M]$ for the determination of C_M and C_S .

vinyl acetate but also lower the number average molecular weight, though the difference in molecular weight at different concentration of DDM is little. This little difference in molecular weight of various concentration of dodecyl mercaptan concludes that DDM may serve as a molecular weight regulator. Poly vinyl acetate carrying out molecular weight $1 \times 10^4 - 1.1 \times 10^4$ may be easily prepared by the addition of 0.0 - 2.65 % DDM during the benzoyl peroxide initiated polymerization of vinyl acetate. Hence DDM acts as chain transfer agent and molecular weight regulator.

REFERENCES

1. W.H. Stockmayer and Reebles, *J. Am. Soc.*, **75**, 2278 (1953).
2. P.D. Bartlett and H. Kwart, *J. Am. Chem. Soc.*, **72**, 1051 (1950).
3. G.M. Burnett and L.D. Loan, *Trans. Faraday Soc.*, **51**, 219 (1955).
4. S. Kamerskya and S.S. Medveder, *ACTA Physicochine USSR*, **13**, 565 (1940).
5. L. Meuniar and G. Vaissiere, *Comp. Redn.*, **206**, 677 (1938).
6. I.M. Kolthoff and W.J. Dale, *J. Am. Chem. Soc.*, **67**, 1672 (1945).
7. I.M. Kolthoff and W.E. Harries, *J. Polym. Sci.*, **2**, 41 (1949).

