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by

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Thermal Polymerization of Methyl Acrylate

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SUMMARY

In this article the thermal rate of polymerization of methyl acrylate has been determined as 5.5 x 10^{-5} mol l^{-1} sn^{-1} From this experimental results we come to the conclusion that omitting the thermal rate of polymerization of methyl acrylate in the kinetics treatments brings about some errors when initiator concentration is low.

INTRODUCTION

Vinyl monomers susceptible to free-radical polymerization often polymerize thermally on storage if the free-radical inhibitors are not present. This effect may be due to traces of peroxide impurities, but in some cases a thermal rate of polymerization is observed in highly purified monomers in the obsence of an added initiator.

Some workers (1), investigating the polymerization of carefully purified methyl methacrylate in the temperature range 100–150°C found that the initial rate of polymerization varied from sample to sample.

Styrene has a higher thermal rate of polymerization than methyl methacrylate and is capable of giving more reproducible results.

A study of the thermal polymerization of chloroprene has recently been undertaken by Leeming et al. (2).

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In this article the thermal polymerization of methyl acrylate has been investigated and it is found that this monomer can be polymirized at 60°C when the monomer is highly purified thus in the presence of a free– radical initiator the rates of initiator by the spontaneous and initiated processes are addivite. Since the thermal polymerization of the monomers is complex, a fully established mechanism does not exist. Howewer the kinetics treatment of the thermal polymerization can be made as follows:

In the thermal initiation, if chain initiation is caused by the production of "hot" moleculus, then the ordinary mechanism of binary collision will supply these molecules.

The activation process can be written as follow

$$M + M \xrightarrow{k} M^{*} + M$$

and the proportion of molecules having an energy greater than E_a is proportional to exp $(-E_a/RT)$. The rate of production of active centres is k $[M]^2$, but the active centres can disappear in two different ways.

a) By starting off a polymerization chain at a rate $k_1\ [M^*]$

b) By deactivation through collision with normal moleculus. For pure monomer without a solvent this rate is $k_2\ [M^*].\ [M]$

When a stationary concentration is set up

$$\frac{d\ [M^*]}{dt} = k\ [M]^2 - k_1\ [M^*] - k_2\ [M^*]\ [M] = 0$$

and

$$[M^*] = k\ [M]^2\ /\ (k_1 + k_2\ [M])$$

Only a fraction of the activated molecules, then, will start chains, and the remainder are destroyed before they can cause polymerization. The rate of disappearance of M* to start chains is

$$k_1\ [M^*] = k_1\ k\ [M]^2\ /\ (k_1 + k_2\ [M])$$

or

$$k_1\ [M^*] = k\ [M]^2\ /\ (1 + k_2\ [M]\ /\ k_1)$$

Here two extreme cases may be distinguished:

1) k_2 [M] $\gg$ k_1. The rate at which chains are started is then k k_1 [M] / k_2. This is a first – order reaction.

2) k_2 [M] $\ll$ k_1 . The expression for k_1 [M*] reduces to k $[M]^2$. This is a second - order reaction. This means that the activated molecules react almost as soon as they are created and nearly all of them start off chains. But the rate of thermal initiation is usually proportional to the monomer concentration, making the over all polymerization rate proportional to $[M]^2$.

The activation energy for thermal polymerization is the same order of magnitute as that intitiated reaction, yet thermal polymerization is much slower than normal reaction. The reason for this is that the collision factor for thermal polymerization is extremely low. The normal value of A for a bimolecular reaction is 10^{11} – 10^{13}, for the thermal initiation of polsystyrene it is about 10^6 – 10^4.

EXPERİMENTAL

1) Purification of Monomer:

300 ml of methyl acrylate was washed with two 50 ml portion of 2 % ferrous sulfate solutions. It was then washed twice with water followed by two washings with 50 ml portions of 2 % solution of sodium hydroxide. The monomer was again washed with distilled water and was then dried over anhydrous sodium sulfate. Distillation of the monomer was carried out under vacuum. A Freshly distilled monomer was degassed at least three times under high vacuum, then the reaction vessel sealed off from the vacuum line was put in a thermostat which was kept at 60°C.

The experimental results are shown in Table I

TABLE I

Thermal Rate of Polymerization of Methyl Acrylate $[M]_0$ = 10,45 mole litre^{-1}

Exp. no.	t (min)	Pol %	R_p (mole litre^{-1} sec^{-1})
I	70	2.31	5.7 x 10^{-5}
II	95	3.04	5.6 x 10^{-5}
III	80	2.16	4.7 x 10^{-5}
IV	80	2.69	5.9 x 10^{-5}

If we compare the thermal rate of polymerization in the abowe table with the initiated rate of polymerization given in reference [3], we come to the conclusion that methyl acrylate has a thermal rate of polymerization which introduce some errors into kinetics treatement when initiator concentration is quite low.

ÖZET

Vinil monomerlerinin bir başlatıcı yanında polimerizasyonuna ait kinetik incelemelerde termik hız ihmal edilmektedir. Bu çalışmada metil akrilata ait termik hız tayin edilerek, özellikle başlatıcı konsantrasyonu küçük olduğu zaman bu hızın ihmal edilemiyeceği gösterilmiştir.

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