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Initiation Mechanisms

Kinetics of the Polymerization of Methylmethacrylate with 4,4'-Azobis (4-Cyanopentanol) as Initiator

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Summary

The radical polymerization in bulk of methylmethacrylate in presence of 4,4' azobis(cyanopentanol) (ACP) has been studied at 60°, 67°, 72°, 81° and 84°C. The ratio $kp/kt^{\frac{1}{2}}$ has been determined for each of these temperatures, using the molecular weight method. The rates constants of decomposition and the efficiency of (ACP) were calculated from conversion-time curves. The activation energy of the polymerization was obtained from the slope of Arrhenius plot of Rp.

Introduction

Functional polymers possessing hydroxy terminal groups have generally been synthesized by the anionic polymerization of suitable monomers to give "living polymers" capable of reaction with various electrophilic reagents for the introduction of functionality (Szwarc 1956, Richards 1968, Brody 1958, Uraneck 1960, Brossas 1974). An alternate approach which has received attention is one involving the use of free radical polymerization mechanism employing initiators containing the desired function. Bamford (1960) demonstrates this technique utilizing 4,4' azobis(4-cyanopentanoic acid) and 4,4' azobis(4-cyanopentanol) (ACP) as the initiators for the polymerization of styrene, acrylonitrile and methylmethacrylate.

This work describes the results of determination of the kinetic parameters of polymerization in bulk of methylmethacrylate with (ACP) as the initiator.

Experimental

. Methylmethacrylate (MMA) was washed with 5% sodium hydroxide solution and then, with distilled water. The monomer was dried with calcium chloride before to be distilled at reduced pressure on to calcium hydride and stored at 0°C in the dark; it was redistilled from calcium hydride prior to use.

. 4,4' azobis(4-cyanopentanol) (ACP) was prepared and purified as described previously (Clouet 1984).

. Polymerization were carried out in bulk in the presence of (ACP) in vacuum sealed Pyrex tubes at 60°, 67°, 72°, 81° and 84°C ±0.1°C. Generally for a short time to ensure low conversion (less than 12% conversion). After proper reaction times the tubes were chilled in liquid nitrogen, opened and the polymer formed was precipited into a large excess of petroleum ether. The polymer was separated and dried in a vacuum oven at 40°C.

. Molecular weights are determined by means of Water Associate 200 Gel Permeation Chromatograph connected with a viscosimeter apparatus.

Results and Discussion

The literature for free radical polymerization of MMA by azo initiator is vast and a proportionality of Rp with the square root of initiator concentration and with the monomer concentration has generally been observed.

$$Rp = -d[M]/dt = kp\ (2\ f\ kd[I]/kt)^{\frac{1}{2}}\ [M] \quad (1)$$

(where $|I|$ and $|M|$ are the instantaneous initiator and monomer concentrations, kd the rate constant of initiator decomposition, f the efficiency of initiator, kp and kt the propagation and termination rate constant and t the reaction time).

The rate of initiation, Ri is:

$$Ri = 2\ f\ kd[I] \quad (2)$$

Termination of MMA occurs essentially by disproportionation : the degree of polymerization is equal to the kinetic chain length:

$$\overline{DP}_n = \nu = Rp/Ri \quad (3)$$

An important characteristic of a polymerization process is the ratio kp^2/kt since the main characteristics of polymerization namely the reaction rate and the average chain length, are dependent on this ratio. The expressions (1,2 and 3) yield an equation (4) for the ratio kp^2/kt:

$$kp^2/kt = (2\ \overline{DP}_n/[M].t)\ Ln\ [M_0]/[M] \quad (4)$$

At five temperatures: 60°, 67°, 72°, 81° and 84°C , six polymerizations of methylmethacrylate in bulk were carried out keeping ACP initial concentration $|I|$ fixed. At known interval of time one of the samples was cooled in liquid nitrogen, the polymer formed was precipitated, collected, dried and weighed. The number average molecular weight was then determined by GPC from the universal calibration law $[\eta]M$. The parameters kp^2/kt calculated from the corresponding rates and degrees of polymerization are set out in table 1 for the five temperatures.

Table 1 - Ratio of constants kp^2/kt of polymerization of bulk methylmethacrylate initiated by ACP
$[ACP] = 4 . 10^{-3}$ mol.l^{-1}

Temperature	60°C	67°C	72°C	81°C	84°C
$^*kp^2/kt. 10^2$	2.25	4.84	5.43	4.81	9.06

* : in $mol^{-1} l^{-1} s^{-1}$

The ratio of rate constants $kp(2\ f\ kd/kt)^{\frac{1}{2}}$ can be evaluated from the slopes of the straight lines obtained from the first order consumption of methylmethacrylate [M] (figure 1).

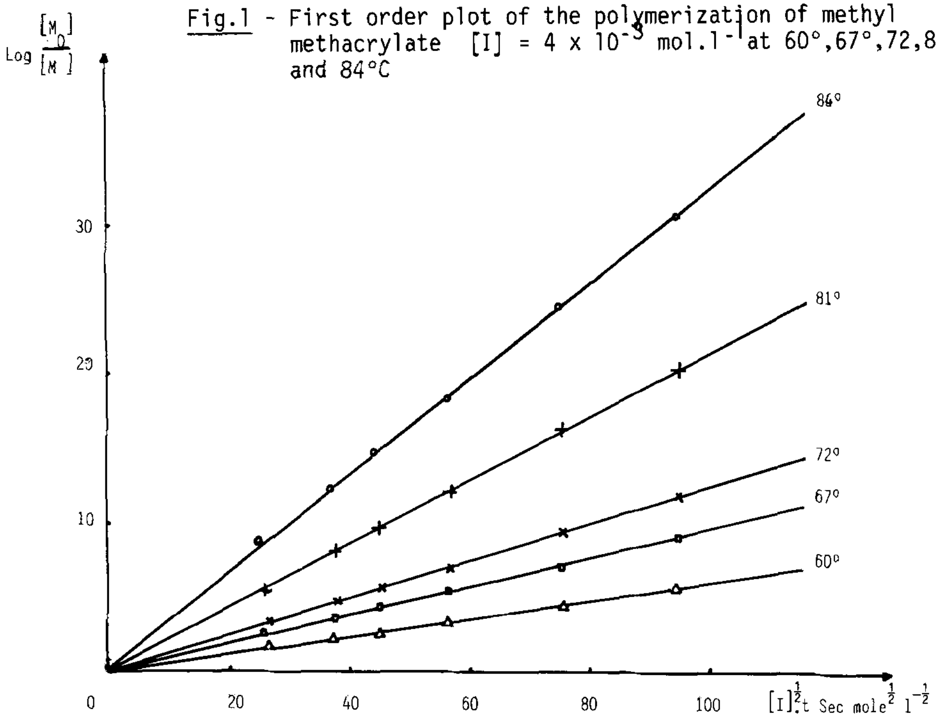


Fig.1 - First order plot of the polymerization of methyl methacrylate $[I] = 4 \times 10^{-3}$ mol.l^{-1} at 60°,67°,72,81° and 84°C

Knowing the ratio kp^2/kt, it is possible to determine the product kd.f with the expression (5) obtained from (1).

$$\text{Ln } [M_0]/[M] = kp(2\ f\ kd/kt)^{\frac{1}{2}}\ [I]^{\frac{1}{2}}\ t \qquad (5)$$

The values of kd for (ACP) has been previously determined in the range 60°-84°C (Clouet 1984). Thus f value can be calculated (table 2).

Table 2 - Determination of the efficiency of initiation of ACP in methylmethacrylate polymerization

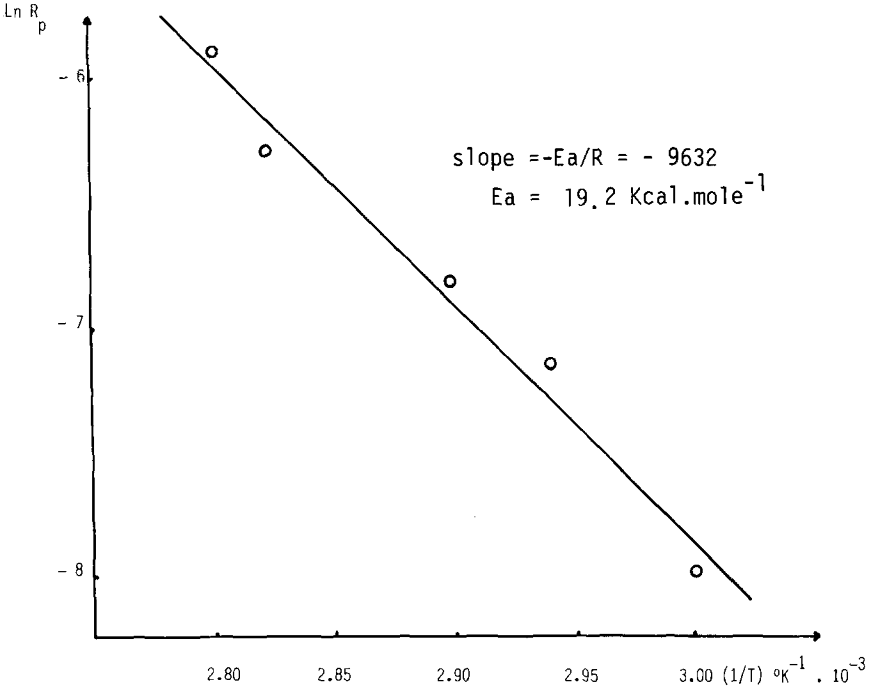
Temperature °C	$kp(2\ f\ kd/kt)^{\frac{1}{2}}.10^3$ *	$kp/kt^{+\frac{1}{2}}$ *	kd . 10^5	f	
60	0.56	0.150	1.28	0.55	0.55
67	1.35	0.220	3.12	0.61	
72	1.81	0.233	5.77	0.52	
81	3.02	0.222	16.73	0.56	
84	4.62	0.301	23.56	0.50	

*: mole$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s$^{-3/2}$

The average of f value is much less than unity for MMA polymerization under varying experimental conditions and does not vary much with changing initiator. Effectively the literature give 0.60 with azobisisobutyronitrile and 0.68 (Pramanick 1981) with 4,4' azobis(4-cyanopentanoic acid).

The temperature dependence of the polymerization reaction is shown in figure 2. The overall activation energy Ea, as obtained from the slope of the line is 19.2 $\mathrm{Kcal.mol^{-1}}$.

Figure 2 - Arrhenius plot of the rate of polymerization of methylmethacrylate



Ea = Ep-(Et/2 + Ed/2) where Ep, Et and Ed are the energy of activation of propagation,termination and decomposition respectively.

Previously, we have reported that Ed = 28.9 $\mathrm{Kcal.mol^{-1}}$ for the thermal decomposition of ACP in DMSO. These lead to Ep - Et/2 = 4.75 $\mathrm{Kcal.mol^{-1}}$ for methylmethacrylate polymerization.

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