Radical Polymerization of Zinc Acrylate Initiated by As_2S_3 - Styrene Complex

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RADICAL POLYMERIZATION OF ZINC ACRYLATE INITIATED BY As_2S_3 - STYRENE COMPLEX

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ABSTRACT

The kinetics of polymerization of zinc acrylate (ZnA_2) initiated by As_2S_3 - styrene complex(I) in dimethylsulphoxide (DMSO) at 90°±0.1°C for 1 hr followed non-ideal kinetics due to primary radical termination. The rate of polymerization was direct function of [polar solvent] but reverse function of [non-polar solvent] and [hydroquinone].

The overall activation energy (Ea) and value of k_p^2/k_t are 26 kJ/mol and 1.55 x10^{-4} l mol^{-1} s^{-1} respectively. The glass transition temperature (T_g) of polymer was 421°C and the polymer was characterized by IR and NMR spectroscopy.

INTRODUCTION

Reports on the kinetics and mechanism of polymerization of metal containing monomers have recent appearance in various polymer journals, probably, because of their excellent applications. A search of literature[1-2] shows that polymerization of Zn, Co, Ni and Cu acrylates in methanol has been carried out with conventional initiators like AIBN or BPO which needs high temperature and long time for desirable conversion. Therefore, it is desirable

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to examine potentiality of other compounds as novel
initiators for polymerization of such monomers.

The aim of the paper is the determination of
the overall rate constants, order of reaction with
regard to monomer and initiator and the overall
energy of the polymerization of ZnA_2 in dimethyl
sulphoxide using As_2S_3 – styrene complex as new
novel initiator. The results show that the initiator
needs moderate temperature and less time for the
polymerization of zinc acrylate.

MATERIAL

The zinc acrylate was prepared according to the new
method reported in literature (3). ZnO(1 mol) and
acrylic acid (2 mol) were stirred in 20% acetone
solution for about 20 hrs till ZnO was completely
dissolved. The solution was evaporated upto complete
dryness.

The synthesis and characterization of As_2S_3 –
styrene complex has already been reported elsewhere
(4-6). Reagent grade styrene and other solvents were
purified by method given by Overberger(7) and Vogel
(8) respectively.

METHOD

The solution polymerization of ZnA_2 in DMSO was
carried out at 90±0.1°C for 1hr using dilatometry
technique. The polymer, precipitated by methanol
was dried to constant weight to calculate percentage
conversion. The rate of polymerization was deter-
mined from the linear portion of the % conversion
vs time plots.

The intrinsic viscosity of polymer was
determined in chloroform at 15±0.1°C using Ubbelhode
viscometer.

The metal content was determined from atomic
spectrometer. The IR and NMR spectra of polymer were
obtained on Perkin-Elmer 599 B and varian 100HA
spectrometer respectively.

TABLE - I

Effect of As_2S_3-styrene complex on the rate of polymerization of ZnA_2

$[I] \times 10^3$ mol l^{-1}	% conversion	$R_p \times 10^6$ mol $l^{-1} s^{-1}$	η_{int}
1.069	15.99	1.09	0.012
2.138	16.68	1.44	0.016
5.345	19.09	2.12	0.020
7.483	20.05	2.42	0.024
10.693	21.83	2.82	0.030
12.820	22.43	2.09	0.032

Polymerization time= 60min., Temp. = 90±0.1°C
$[ZnA_2]$ = 1.271 x 10^{-2} mol/l

TABLE - II

Effect of $[ZnA_2]$ on the rate of polymerization of ZnA_2

$[ZnA_2] \times 10^2$ mol l^{-1}	% conversion	$R_p \times 10^6$ mol $l^{-1} s^{-1}$	η_{int}
0.635	17.50	1.52	0.018
1.271	19.09	2.12	0.020
1.907	20.15	2.59	0.026
2.542	21.65	2.72	0.028
3.178	22.80	3.18	0.032

$[I]$ = 5.345x10^{-3} mol/l, Time = 60 min.,Temp.-90±0.1°C

TABLE - III

Effect of additives on the rate of polymerization of ZnA_2 initiated by As_2S_3- styrene complex

Additive's name	[Additive] mol l^{-1}	% Conversion	$R_p \times 10^6$ mol$l^{-1}s^{-1}$	η_{int}
dioxane	1.54	19.39	2.23	0.008
	3.08	23.58	2.75	0.020
DMF	1.70	24.73	2.23	0.008
	3.40	25.88	2.79	0.012
Toluene	1.49	15.36	1.83	0.018
	2.98	14.43	1.76	0.016
Xylene	1.09	17.92	1.91	0.028
	2.18	16.68	1.89	0.026
Hydroquinone	1.19	17.25	2.01	0.012
	4.76	14.43	1.72	0.004

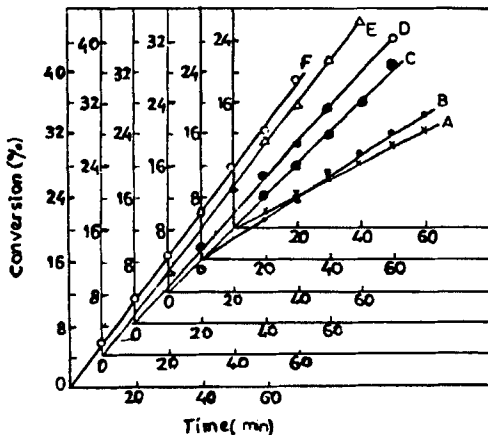Polymerization time= 60min., Temp. = $90 \pm 0.1°C$

$[I]$ = 5.345×10^{-3} mol/1, $[ZnA_2]$= 1.27×10^{-2} mol/1

        Glass transition temperature of the polymer was measured under N_2 atmosphere using a DuPont 910-differential scanning calorimeter, 200 µW/mV. The weight of each dry sample was 3 mg. The scanning rate was 10° per minute. The temperature of the point at which the DSC curves deflects from the base line, i.e. intersection of extra base line and the sloping portion of DSC curve, was taken as the glass transition temperature.

RESULTS AND DISCUSSION

The polymerization conditions and results are presented in Table 1 to 3 and Fig. 1 to 10.

A study of fig.1 shows that the polymerizations run were associated with short induction period (2- 5 minutes). R_p is a direct function of [initiator] and [monomer] and the values of reaction order with respect to initiator (Fig.2) and monomer (Fig.3) equal to 0.4 and 1.0 respectively These values reveal essential differences from those assumed by the classical polymerization equation $R_p = K[M][I]^{0.5}$ This is further confirmed by the fact that the plot between $1/\eta_{int}$ vs $[I]^{0.5}$ does not pass through the origin (Fig.4) Such deviations from the expected monomer and initiator exponent of 1.0 and 0.5, respectively are common for polymerization of transitional metals like Zn(2) and Ni, Co(1) this may be explained in different ways (9). The values for energy of activation (Fig.5) and k_p^2/k_t (Fig.6) as


(a) $[I] = (A) 1.07 \times 10^{-3}$ mol 1^{-1} (B) 2.14×10^{-3} mol 1^{-1}, (C) 5.35×10^{-3} mol 1^{-1}, (D) 7.48×10^{-3} mol 1^{-1} (E) 10.69×10^{-3} mol 1^{-1}, (F) 12.82×10^{-3} mol 1^{-1}

(b) $[ZnA_2] = 1.27 \times 10^{-2}$ mol 1^{-1}
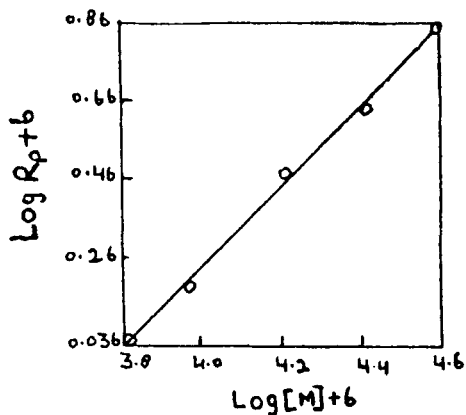
(c) Temperature = $90 \pm 0.1°C$

(d) Time = 60 minutes

(Fig. 1)

26 kJ/mol and 1.55×10^{-4} 1 mol^{-1} s^{-1} is comparatively low than the reported in lit.(1) for the polymerization of Zn-acrylate in DMF using AIBN as initiator.
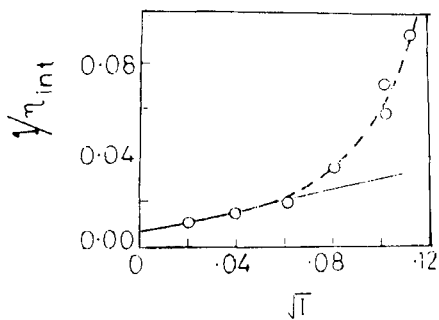
Characterization of polymers are as follows :-

(i) The IR spectra of polymers shows the band at 1750-1735 cm^{-1} which confirms the presence of carbonyl group of acrylate (Fig.8).
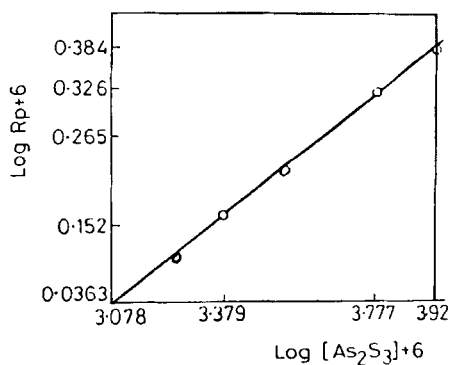
(a) $[ZnA_2] = 1.27 \times 10^{-2}$ mol l^{-1}
(b) Temperature = $90 \pm 0.1°C$
(c) Time = 60 minutes

(Fig.2)

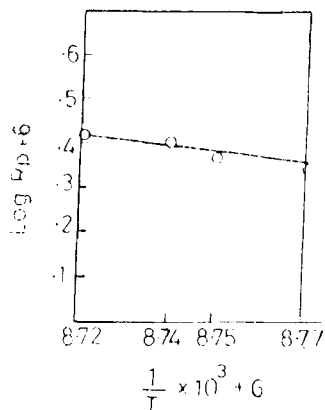(a) $[I] = 5.35 \times 10^{-3}$ mol l^{-1}
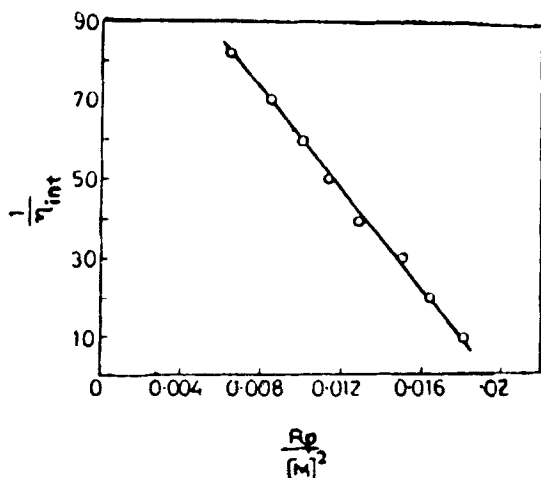(b) Temperature = $90 \pm 0.1°C$
(c) Time = 60 minutes

(Fig. 3)

(a) $[ZnA_2] = 1.27 \times 10^{-2}$ mol l^{-1}
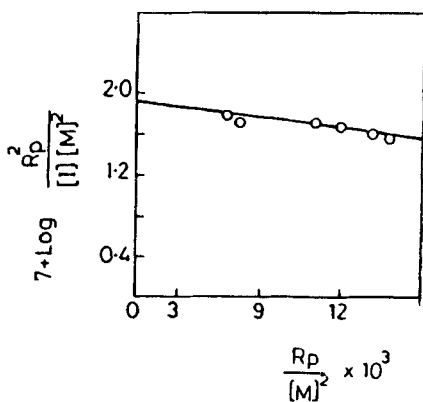(b) Temperature = $90 \pm 0.1°C$
(c) Time = 60 minutes

(Fig.4)

(a) $[I] = 5.35 \times 10^{-3}$ mol l^{-1}
(b) $[ZnA_2] = 1.27 \times 10^{-2}$ mol l^{-1}
(c) Temperature = $90 \pm 0.1°C$
(d) Time = 60 minutes.

(Fig.5)

(a) $[I]=5.35 \times 10^{-3} mol\ l^{-1}$

(b) Temperature=90±0.1°C

(c) Time = 60minutes

(Fig.6)

(a) $[ZnA_2]=1.27 \times 10^{-2} mol\ l^{-1}$

(b) Temperature =90±0.1°C

(c) Time = 60 minutes

(Fig.7)

(a) $[I]=5.35 \times 10^{-3} mol\ l^{-1}$

(b) $[ZnA_2]=1.27 \times 10^{-2} mol\ l^{-1}$

(c) Temperature =90±0.1°C

(d) Time = 60 minutes

(Fig.8)
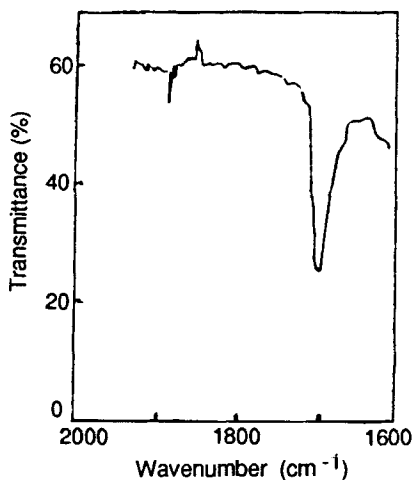
(a) $[I] = 5.35 \times 10^{-3}$ mol 1^{-1}

(b) $[ZnA_2] = 1.27 \times 10^{-2}$ moll^{-1}

(c) Temperature = $90 \pm 0.1°C$

(d) Time = 60 minutes

    (Fig.9)

(δ) ppm

(ii)   NMR spectra shows only the peak due to $-CH_2-$ group at $(2-1)\,\delta$ and there is no peak at about $7\,\delta$ which excludes possibility of styrene of complex in polymer (Fig.9).

(iii) The polymer showed absence of S and As in element analysis.

(iv) The glass transition is an important character-istic of a polymer.This is the temperature at which an amorphous materials ch-anges from a brittle vit-reous state to plastic state and at this point dramatic changes take pl-ace, in polymer proper-ties. The T_g of polyzinc acrylate, measured from DSC, is 421°C(Fig.10) which is close to that reported earlier for other transi-tional metals(10).
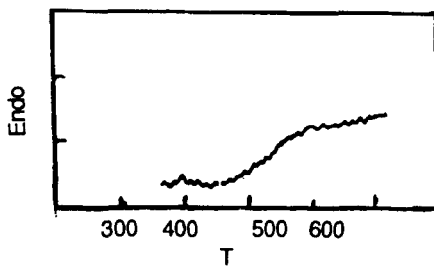
plot of C_p Vs $T''C$ for Poly ZnA_2

    (Fig.10)

(v)   A polymer was soluble in $CHCl_3$, CCl_4 and toluene but insoluble in HCl, H_2SO_4, etc.

Mechanism -   The mechanism of polymerization of the
salt dissociated in solvent was discussed in terms
of ion-pair theory (11). However, it is not fitted
for ZnA_2 which in DMSO is undissociated(12).

     We have already reported (4,5) that complex
$As_2 S_3$ -styrene dissociates to form radical $\overset{\bullet}{R}$ the
exact nature of which was not elucidated. However,
absence of S, As and styrene in the polymer shows
that $\overset{\bullet}{R}$ is H which brings about polymerization. The
steps are as follows

(i)
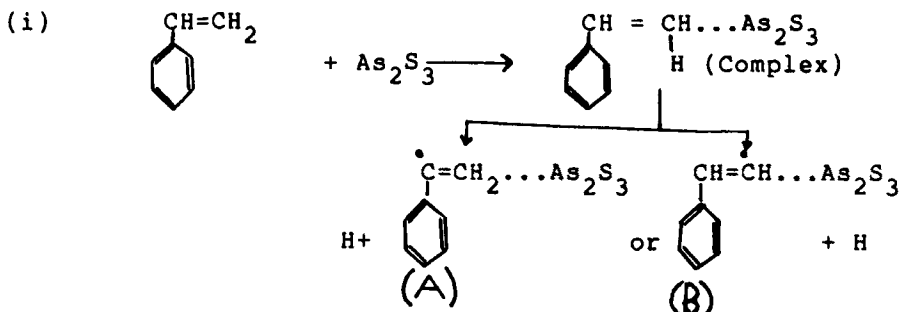
(ii)   Dissociation of complex gives either (A) or
       (B) with H since (A) is intertiary form and
       (B) is in secondary form, therefore, stabi-
       lity of A (Ter.) $>$ B (Sec.). Hence step(A)
       is likely to be involved.

Thus on the basis of above discussion following stru-
cture can be proposed for polyzinc acrylate.
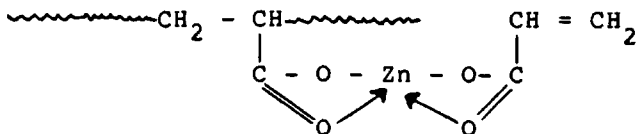
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