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### Copolymerization of Styrene with Chromium Acrylate Initiated by Styrene-Arsenic Sulfide Complex

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**COPOLYMERIZATION OF STYRENE WITH CHROMIUM ACRYLATE  
INITIATED BY STYRENE-ARSENIC SULFIDE COMPLEX**

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**ABSTRACT**

The radical copolymerization of styrene with chromium acrylate in dimethyl formamide at  $85 \pm 0.1^\circ\text{C}$  was studied in presence of styrene-arsenic sulfide complex. The kinetic expression for the system is  $R_p \propto [\text{As}_2\text{S}_3]^{0.5} [\text{Sty}]^{1.0} [\text{Cr-acrylate}]^{1.0}$ , i.e. it follows ideal radical kinetics. The overall activation energy and average value of  $k_p^2/k_t$  are  $77.0 \text{ kJ mol}^{-1}$  and  $0.45 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$  respectively. The monomer reactivity ratios was determined as follows  $r_1(\text{sty}) = 0.82$  and  $r_2(\text{Cr-acrylate}) = .08$ . The product of reactivity ratios reflect ideal copolymerization and therefore a strong alternating tendency in propagation reaction. The Alfrey-Price Q-e parameters for the metal acrylate was calculated and discussed.

**INTRODUCTION**

The polymerization and copolymerization of salts of acrylic and methacrylic acid in aqueous solutions [1-4] and in solid state [5-7] revealed the influence of cations on salt reactivities, reaction rates and molecular weight of the products. The copolymerization of acrylic salts with styrene in emulsion [8-9] indicated the role of the metal on reaction yields, composition and copolymer properties. However data on polymerization of chromium acrylate still scarce, is formed in patent literature.

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We have recently described the application of styrene-arsenic sulfide complex as radical initiator for the polymerization of some vinyl monomers like methyl methacrylate [10], styrene [11], and methyl acrylate [12].

The present communication reports the kinetics of the copolymerization of styrene with chromium acrylate in dimethyl formamide initiated by styrene-arsenic sulfide complex at  $85 \pm 0.1^\circ\text{C}$  and an investigation of reactivity ratios of the copolymer.

### MATERIAL

Reagents grade styrene (Robert Johnson) and other solvents were purified by methods given by Overberger [13] and Vogel [14] respectively. Arsenic sulfide (Merck) was used as such without further purification.

The synthesis and characterization of complex of arsenic sulfide with styrene has already been reported [10-12].

Chromium acrylate was prepared according to the method of Sayyah et.al. [15].

### METHOD

A solution containing styrene, chromium acrylate and complex in dimethyl formamide was injected into a dilatometer and polymerization was carried out at  $85 \pm 0.1^\circ\text{C}$  for 2 hrs., under an inert atmosphere of  $\text{N}_2$ . The copolymer, precipitated with a mixture of methanol and water (1:1), was dried to constant weight. It was then subjected to solvent treatment (to remove homopolymers), using soxhlet apparatus and then dried to constant weight. No significant weight loss was observed.

Rate of polymerization ( $R_p$ ) was calculated from the slope of linear portion of conversion vs time plots.

The intrinsic viscosity  $[\eta]$  of the copolymer was determined in toluene at  $27^\circ\text{C}$  using an Ubbelohde viscometer.

The i.r., n.m.r. and e.s.r. spectra of copolymer were obtained on Perkin-Elmer 599B, Varian 100HA and X-band EPR-109E-line century series spectrometers respectively.

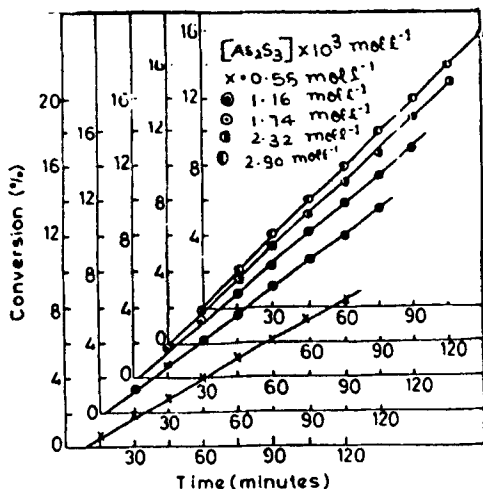


Fig. 1a

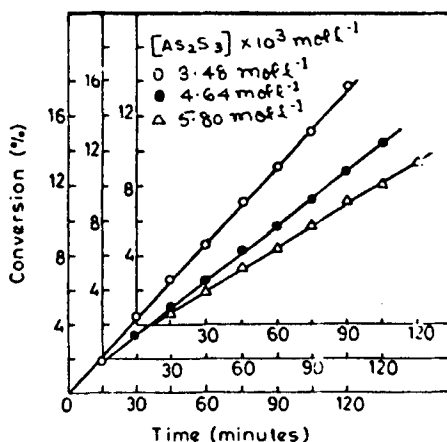


Fig. 1b

Conversion versus time plots for copolymerization of styrene with chromium acrylate:  $[\text{Sty}] = 2.47 \text{ mol. l}^{-1}$ ,  $[\text{Cr-acrylate}] = 0.107 \text{ mol. l}^{-1}$ , time = 2 hr., temp =  $85 \pm 0.1^\circ \text{C}$

## RESULTS AND DISCUSSION

The polymerization conditions and results have been summarized in Table 1 to 5 and Figs. 1 to 11.

### (i) Effect of arsenic sulfide

The effect of arsenic sulfide on rate of polymerization was studied by varying  $[\text{As}_2\text{S}_3]$  from  $0.58 \times 10^{-3} \text{ mol l}^{-1}$  to  $5.80 \times 10^{-3} \text{ mol l}^{-1}$  and keeping the total monomer concentration constant. Fig. 1a and 1b shows that polymerization runs have been associated with short induction period of about 2-8 minutes which decreases upto a concentration of  $\text{As}_2\text{S}_3$  as  $3.48 \times 10^{-3} \text{ mol l}^{-1}$  then it becomes almost constant. Table 1 reveals that  $R_p$  increases with increasing  $[\text{As}_2\text{S}_3]$  upto  $3.48 \times 10^{-3} \text{ mol l}^{-1}$  and then decreases with increasing  $[\text{As}_2\text{S}_3]$  upto  $5.80 \times 10^{-3} \text{ mol l}^{-1}$ . Probably, at higher concentration the initiator acts as a retarder as well as slowly dissociating to form initiating radicals.

TABLE - 1  
Effect of arsenic sulfide concentration on rate of polymerization

S.No.	$[As_2S_3] \times 10^3$ mol l <sup>-1</sup>	Percentage conversion	$R_p \times 10^5$ mol l <sup>-1</sup> s <sup>-1</sup>	$\eta_{int}$
1	0.58	7.9	2.57	.38
2	1.16	11.5	3.42	.30
3	1.74	13.4	4.56	.26
4	2.32	15.0	5.40	.21
5	2.90	16.0	5.81	.18
6	3.48	17.8	6.20	.14
7	4.64	12.6	4.09	-
8	5.80	9.6	3.12	-

[Sty] = 2.47 mol l<sup>-1</sup>, [Cr-acrylate] = 0.107 mol l<sup>-1</sup>  
polymerization time = 2hr., polymerization temp. = 85 ± 0.1°C

The order of reaction with respect to  $[As_2S_3]$  calculated from the linear portion of slope of  $\log R_p$  Vs  $\log [As_2S_3]$  is 0.5 (Fig.2), shows that the system follows ideal radical kinetics. This is further confirmed by the plot between  $1/\eta_{int}$  Vs  $[I]^{0.5}$  which passes through origin (Fig.3). The intrinsic viscosity decreases with increase in initiator concentration and the value for the ratio of the square propagation rate constant  $k_p^2/k_t$  calculated from the slope of the plot  $1/\eta_{int}$  Vs  $R_p/[M]^2$  is  $0.45 \times 10^{-5} l^2 mol^{-1} s^{-1}$  (Fig.4)

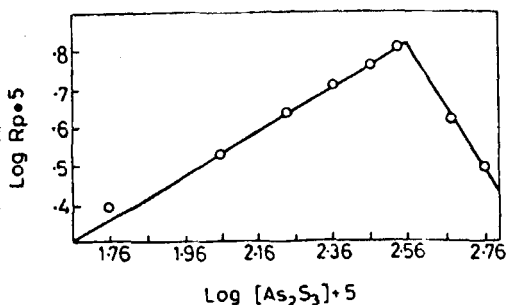


Fig.2 Relationship between  $\log R_p$  and  $\log As_2S_3$  for the copolymerization of styrene with Cr-acrylate where [Sty]=2.47 mol l<sup>-1</sup> [Cr-acrylate]=0.107 mol l<sup>-1</sup>, time = 2hr. temp. = 85 ± 0.1°C

#### (ii) Effect of monomer concentration

The influence of [Sty] and [Cr-acrylate] on rate of polymerization were studied by varying their concentrations 0.98 mol l<sup>-1</sup> to 2.96 mol l<sup>-1</sup> respectively at fixed  $[As_2S_3] = 3.48 \times 10^{-3}$  mol l<sup>-1</sup>.  $R_p$  is a direct function of [monomers] and monomer exponent, calculated from the slope of linear portion of  $\log R_p$  Vs  $\log [monomer]$  for both the cases styrene and chromium acrylate, is unity (Fig.5). The intrinsic viscosity of the copolymer increases with increase of monomer concentration (Table 2).

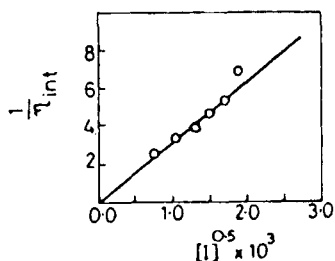


Fig.3 Relationship between  $1/r_{int}$  and  $[I]^{0.5}$  for the copolymerization of styrene and chromium acrylate

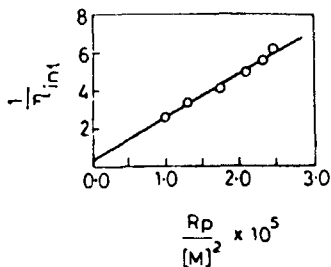


Fig.4 Relationship between  $1/r_{int}$  and  $R_p/[M]^2$  for the copolymerisation of styrene with chromium acrylate

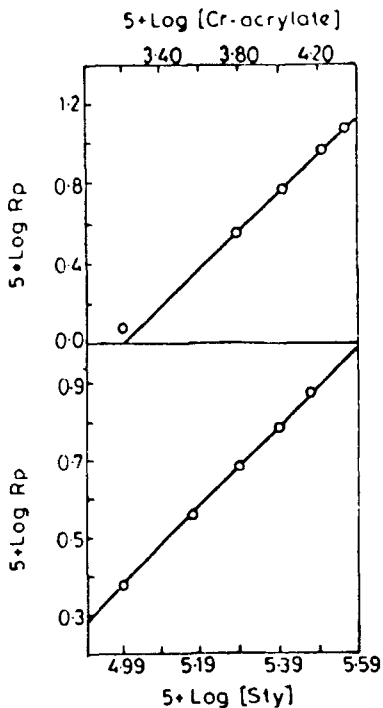


Fig.5a Relationship between  $\log [\text{Cr-acrylate}]$  and  $\log R_p$  for the copolymerization of styrene with chromium acrylate where  $[\text{As}_2\text{S}_2]=3.48 \times 10^{-3} \text{ mol l}^{-1}$ ,  $[\text{Sty}]=2.47 \text{ mol l}^{-1}$ , time = 2hr., temp. =  $85 \pm 0.1^\circ\text{C}$

Fig.5b Relationship between  $\log [\text{Sty}]$  and  $\log R_p$  for the copolymerization of styrene with chromium acrylate where  $[\text{As}_2\text{S}_2]=3.48 \times 10^{-3} \text{ mol l}^{-1}$ ,  $[\text{Cr-acrylate}]=0.107 \text{ mol l}^{-1}$ , time=2hr, temp.= $85 \pm 0.1^\circ\text{C}$

TABLE - 2

Effect of concentration of monomer on rate of polymerization

S.No.	[Sty] mol l <sup>-1</sup>	[Cr-acrylate] mol l <sup>-1</sup>	percen- tage con- version	R x 10 <sup>5</sup> mol <sup>-1</sup> s <sup>-1</sup>	$\eta_{int}$
1		.021	3.4	1.21	-
2		.064	10.5	3.40	.10
3	1*	.107	17.8	6.20	.14
4		.172	26.4	9.32	.20
5		.215	29.9	11.90	.28
6	.98		7.0	2.42	-
7	1.48		10.7	3.65	.10
8	1.97	2*	14.2	4.82	.18
9	2.47		17.8	6.20	.20
10	2.96		21.2	7.45	.30

[As<sub>2</sub>S<sub>3</sub>]=3.48x10<sup>-3</sup> mol l<sup>-1</sup>, 1\* = 2.47 mol l<sup>-1</sup>, 2\* = 0.107 mol l<sup>-1</sup>

Polymerization time = 2hr., polymerization temp. = 85±0.1°C

## (iii) Effect of temperature

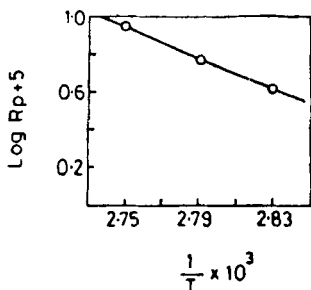


Fig.6 Plot of log R<sub>p</sub> Vs polymerization temp. (Arrhenius plot), [As<sub>2</sub>S<sub>3</sub>]=3.48x10<sup>-3</sup> mol l<sup>-1</sup> [Sty]=2.47 mol l<sup>-1</sup>, [Cr-acrylate]=0.107 mol l<sup>-1</sup>, time=2hr.

The polymerization was also carried out at 80°C, 85°C and 90°C to study the effect of temperature. Rate of polymerization increases with increase in polymerization temperature. The overall energy of activation, calculated from the linear Arrhenius plot is 77.0 kJ mol<sup>-1</sup> (Fig.6).

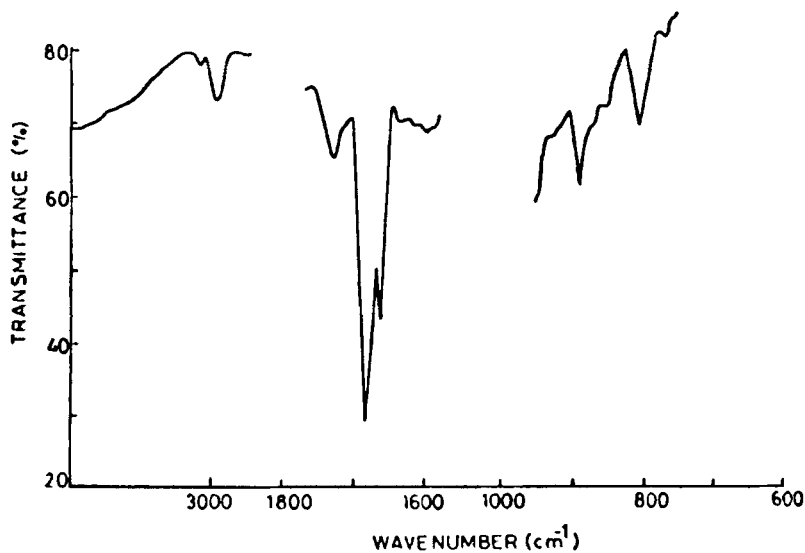
## (iv) Effect of additives

Table 3 shows that hydroquinone retards the reaction, confirming a radical mechanism. The copoly-

TABLE - 3  
Effect of additives on rate of polymerization

S.No.	Additives	[Additive] mol l <sup>-1</sup>	Percentage conversion	R <sub>p</sub> x 10 <sup>5</sup> mol l <sup>-1</sup> s <sup>-1</sup>
1	No additive	0.0	17.8	6.20
2	Dimethyl sulphoxide	.731 1.46	22.0 24.3	7.75 8.01
3	Dioxane	1.29 1.95	15.2 13.5	5.21 4.84
4	Cyclohexane	.952 1.42	13.3 12.6	4.54 4.30
5	Hydroquinone	1.29x10 <sup>-2</sup> 2.59x10 <sup>-2</sup>	11.2 5.7	3.81 1.90

[As S ]=348x10<sup>-3</sup> mol l<sup>-1</sup>, [Sty]=2.47 mol l<sup>-1</sup>, [Cr-acrylate]=.107 mol l<sup>-1</sup>, time = 2hr., temp.= 85±0.1°C



(Fig.7)

IR spectrum of copolymer



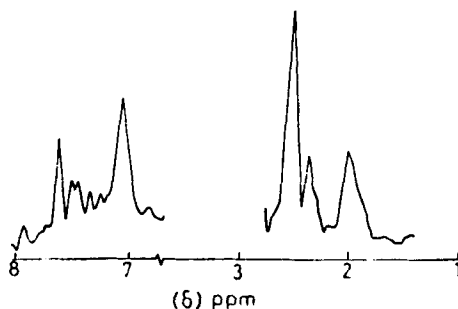
merization of styrene with chromium acrylate was also carried out in presence of dimethylsulphoxide, dioxane and cyclohexane. Rate of polymerization is retarded in presence of dioxane and cyclohexane whereas dimethylsulphoxide enhanced the reaction rate.

#### Characterization of copolymer structure

(1) IR spectrum of copolymer consist of following group of bands :

- (a) The range of C-H stretching vibrations due to aromatic rings of polystyrene is present at  $3000 \text{ Cm}^{-1}$  to  $2962 \text{ Cm}^{-1}$ .
- (b) The range of C-H bending vibrations shows bands at  $880 \text{ Cm}^{-1}$  -  $800 \text{ Cm}^{-1}$ .
- (c) The -CH bending vibrations of (-CH-CH<sub>2</sub>) appears in the region  $985$ - $915 \text{ Cm}^{-1}$ .
- (d) The ester carbonyl band of polychromium acrylate is present at  $1760$ - $1735 \text{ Cm}^{-1}$ (Fig.7).

(2) NMR spectrum shows the peaks due to -CH<sub>2</sub>- protons at  $\delta = 2-3 \text{ ppm}$  and due to phenyl protons at  $\delta = 7-8 \text{ ppm}$ (Fig.8)

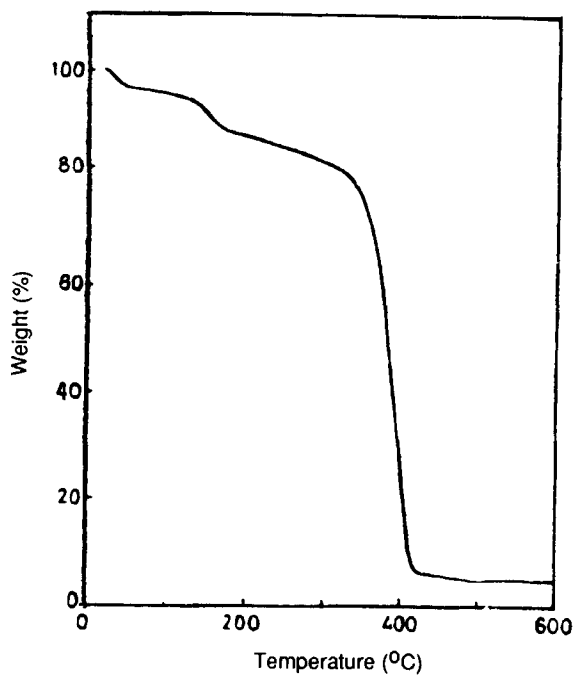


(Fig.8)

NMR spectrum of copolymer

(3) The TGA curve (Fig.9) shows that copolymer has thermal stability upto  $330^\circ\text{C}$ . This data matches than that reported for other acrylates like  $\text{CuA}_2$  &  $\text{ZnA}_2$ [16].

(4) The elemental analysis of the copolymer rules out the presence of arsenic or sulphur in the copolymer.



(Fig.9)  
TGA of Copolymer

TABLE - 4

S.N.	Molar ratio in feed(F)	Percentage conversion	Moles fra- ction of Styl <sup>1*</sup>	Moles fra- ction of Cr-acrylate <sup>2*</sup>
1.	27	22.1	.930	.093
2	25	17.8	.920	.096
3	17	14.2	.901	.098
4	15	10.7	.888	.111

1\* From NMR, 2\* From metal content,

## COMPOSITION AND VALUES OF REACTIVITY RATIOS

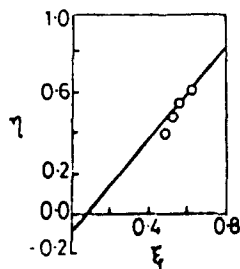
The data concerning the copolymerization system is summarized in Table 4.  $F=M_1/M_2$  ( $M_1=Sty.$ ,  $M_2=(Cr\text{-acrylate})$ ) is the initial ratio of monomer and  $f = m_1/m_2$  is the molar ratio of copolymer. [15]

The monomer reactivity ratios were determined according to the Kelen-Tüdös method (Fig.10). The styrene content of the copolymer is calculated from NMR spectrum (phenyl protons) and chromium content is estimated using inductively coupled plasma emissions spectrometer.

The  $e_2$  and  $Q_2$  values were calculated using  $e_1 = -0.80$  and  $Q_1 = 1.0$  assumed for the styrene by following equations [17,18]

$$e_2 = e_1 \pm (\log r_1 r_2)^{0.5}$$

$$Q_2 = \frac{Q_1}{r_1} \exp [-e_1(e_1 - e_2)]$$



(Fig.10)

Kelen-Tüdös plot of styrene and chromium acrylate

The product of  $r_1$  and  $r_2$  is .0656 which is much less than unity suggesting higher tendency of alternating copolymerization which follows from the high difference of  $e$  values of both comonomers ( $e_{sty} = -0.80$  and  $e_{CrA_3} = +.286$ )

The  $Q_2$  value, less than one reflect reactivities of the investigated chromium acrylate lower than those of styrene.

## MECHANISM

We have already reported [10-12] that complex  $As_2S_3$ -styrene complex dissociates to form radical H. It is

TABLE - 5  
Reactivity Parameters

$r_1$	$r_2$	$r_1 r_2$	$Q_2$	$e_2$
0.82	.08	.0656	.809	.286

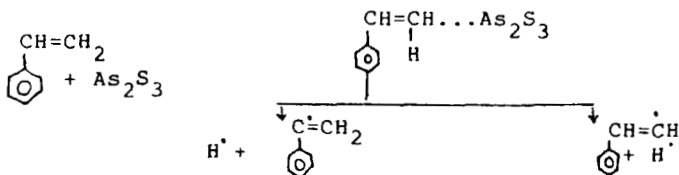
For styrene  $e_1 = -0.80$ ,  $Q_1 = 1.0$

confirmed by the ESR spectrum (Fig.11). The value of 'g' is calculated as 1.95722.

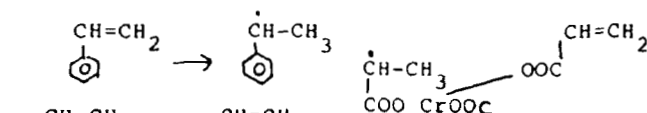
The dissociation of complex gives either A or B with H . Since A is tertiary radical, therefore A is more stable than B. Hence step A is likely to be formed. The steps are as follows :

Initiation

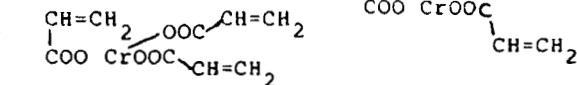
(i)



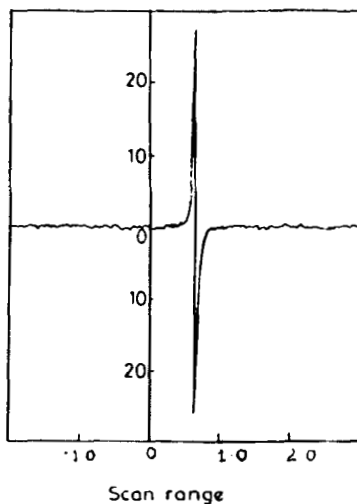
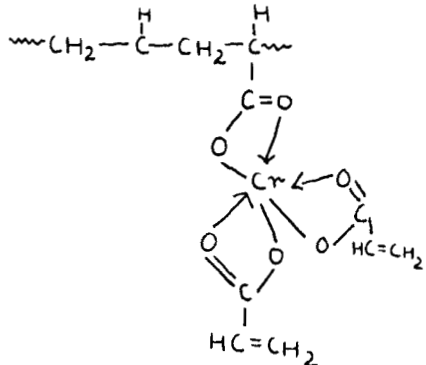
(ii)



(iii)



The propagation and termination follows the same usual methods. Thus on the above basis the structure of copolymer may be written as



(Fig.11)  
ESR spectrum of copolymer

## ACKNOWLEDGEMENT

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