

Synthesis and polymerization of 3,2-thienyl chromium acrylate

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3,2-Thienyl chromium acrylate has been synthesized and its polymerization carried out in the presence of a styrene-arsenic sulphide complex in dimethylformamide at $90 \pm 0.1^\circ\text{C}$ for 4 h. The reaction order with respect to initiator and monomer revealed essential differences from those assumed using the classical polymerization rate equation. The overall activation energy and the average value of the ratio of the square of the propagation constant to the termination rate constant (k_p^2/k_t) are 53.3 kJ mol^{-1} and $0.80 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$, respectively.

(Keywords: 3,2-thienyl chromium acrylate; styrene-arsenic sulphide complex; initiator; kinetics; dilatometric technique; Ubbelohde viscometer)

Introduction

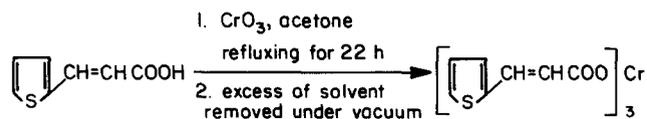
Studies on the polymerization of heterocycles due to properties such as electrical conductance, thermal photostability, incombustibility, etc., are increasingly being reported^{1,2}. Most of the reports involve polymerization by a limited number of doping agents³⁻⁵. It is, therefore, of interest to synthesize heterocycles like thiophene containing a vinyl group so that conventional radical/ionic initiators may be employed for their polymerization. To this end, the present work involves the synthesis and polymerization of 3,2-thienyl chromium acrylate. An advantage of this polymer is the presence of the chromium ion which affects a number of the properties of the polymer compared to those of polythiophene.

Experimental

Reagent grade styrene (Robert Johnson) and other solvents were purified by methods given by Overberger and Yamamoto⁶ and Vogel⁷, respectively. Arsenic sulphide, As_2S_3 (Merck), was used without further purification.

The synthesis and characterization of the arsenic sulphide-styrene complex has been reported elsewhere⁸⁻¹⁰.

Synthesis of 3,2-thienyl chromium acrylate. Chromium trioxide (calcinated for 4 h) was added to 3,2-thienyl acrylic acid in acetone in a stoichiometric amount. The reaction mixture was then refluxed with continuous stirring for 22 h and the excess solvent was subsequently evaporated. The monomer was obtained as a greenish solid.



I.r. (dimethyl formamide, DMF): 1120 (C=S band), 1660 (ester group) and 3000 cm^{-1} (aromatic) (Figure 1).

N.m.r. [CDCl_3 , tetramethylsilane, δ (ppm)]: 2–3 δ ($-\text{CH}_2$ proton) and 7–8 δ (aromatic proton) (Figure 2).

Thermogravimetric analysis was carried out on a Stanton Redcroft thermal analyser at a heating rate of $10^\circ\text{C min}^{-1}$. The sample weight was 7 mg.

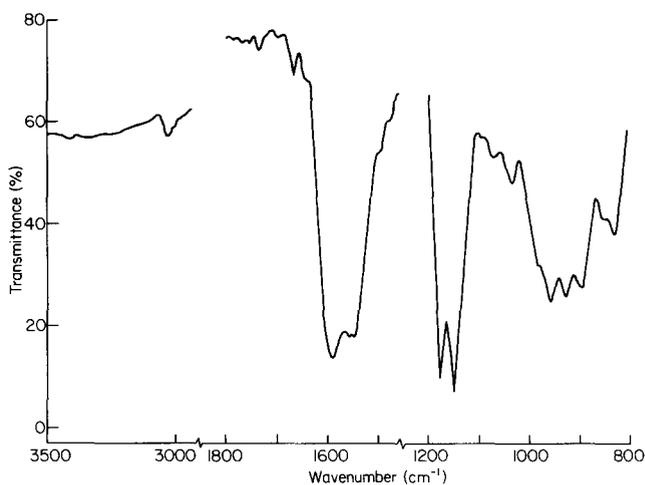


Figure 1 I.r. spectrum of 3,2-thienyl chromium acrylate

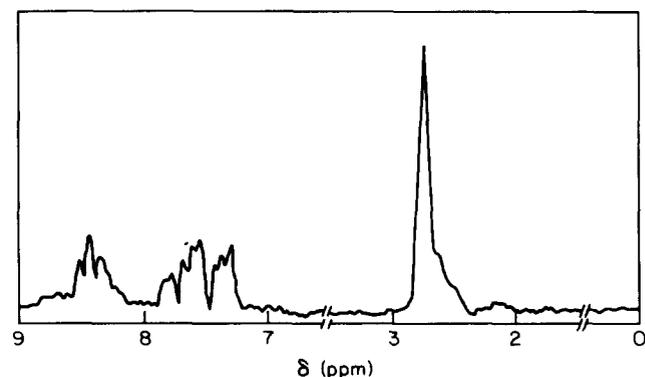


Figure 2 N.m.r. spectrum of 3,2-thienyl chromium acrylate

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Polymerization procedure. The polymerization of 3,2-thienyl chromium acrylate initiated by the styrene-arsenic sulphide complex in DMF was carried out at $90 \pm 0.1^\circ\text{C}$ under an inert atmosphere of N_2 using dilatometry. The progress of the reaction, monitored as meniscus movement per unit volume per unit time, with the help of a cathetometer, was converted into percentage conversion. The polymer precipitated with acidified methanol and water (1:1) was dried to constant weight.

The rate of polymerization (R_p) was calculated from

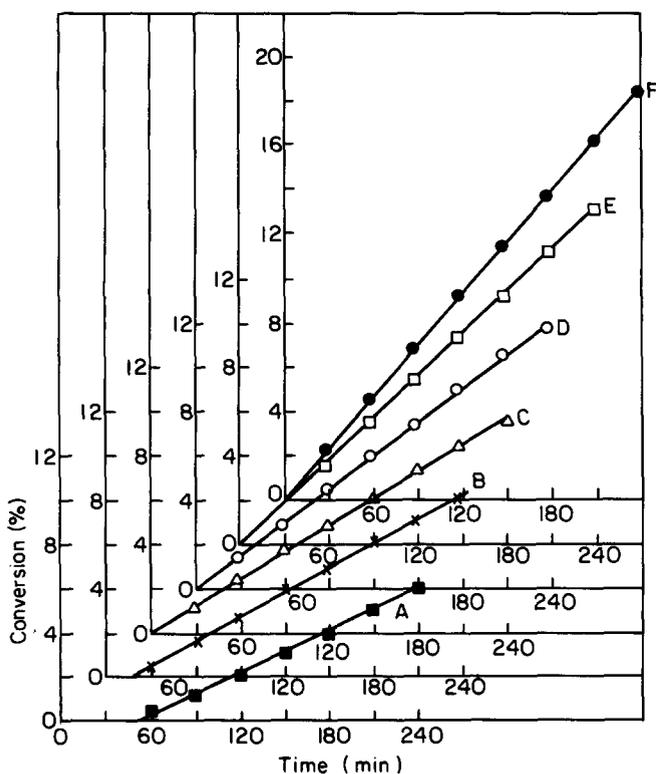


Figure 3 Conversion-time plots of radical polymerization of 3,2-thienyl chromium acrylate initiated by the styrene-arsenic sulphide complex. $[\text{As}_2\text{S}_3]$: (A) 1.35×10^{-3} ; (B) 2.71×10^{-3} ; (C) 4.06×10^{-3} ; (D) 5.42×10^{-3} ; (E) 6.77×10^{-3} ; (F) $8.13 \times 10^{-3} \text{ mol l}^{-1}$. $[\text{3,2-Thienyl chromium acrylate}] = 0.174 \text{ mol l}^{-1}$; polymerization time = 4 h; polymerization temperature = $90 \pm 0.1^\circ\text{C}$

the slope of the linear portion of the conversion versus time plots (Figure 3).

The intrinsic viscosity (η_{int}) of the polymer was determined in DMF at $30 \pm 0.1^\circ\text{C}$ using an Ubbelohde viscometer.

Results and discussion

The reaction conditions are given in Tables 1 and 2. A study of Figure 3 shows that polymerization runs are associated with a maximum induction period of ~ 48 min. Table 1 shows that R_p is a direct function of the concentrations of As_2S_3 and 3,2-thienyl chromium acrylate. The η_{int} of the polymer decreases with increase in initiator concentration, $[\text{I}]$, but increases with increase in monomer concentration, $[\text{M}]$. The reaction order with respect to initiator and monomer is one-half and one, respectively. Thus the system follows the classical polymerization equation, i.e. $R_p = K[\text{M}][\text{I}]^{0.5}$, although reports regarding polymerization of other metal salts, such as Zn^{11} , Ni and Co^{12} , show deviations from the classical equation. The fact that the system follows ideal kinetics is further strengthened by the nature of the plot of $1/\eta_{\text{int}}$ versus $[\text{I}]^{0.5}$ which passes through the origin (Figure 4). The average value of the ratio of the square of the propagation constant to the termination rate constant (k_p^2/k_t), determined from the slope of the linear plot of $1/\eta_{\text{int}}$ versus $R_p/[\text{M}]^2$, is $0.80 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$.

Hydroquinone retards the reaction confirming radical polymerization, whereas dimethyl sulphoxide (DMSO) enhanced the reaction rate (Table 2), probably due to high polarity in comparison to DMF.

Table 2 Effect of additives on the rate of polymerization^a

Sample	Additive	[Additive] (mol l ⁻¹)	Conversion (%)	$R_p \times 10^6$ (mol l ⁻¹ s ⁻¹)
1	No additive	0.00	9.6	1.45
2	DMSO	0.76	11.6	1.69
		1.51	15.0	2.19
3	Hydroquinone	0.015	7.2	1.10
		0.03	5.2	0.70

^a $[\text{3,2-Thienyl chromium acrylate}] = 0.174 \text{ mol l}^{-1}$; $[\text{As}_2\text{S}_3] = 4.06 \times 10^{-3} \text{ mol l}^{-1}$; time = 4 h; temperature = $90 \pm 0.1^\circ\text{C}$

Table 1 Effect of arsenic sulphide and 3,2-thienyl chromium acrylate concentration on the rate of polymerization^a

Sample	$[\text{As}_2\text{S}_3] \times 10^3$ (mol l ⁻¹)	3,2-thienyl chromium acrylate (mol l ⁻¹)	Conversion (%)	$R_p \times 10^6$ (mol l ⁻¹ s ⁻¹)	η_{int} (dl g ⁻¹)
1	1.35	0.174	6.2	1.00	0.22
2	2.71		7.8	1.25	0.20
3	4.06		9.6	1.45	0.17
4	5.42		12.2	2.00	0.15
5	6.77		15.5	2.50	0.12
6	8.13		18.4	3.00	-
7		0.116	6.2	1.00	-
8		0.174	9.6	1.45	-
9	4.06	0.203	10.8	1.75	-
10		0.232	12.2	2.00	-
11		0.261	13.6	2.20	-
12		0.290	15.5	2.50	-

^aTime = 4 h; temperature = $90 \pm 0.1^\circ\text{C}$

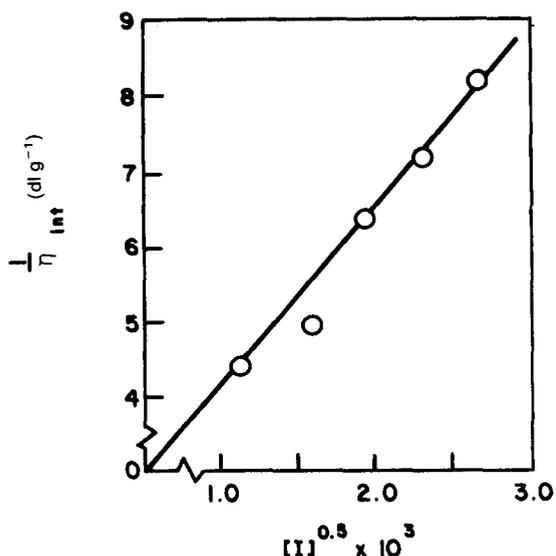


Figure 4 Plot of $1/\eta_{int}$ versus $[I]^{0.5}$ for the polymerization of 3,2-thienyl chromium acrylate initiated by the styrene–arsenic sulphide complex. $[3,2\text{-Thienyl chromium acrylate}] = 0.174 \text{ mol l}^{-1}$; polymerization time = 4 h; polymerization temperature = $90 \pm 0.1^\circ\text{C}$

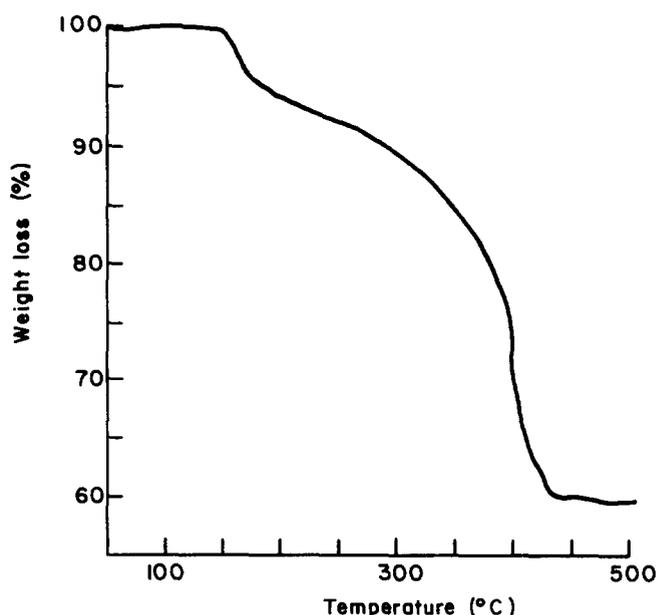


Figure 6 T.g.a. trace of the polymer

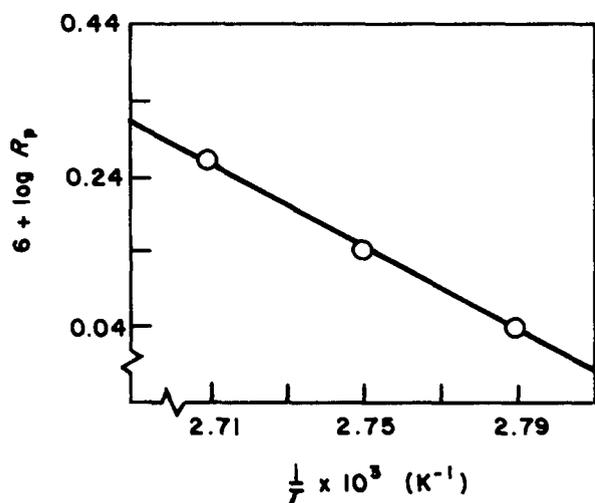


Figure 5 Logarithm of the rate of polymerization versus polymerization temperature (Arrhenius plot). $[\text{As}_2\text{S}_3] = 4.06 \times 10^{-3} \text{ mol l}^{-1}$; $[3,2\text{-thienyl chromium acrylate}] = 0.174 \text{ mol l}^{-1}$; polymerization time = 4 h

The overall activation energy calculated from the Arrhenius plot (see Figure 5) is 53.3 kJ mol^{-1} .

Polymer characterization. I.r.: 1200–1050 ($\text{C}=\text{S}$ band), 1730–1650 (ester group) and 3300 cm^{-1} (aromatic bands). The t.g.a. curve (Figure 6) shows that the polymer is thermally stable up to 175°C . The polymer

was soluble in DMF, DMSO and insoluble in chloroform, carbon tetrachloride, benzene and acetone.

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