Copolymerization of acrylonitrile with chromium acrylate initiated by a styrene–arsenic sulfide complex

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The styrene–arsenic sulfide complex initiated radical copolymerization of acrylonitrile (AN) with chromium acrylate (CrA_3) at 85±0.1°C, using dimethylformamide (DMF) as an inert solvent, yields an alternating copolymer as evidenced by the reactivity ratios $r_1 = 0.18$ and $r_2 = 0.03$ ($M_1 = AN$, $M_2 = CrA_3$). The kinetic equation for the system is $R_p \propto [As_2S_3]^{0.5}[AN]^{1.0}[CrA_3]^{1.0}$. The value of the activation energy and the average value of k_p^2/k_t are 96.2 kJ mol^{-1} and 1.0×10^{-5} l mol^{-1} s^{-1}, respectively. The properties of the resulting copolymer were studied in the form of films. Nitric acid was strongly absorbed by these films, while the absorption of hydrochloric acid was comparatively low.

(Keywords: radical copolymerization; initiator complex; kinetics)

INTRODUCTION

Metal containing polymers, as a result of their interesting reactivities and usefulness in preparative organic chemistry, have become of increasing significance[1–3].

A search of the literature reveals that the choice of an initiator for the radical polymerization of chromium acrylate (CrA_3) is very limited[4]. In addition, these initiators need high temperatures and long polymerization times to obtain any reasonable conversions. After reporting the application of a styrene–arsenic sulfide complex as an initiator for the radical polymerization of monomers such as methyl methacrylate[5], styrene[6] and methyl acrylate[7], we have examined this complex in the copolymerization of acrylonitrile (AN) with CrA_3. The maximum conversion achieved was 33.6% after which gelation takes place. The particular advantage of this system is that polymerization could be easily carried out at relatively low temperatures and over shorter times. The copolymer produced in this way has been characterized by i.r. and n.m.r. spectroscopy. This present communication reports the kinetics of the copolymerization of AN with CrA_3 initiated by the styrene–arsenic sulfide complex and also describes some of the properties of the copolymer that is produced.

EXPERIMENTAL

Materials

Reagent grade styrene (Robert Johnson) and other solvents were purified by methods given by Overberger and Yamamoto[8] and Vogel[9], respectively. Arsenic sulfide (As_2S_3) (Merck), was used without further purification. CrA_3 was prepared according to the method of Sayyah *et al.*[4].

Formation and characterization of the styrene–arsenic sulfide complex

A solution containing varying amounts (1–10 wt%) of As_2S_3 in styrene (1.9 mol l^{-1}) was stirred for 2.5 h until a transparent and viscous mixture was obtained. Excess styrene was removed by vacuum distillation. The density and refractive index of the resulting complex (measured at 35°C without any further treatment) were 1.3 g cm^{-3} and 1.533, respectively. The complex is soluble in benzene, tetrachloromethane, dimethylformamide (DMF) and dimethyl sulfoxide.

Polymerization

A solution containing AN, CrA_3 and the initiator complex in DMF was injected into a dilatometer and the polymerization was carried out at 85±0.1°C for a period of 90 min under an inert atmosphere (N_2). The copolymer was precipitated by adding a mixture of methanol and water (1:1) and was dried to constant weight under vacuum at 40±0.5°C. Any residual homopolymers of AN and CrA_3 were removed by solvent extraction using a Soxhlet apparatus. No significant weight loss was observed after a final drying to constant weight.

The rate of polymerization (R_p) was calculated from the plots of polymer conversion *versus* time (see *Figure 1*).

The intrinsic viscosity (η_{int}) of the copolymer was measured in DMF at 25°C using an Ubbelohde viscometer, with the results being expressed in dl g^{-1}.

Preparation of films

Films were cast by pouring a solution of the copolymer in DMF onto a dry glass plate and then tilting the latter backwards and forwards so as to spread the solution uniformly over the surface. These films were stored at room temperature.

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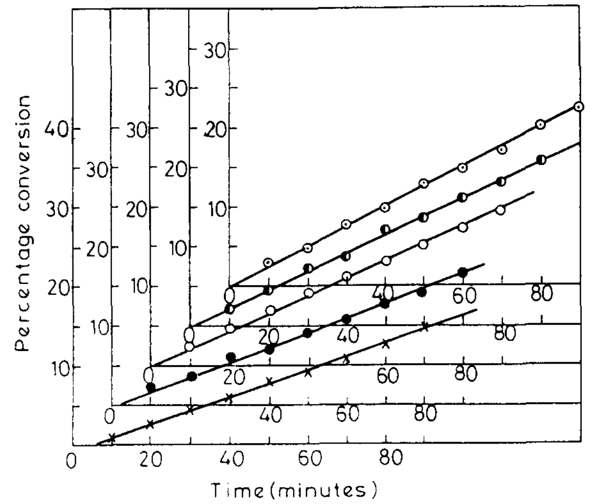

Figure 1 Conversion–time plots of the copolymerization of acrylonitrile with chromium acrylate initiated by the styrene–arsenic sulfide complex. $[As_2S_3]$: ×, 1.16×10^{-3}; ●, 1.74×10^{-3}; ○, 2.32×10^{-3}; ◐, 2.90×10^{-3}; ⊙, 3.48×10^{-3} mol l^{-1}. [AN] = 4.3 mol l^{-1}; $[CrA_3]$ = 0.107 mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

Table 1 Effect of the concentration of arsenic sulfide on the rate of copolymerization[a]

Sample	$[As_2S_3]\times10^3$ (mol l^{-1} s^{-1})	Conversion (%)	$R_p\times10^5$ (mol l^{-1} s^{-1})	η_{int} (dl g^{-1})
1	1.16	15.5	2.15	0.45
2	1.74	16.8	2.38	0.38
3	2.32	19.7	2.73	0.35
4	2.90	20.8	2.88	0.28
5	3.48	23.5	3.25	0.26
6	4.64	28.1	3.89	0.22
7	5.80	25.9	3.60	–
8	6.96	24.7	3.40	–

[a] [AN] = 4.3 mol l^{-1}; $[CrA_3]$ = 0.107 mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

Solubility and chemical resistance

Film strips (wt ~50 mg) were immersed in various organic solvents for periods up to seven days, and the subsequent changes in weight were recorded.

Absorption experiments

Absorption was investigated by immersing strips of the films (wt ~50 mg) in various liquids (e.g. methanol, nitric acid and hydrochloric acid) at 40°C, with any increase in weight (as a result of absorption) being recorded.

Spectroscopic and thermal measurements

I.r. spectra were recorded on a Perkin–Elmer 599B spectrometer, and n.m.r. spectra were recorded using a Varian 100H A spectrometer. Thermogravimetric analysis (t.g.a.) measurements were carried out by using a Stanton Redcroft thermal analyser operating at a heating rate of 10°C min^{-1} with sample weights of 10.0 mg.

RESULTS AND DISCUSSION

The copolymerization of AN with CrA_3 in DMF has been carried out at 85 ± 0.1°C by varying $[As_2S_3]$ from 1.16×10^{-3} to 6.96×10^{-3} mol l^{-1}, [AN] from 1.72 to 5.14 mol l^{-1} and $[CrA_3]$ from 0.041 to 0.113 mol l^{-1}.

Polymerization runs were associated with a short induction period of approximately 2–5 min. Synthesis of the copolymer was also carried out at 85 ± 0.1°C by varying $[As_2S_3]$ from 2.32×10^{-3} to 4.64×10^{-3} mol l^{-1}, [AN] from 4.3 to 5.1 mol l^{-1} and $[CrA_3]$ from 0.053 to 0.107 mol l^{-1}.

Effect of As_2S_3

The rate of polymerization (R_p) increases with an increase in $[As_2S_3]$ from 1.16×10^{-3} to 4.64×10^{-3} mol l^{-1} and then decreases with further increases in $[As_2S_3]$ up to a level of 6.96×10^{-3} mol l^{-1} (see *Table 1*).

The initiator (I) exponent value, calculated from the slope of the plot of log R_p against log$[As_2S_3]$ is 0.5 ± 0.01, as expected for a radical polymerization process (*Figure 2*). This fact is confirmed by the plot of $1/\eta_{int}$ *versus* $[I]^{0.5}$ which passes through the origin (see *Figure 3*).

The intrinsic viscosity of the copolymers is decreased as $[As_2S_3]$ is increased. The value of k_p^2/k_t over the temperature range 83–87 ± 0.1°C, determined from the slope of the linear plot of $1/\eta_{int}$ *versus* $R_p/[M]^2$ is $1.0(\pm0.02)\times10^{-5}$ l mol^{-1} s^{-1} (*Figure 4*).

Effect of comonomer concentrations

The effect of [AN] and $[CrA_3]$ was studied by varying these concentrations from 1.72 to 5.14 mol l^{-1}, and from 0.041 to 0.113 mol l^{-1}, respectively, at a fixed $[As_2S_3]$ of 4.64×10^{-3} mol l^{-1} (*Table 2*). The rate R_p is a direct

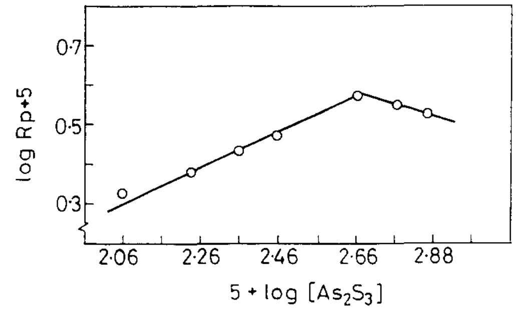

Figure 2 Relationship between the rate of copolymerization and $[As_2S_3]$: [AN] = 4.3 mol l^{-1}; $[CrA_3]$ = 0.107 mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

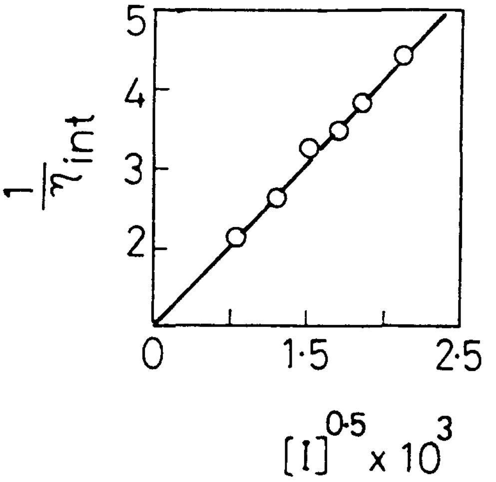

Figure 3 Reciprocal of the intrinsic viscosity *versus* the square root of the initiator concentration [I]: [AN] = 4.3 mol l^{-1}; $[CrA_3]$ = 0.107 mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

function of the monomer concentration and the monomer exponent, with the latter calculated from the slope of the plot of log R_p *versus* log[monomer] (*Figure 5*). For both of the comonomers this exponent is unity, as would be expected for an ideal radical polymerization process. The intrinsic viscosities of the copolymers increase with increasing comonomer concentration (see *Table 2*).

Effect of additives

The effect of a number of additives on the rate of copolymerization is shown in *Table 3* where it can be seen that hydroquinone significantly retards the reaction rate, thus confirming a radical mechanism. An examination of the data presented in this table reveals that polar as well as non-polar solvents have a significant influence on the percentage conversion. It has already been reported[10] that if the polarity of the solvent medium decreases, then the conversion also decreases. It appears that the dissociation of the complex is a direct function of the polarity of the medium, as has been previously

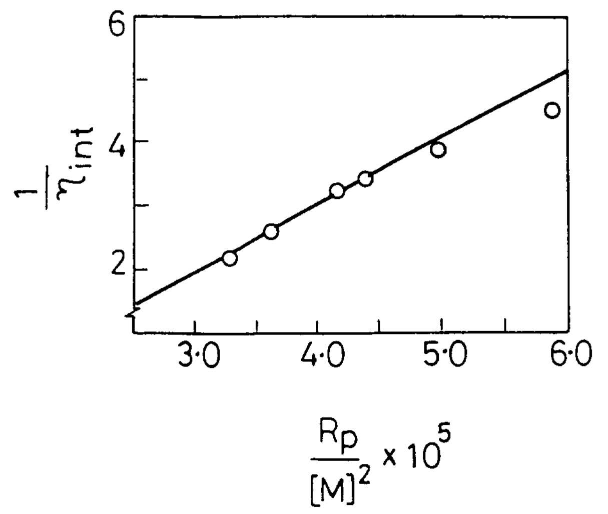

Figure 4 Reciprocal of the intrinsic viscosity *versus* the ratio of the copolymerization rate over the square of the monomer concentration, $R_p/[M]^2$: [AN] = 4.3 mol l^{-1}; [CrA$_3$] = 0.107 mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

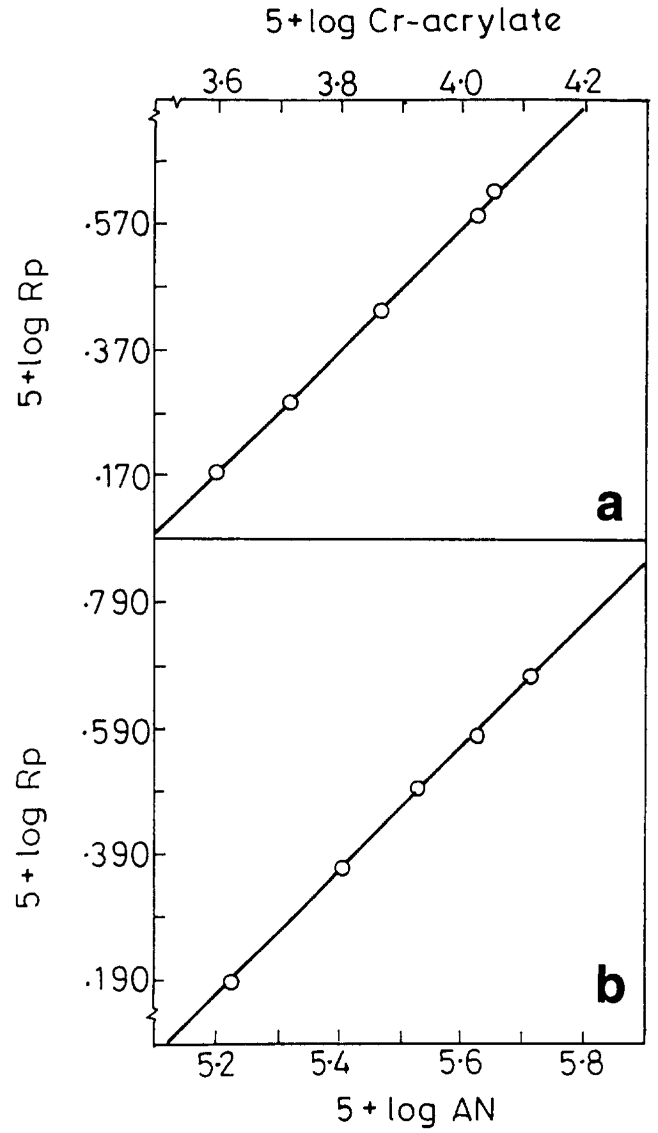

Figure 5 Relationship between the rate of copolymerization and comonomer concentration: (a) [CrA$_3$] with constant [AN] = 4.3 mol l^{-1}; (b) [AN] with constant [CrA$_3$] = 0.107 mol l^{-1}. [As$_2$S$_3$] = 4.64 × 10^{-3} mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

Table 2 Effect of the concentrations of the comonomers on the rate of copolymerization[a]

Sample	[AN] (mol l^{-1})	[CrA$_3$] (mol l^{-1})	Conversion (%)	$R_p \times 10^5$ (mol l^{-1} s^{-1})	η_{int} (dl g^{-1})
1	1.72	0.107	11.2	1.55	–
2	2.58	0.107	16.8	2.3	0.10
3	3.45	0.107	22.4	3.10	0.12
4	4.31	0.107	28.1	3.89	0.22
5	5.14	0.107	33.6	4.65	0.28
6	4.3	0.041	10.6	1.48	0.10
7	4.3	0.053	13.8	1.92	0.14
8	4.3	0.075	19.6	2.72	0.18
9	4.3	0.107	28.1	3.89	0.22
10	4.3	0.113	29.6	4.10	0.26

[a] [As$_2$S$_3$] = 4.64 × 10^{-3} mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

Table 3 Effect of additives on the rate of copolymerization[a]

Sample	Additive	[Additive] (mol l^{-1})	Conversion (%)	$R_p \times 10^5$ (mol l^{-1} s^{-1})
1	No additive	0.0	28.1	3.89
2	Dioxane	0.649	26.3	3.42
		1.29	19.5	2.70
3	Toluene	0.496	17.2	2.38
		0.993	14.2	1.96
4	Cyclohexane	0.479	15.5	2.15
		0.952	12.0	1.90
5	Hydroquinone	1.29×10^{-2}	12.4	1.95
		2.59×10^{-2}	3.2	0.51

[a] $[As_2S_3] = 4.64 \times 10^{-3}$ mol l^{-1}; [AN] = 4.3 mol l^{-1}; $[CrA_3] = 0.107$ mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

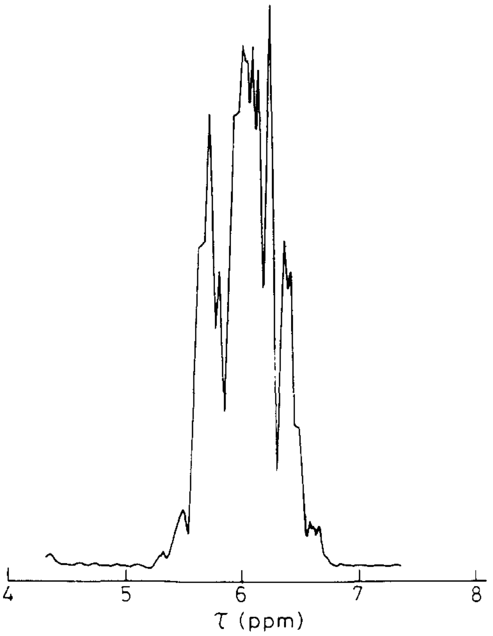

Figure 6 N.m.r. spectrum of the copolymer: $[As_2S_3] = 4.64 \times 10^{-3}$ mol l^{-1}; [AN] = 4.3 mol l^{-1}; $[CrA_3] = 0.107$ mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

reported for a number of donor–acceptor complexes. It is known[11] that As_2S_3 is acidic in nature and styrene behaves as an electron-donor monomer. Therefore, a donor–acceptor complex may be formed *in situ*, which then dissociates to give a free radical, as indicated from the kinetic studies.

Effect of temperature

The activation energy (ΔE) was determined at three different temperatures, i.e. 83, 85 and 87°C, and was found to have an overall value of 96.2 ± 0.2 kJ mol^{-1}. It was found that R_p was a direct function of the temperature.

Characterization of the copolymer

Infra-red spectroscopy. I.r. spectra were obtained using DMF as a solvent, and showed peaks at 1735–1760 and 2210 cm^{-1}, which were assigned to the ester group of the acrylate species and the cyanide group of the AN component, respectively.

Nuclear magnetic resonance spectroscopy. ^{1}H n.m.r. (? MHz, $CDCl_3$, TMS) spectra showed signals at $\tau =$ 6.4–7.8 ppm (CH, CH_2 protons) (see *Figure 6*).

Thermal analysis. A typical t.g.a. curve (*Figure 7*) shows that the copolymer is thermally stable up to 300°C.

Copolymer composition and determination of reactivity ratios. The relationship between the feed composition and the composition of the low-conversion copolymers was used to calculate the reactivity ratios by applying the Finemann–Ross method[12], taking $M_1 = AN$ and $M_2 = CrA_3$. The AN content of the copolymer is calculated from the percentage of nitrogen, and the chromium content is estimated by using an atomic emission spectrometer with an inductively coupled plasma. Composition data are summarized in *Table 4*.

The Finemann–Ross plot of $F^2(f-1)/f$ *versus* F^2/f is given in *Figure 8*, from which values of r_1(AN) and r_2(CrA_3) of 0.18 and 0.03, respectively, are obtained. It is noticeable that the product, r_1r_2, is very nearly zero, which is a sign of alternating copolymerization. This value matches well those previously obtained for the copolymerization of AN with a number of other transition-metal acrylates[13].

Properties of copolymer films

Films of the copolymer were colourless and transparent. The effect of organic solvents and various inorganic reagents was used to check the solubility and chemical resistance of the films. It was found that the copolymer was insoluble in strong acids but soluble in most organic solvents (see *Table 5*). Details of the copolymer films are given in *Table 6*.

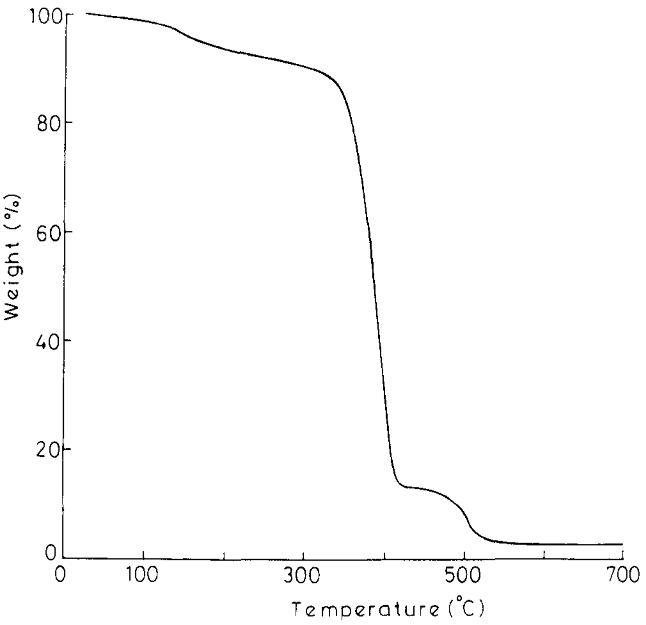

Figure 7 A typical t.g.a. trace of copolymer

Table 4 Composition of the copolymers[a]

Sample	Molar ratio in feed $[AN]/[CrA_3]$	Conversion (%)	Mole fraction of AN	Mole fraction of CrA_3
1	0.498	25.4	0.64	0.35
2	0.458	23.1	0.61	0.39
3	0.397	28.1	0.58	0.41
4	0.378	30.4	0.56	0.43

[a] $[As_2S_3] = 4.64 \times 10^{-3}$ mol l^{-1}; copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

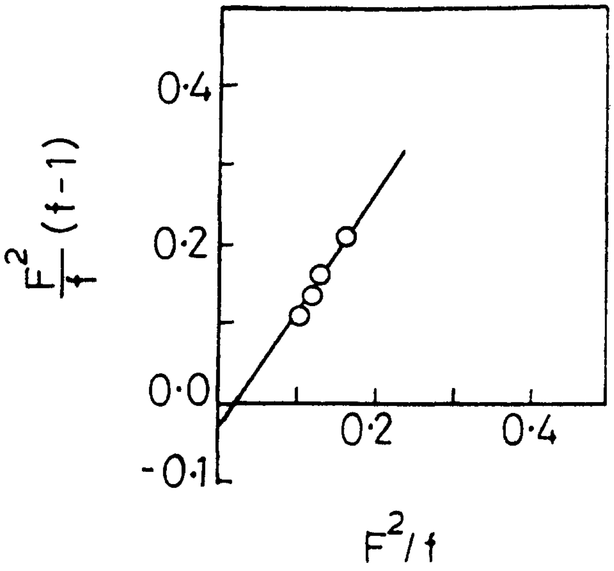

Figure 8 Fineman–Ross plot[12] of acrylonitrile and chromium acrylate, used to calculate the reactivity ratios r_1 (AN) and r_2 (CrA_3)

Table 5 Solubility of the copolymer films[a]

		Polymer film sample[b]		
Sample system	Solvent/reagent	PF_1	PF_2	PF_3
1	Dimethylformamide	+ +	+ +	+ +
2	Dimethyl sulfoxide	+ +	+ +	+ +
3	Dioxane	+ +	+ +	+ +
4	Toluene	+ +	+ +	+ +
5	Acetone	+ +	+ +	+ +
6	Methanol	− −	− −	− −
7	Benzene	+ +	+ +	+ +
8	NH_4OH	− −	− −	− −
9	NaOH	+ −	+ −	+ −
10	H_2SO_4	− −	− −	− −
11	HCl	− −	− −	− −
12	HNO_3	− −	− −	− −
13	H_2O	− −	− −	− −
14	Tetrachloromethane	− −	− −	− −
15	Tetrahydrofuran	− +	− +	− +

[a] (+ +) Soluble at room temperature; (+ −) sparingly soluble at room temperature; (− −) insoluble at room temperature; (− +) sparingly soluble on heating

[b] Details of the samples used are shown in *Table 6*

Film absorption studies were carried out using hydrochloric acid, nitric acid and methanol as test liquids. As shown in *Figure 9* nitric acid was most strongly absorbed by the films; high absorption for methanol was also observed, while the absorption of hydrochloric acid was relatively low.

A likely structure for the copolymer is as follows:

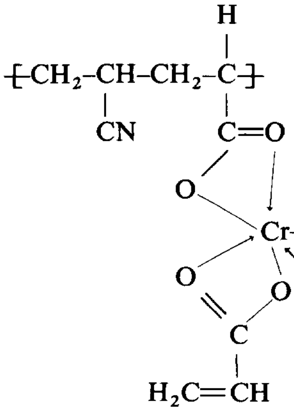

Table 6 Amounts of components used to prepare various copolymer films: copolymerization time = 90 min; copolymerization temperature = 85 ± 0.1°C

	Component		
Polymer film sample	$[As_2S_3] \times 10^3$ ($mol\,l^{-1}$)	$[CrA_3]$ ($mol\,l^{-1}$)	[AN] ($mol\,l^{-1}$)
PF_1	2.32	0.107	4.3
PF_2	4.64	0.107	4.3
PF_3	4.64	0.053	4.3
PF_4	4.64	0.107	5.1

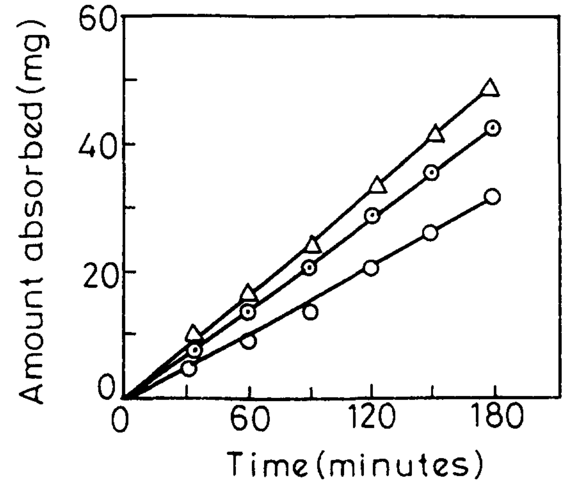

Figure 9 Amount of different liquids absorbed by the copolymer films as a function of time: △, HNO_3; ⊙, methanol; ○, HCl

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