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Redox polymerisation of acrylamide on aqueous montmorillonite surface: kinetics and mechanism of enhanced chain growth

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Aqueous polymerisation of acrylamide by Fe(III)–thiourea redox couple has been studied in homogeneous conditions as well as by loading Fe(III) ions in the interlayer spaces of montmorillonite. A dramatic effect was observed in the latter case, resulting in a very high degree of polymerisation and yielding polymers having high intrinsic viscosity due to imposed constraint on linear termination process. The technique, in general, demonstrates a promising method of achieving high molecular weight polymers by redox initiators. Polymerisation locus was identified and propagating radicals were characterised by XRD and e.s.r., respectively. The polymers were characterised by ^1H and ^{13}C n.m.r. spectroscopy. Kinetics of the polymerisation reaction is investigated and the mechanism of the reaction is discussed. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: aqueous polymerisation; acrylamide; montmorillonite)

INTRODUCTION

Ability of clay minerals to intercalate various molecules and their catalytic properties are long known. The clay–polymer interaction has found many and varied applications[1]. Interest in clay–polymer combinations stems from the use of clay minerals as fillers and reinforcers in polymer systems. All things being equal, the efficiency of a filler in improving the physico-chemical properties of a polymer system is primarily determined by the degree of its dispersion in the polymer matrix. The most effective way of achieving such compatibility is to graft a suitable polymer on to filler surface and/or to encapsulate the mineral particles with the former by polymerising monomers directly on filler surfaces[2]. Montmorillonite, a smectite clay has been shown to catalyse the polymerisation of some unsaturated organic compounds such as styrene and hydroxy ethyl methacrylate and yet to inhibit polymer formation from other structurally related monomers such as methyl methacrylate[3]. This behaviour is believed to be due to the electron accepting or electron donating sites on the clay minerals. However, it has been shown recently that montmorillonite can be used in conjunction with organic substances, viz., alchols, thioureas, etc. to polymerise methyl methacrylate in aqueous medium[3,4].

In view of increasing industrial applications of water soluble acrylamide polymers, clay minerals and their combinations in various fields including the use of polyacrylamide as water soluble viscofier in enhanced oil recovery, we undertake the present study with two major objectives: (i) to examine the catalytic activity of montmorillonite on the polymerisation of acrylamide in aqueous medium and, (ii) to prepare acrylamide polymer having large hydrodynamic volume and molecular weights by Fe(III)/thiourea redox initiator in presence of montmorillonite.

EXPERIMENTAL

Materials

Acrylamide (AM, reagent grade, Fluka) was purified by recrystallisation from methanol (two times) and dried in vacuum oven at 45°C overnight. Thiourea (TU, E.Merck) was used after recrystallisation three times from distilled water (m.p. 180°C). A suspension of montmorillonite (Mo) having particle size less than 2 μm (diameter) was prepared by sedimentation[3]. Free iron oxides were removed by dithionite–citrate method. Organic matters were removed following method described elsewhere[5]. H^+-montmorillonite (HM) was prepared by shaking the stock of the mineral (3% w/v) in presence of 0.5 M HCl for about 6 h followed by repeated centrifugation (20 000 rpm) and washing with double distilled water. The cation exchange capacity (CEC) of montmorillonite was determined by potentiometric titrations with standard KOH solution under nitrogen atmosphere and was found to be 0.91 meq g^{-1}. Fe(III)-montmorillonite (FeM) was prepared by shaking HM suspension (3% w/v) in presence of 0.5 M $FeCl_3$ (reagent grade) at pH 2.5 for 6 h followed by purification by repeated centrifugation and washing with distilled water until the test of Fe(III) ions in the supernatent was negative. A separate experiment on the sorption of Fe(III) on to montmorillonite shows that the maximum intake of Fe(III) ions by HM samples slightly exceeds the CEC value viz., 0.98 meq g^{-1}.

Polymerisation

Measured quantities of aqueous solutions of AM were added to known amounts of HM or FeM suspension or their various mixtures in well stoppered pyrex bottles under nitrogen atmosphere and were equilibrated at required temperature. Deaerated TU solutions were then added to these solutions and the reactions were allowed to continue for desired time span in absence of any light. Polymerisation reactions were stopped by diluting the mixture with chilled

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water keeping the reaction vessels in ice bath. The mixtures were then centrifuged to remove HM/FeM. The polyacrylamide (PAM) was precipitated out by adding excess of acetone, washed repeatedly with acetone and dried in vacuum at 40°C for 48 hours. Molecular weights of the polymer were determined by viscosity measurement in aqueous 0.1 M NaCl solution using a Ubbelohde viscometer and a Mark–Houwink relationship of the type[6,7]:

$$[\eta] = 9.33 \times 10^{-3} \bar{M}^{0.75}\ \mathrm{cm^3/g}$$

E.s.r., n.m.r. and XRD measurements

E.s.r. spectra were recorded at room temperature with a Varian V4502 spectrometer using 100 kHz magnetic field modulation. Instrumental setup and technique were the same as described previously[8]. ^{1}H and ^{13}C n.m.r. spectra were recorded on a Varian XL-300 spectrometer in D_2O. Chemical shifts were measured with reference to dioxane at $\delta = 67.40$ ppm. The X-ray powder diffraction patterns of solid minerals were recorded with a Philips PW 1730 machine using Ni-filtered CuK$_\alpha$ radiation. X-ray generator was operated at 40 kV/20 mA.

RESULTS AND DISCUSSION

Montmorillonite possesses a layered structure and has strong sorptive properties due to expandability of the mineral layers. It is a 2:1 type or trimorphic layered phyllosilicate in which the central octahedral aluminium is surrounded by two tetrahedral silica sheets. Substitution by Fe^{2+}, Fe^{3+} or Mg^{2+} normally occurs in the octahedral position of aluminium. The isomorphous replacement of both bi and trivalent metals from the lattice position to the mineral surface may also take place slowly on standing. The mineral can accept electrons via the aluminium at the crystal edges and the transition metals, such as Fe(III), in the silicate layers. Aluminium in octahedral coordination acts as a Lewis acid if its coordination water molecules are removed by drying. On the other hand, the electron donor sites are transition metals in the reduced state. Iron in the crystal lattice of montmorillonite participates in various chemical reactions in the layered spaces. One of the examples is the well known reaction of montmorillonite with benzidine molecule to form benzidine blue in which the lattice substituted Fe(III) ions are involved[9].

Montmorillonite especially, and other clay minerals in general, give powder e.s.r. spectra containing a multiplicity of lines, which essentially fall into three zones. *Figure 1a* shows e.s.r. spectra of the present montmorillonite sample containing 0.03% and 2.14% (w/w with respect to mineral wt.) iron in exchangeable and lattice positons respectively. Signal near $g = 4.3$ due to paramagnetic Fe^{3+} cations may be attributed to cis and trans octahedral sites, having axial and rhombic symmetry. A very broad signal near $g = 2.2$ arises from exchange interactions between clusters of Fe^{3+} ions which may be present on the surfaces of the smectite as well as due to hydrated Fe^{3+} in the exchangeable sites[10]. A very small but sharp signal at $g = 2.00$ has been assigned to structural defects. *Figure 1b* shows the e.s.r. spectrum that arises from the same montmorillonite sample but pretreated with excess of TU at 50°C for 30 min under nitrogen. Significant decrease of the intensity at $g = 4.3$ signal indicates that TU reacts with lattice Fe(III) and forms non-Kramers species which are e.s.r. silent. Bhattacharya and coworkers put forward chemical and electrochemical evidences to show that isothiocarbamido radicals (I) formed in above reaction can activate radical polymerisation of methyl methacrylate in aqueous medium[11].

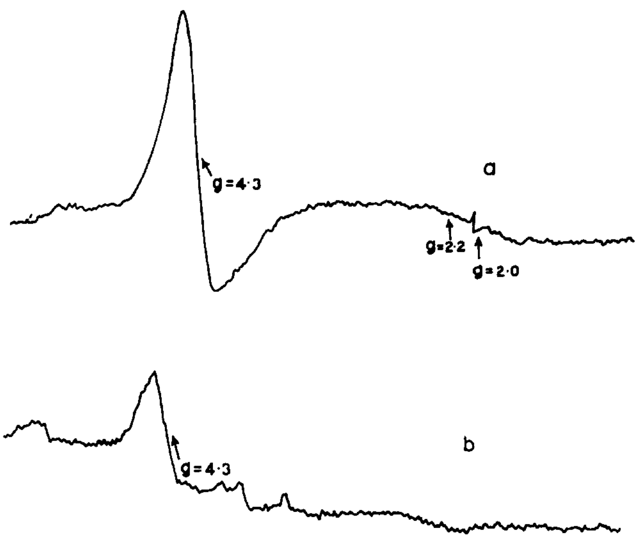


Figure 1 E.s.r. spectra of air dried powder montmorillonite sample at 20°C: (a) H^+ exchanged; (b) pretreated with thiourea at 50°C under N_2

However, in the present study, attempts to polymerise water soluble acrylamide monomers by lattice-Fe(III)/TU combination were unsuccessful at a wide range of temperature. This is probably due to efficient inhibition of radical polymerisation of acrylamide by montmorillonite via electron transfer from initiating or propagating radicals to the Lewis acid sites. On the other hand, montmorillonite microenvironment seems to have a dramatic effect on the redox polymerisation of acrylamide by Fe(III)–TU combination. In view of the fact that redox initiated polymerisation of acrylamide often yield polymers having not so high molecular weights and intrinsic viscosities primarily because of the fast termination process via transfer to the oxidant (viz., metal ions at higher oxidation state) of the initiating redox couple, we loaded Fe(III) ions in the interlayer spaces of the mineral to control the rate of termination and examined the effect on acrylamide polymerisation in presence of TU[12]. For the purpose of comparison of the results, same experiments were duplicated as controls with Fe(III)/TU redox initiator in absence of the mineral. *Figure 2* shows that the conversion efficiencies are increased dramatically when the Fe(III) ions are loaded in the layered spaces of montmorillonite. Fe(III)/TU redox couple brings about 40% conversion at 45°C (in the absence of any montmorillonite), which is increased slightly with temperature when 4.0×10^{-3} mol l^{-1} $FeCl_3$ is used (TU = 0.04 mol l^{-1}) at pH 2.01. However, 94% conversion is observed for the same concentration of Fe(III) ion when loaded in the interlayer space of montmorillonite ($\overline{\mathrm{Fe}}$(III)) under identical conditions (concentration of $\overline{\mathrm{Fe}}$(III) being moles of interlayer metal ions per 1000 mL of the reaction mixture). No induction period is observed, however, in either case. At lower $FeCl_3$ concentrations, polymer yield (X_L) as well as the initial rate of reaction (R_p) were increased substantially, indicating slower termination rates in the absence of any mineral clay. On the other hand, in the presence of mineral microenvironment, the initial rate of polymerisation was increased from 2.83×10^{-3} to 3.97×10^{-3} mol l^{-1} min^{-1} as the $\overline{\mathrm{Fe}}$(III) concentration increased from 0.60×10^{-3} to 2.07×10^{-3} mol l^{-1}. At a higher concentration of $\overline{\mathrm{Fe}}$(III), however, R_p tends to decrease due to transfer to ferric ions. Conversion

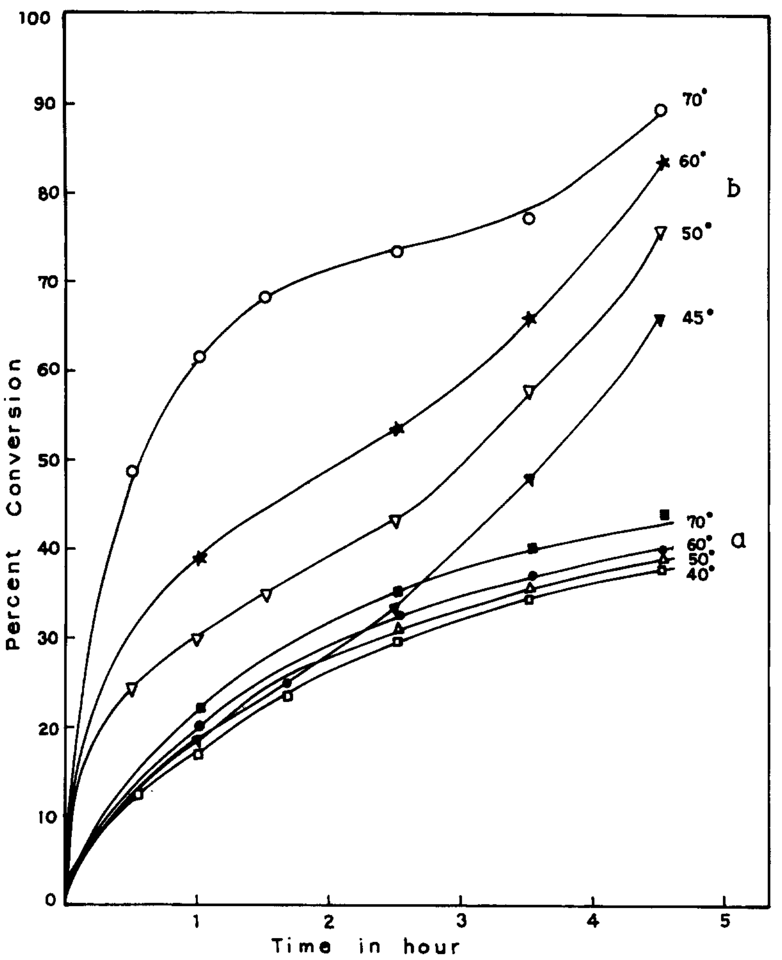
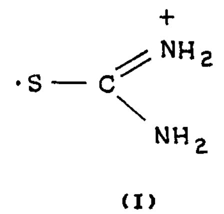


Figure 2 The effect of Fe(III) loading in montmorillonite on the course of polymerisation at various temperatures: (a) [Fe(III)] = 0.004 mol l^{-1}, [Mo] = 0, [TU] = 0.04 mol l^{-1}, [AM] = 0.4 mol l^{-1}, pH 2.01; (b) [Fe(III)] = 0.004 mol l^{-1}, [Mo] = 1.4%, [TU] = 0.04 mol l^{-1}, [AM] = 0.4 mol l^{-1}

efficiencies were also increased regularly with increasing Fe(III) ion concentration up to 2.07×10^{-3} mol l^{-1}. Although R_p and the yield decreased with decreasing TU concentrations, molecular weight of the polymer was higher at lower TU concentrations. Moreover, significant 'gel-effect' was observed in the presence of clay mineral apparently due to decrease in termination rates as mentioned above as well as for comparatively higher viscosity of the medium[13]. 'Gel-effect' was more prominent at lower temparatures than at 70°C. *Table 1* represents the data pertaining to the initial rates of polymerisation (R_p), polymer yeild (X_L), intrinsic viscosity (η) and molecular weight ($\bar{M}_v$) of the polymers formed as functions of the concentration of Fe(III), TU, AM, pH and temperature in the presence as well as in the absence of montmorillonite. The most significant observation of loading Fe(III) ions of the initiating redox couple in the interlayer spaces of montmorillonite is achieving polymers with much higher intrinsic viscosity and molecular weight. The η value of the polymer formed in homogeneous solution and in the absence of the mineral varied from 14 to 90 ml g^{-1} (*Table 1*) under the present experimental condition. Previous reports showed that redox polymerisation always displayed low intrinsic viscosities and molecular weights as are depicted in *Table 2* (which records the highest values of η and $\bar{M}_v$ from each of the References [12,14–17]). On the other hand, η values displayed by polymers formed in presence of montmorillonite were found to vary from 247 to 600 ml g^{-1} under identical experimental conditions. The η is also increased with increasing monomer and TU concentrations while it is increased with temperature up to 50°C but decreased at higher temperatures. The $\bar{M}_v$ values as calculated from viscosity data of present experiments ranged from 0.62×10^6 to 2.5×10^6. However, comparison of $\bar{M}_v$ with literature values should be done carefully because previous workers applied a different Mark–Houwnik equation. The significant role played by montmorillonite probably stems from two factors: (i) polymer initiation in the mineral microenvironment is favoured and (ii) rate of linear termination process decreases significantly because transfer to Fe(III) ions is highly restricted for the latter's location in the layered spaces of the mineral and diffusion of the living radical through montmorillonite gel is rather slow. In general, loading of the oxidant, i.e. metal ions, of the redox couple in the interlayer space of clay minerals, i.e. montmorillonite, offers a potential method of achieving very high degree of polymerisation for a redox initiated reactions.

Generation of primary and propagating free radicals

Previous studies showed that polymerisation of various



(I)

Table 1 The initial rates of polymerisation, polymer yields, intrinsic viscosities and the molecular weights of Fe(III)–TU initiated polymerisation in the presence and absence of montmorillonite at various conditions

Temp. (°C)	pH	[Mo]^a (g l^{-1})	[Fe(III)]^b (mmol l^{-1})	[TU] (mol l^{-1})	[AM] (mol l^{-1})	$R_p \times 10^3$ (mol l^{-1} m^{-1})	$X_L{}^c$ (%)	η (ml g^{-1})	$\bar{M}_v$ (× 10^{-5})
50	2.01	2.0	0.60	0.04	0.40	2.86	61	340	12.0
		3.0	0.90			3.33	62	364	12.2
		5.0	1.50			2.64	76	369	12.5
		7.0	2.07			3.97	77	284	9.5
		9.0	2.67			3.90	60	291	9.8
50	2.01	5.0	1.50	0.01	0.40	1.04	42	487	19.5
				0.02		2.56	50	595	25.0
				0.03		2.60	55	560	23.0
50	2.01	5.0	1.50	0.04	0.30	1.08	63	363	12.2
					0.50	3.60	48	397	14.9
					0.60	5.56	57	480	19.1
45	2.01	5.0	1.50	0.04	0.40	1.02	66	208	6.2
60						3.72	84	432	16.6
70						3.98	94	220	6.8
50	1.52	5.0	1.50	0.04	0.40	2.65	63	300	10.0
	2.10					3.09	40	369	12.5
	2.87					–^{d}	–	–	–
50	2.01	5.0	0.38 (0.008)	0.04	0.40	1.23	36	290	9.8
			0.75 (0.015)			1.99	43	360	13.0
			1.13 (0.023)			2.22	45	355	12.8
50	2.01		1.50^e	0.04	0.40	4.40	73	64	1.3
			3.00^e			5.60	56	73	1.5
			4.00^e			1.02	40	61	0.7
			8.00^e			2.50	26	45	0.8
50	2.01		1.5^e	0.04	0.30	5.0	62	60	1.2
				0.04	0.60	13.00	77	108	2.6
				0.01	0.40	1.78	40	14	0.2

[a] Montmorillonite content

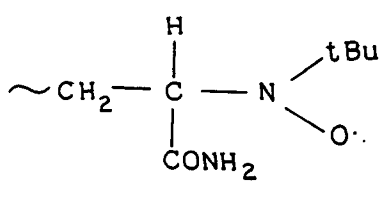
[b] Concentration of interlayer Fe(III) in mmol l^{-1} of the reaction mixture; corresponding concentrations in montmorillonite gel phase is 0.03 mol l^{-1} throughout, except those shown in brackets

[c] Yield after 4.5 hrs. [d] No polymer formed. [e] Concentration of FeCl$_3$ in solution

Figure 3 E.s.r. spectrum of MNP–PAM spin adduct

water insoluble vinyl monomers initiated by redox couples involving TU as the reductant, involved isothiocarbamido primary free radicals (I) in aqueous acid solution[11].

Owing to high '*g*' anisotropy and a very short relaxation time, detection of this radical by e.s.r. spectroscopy was not possible until recently, when e.s.r. study of spin adducts of the radical was reported[8]. In the present system also it is believed that the same primary radical (I) is formed and the propagating radicals from acrylamide are trapped by methyl nitroso propane (MNP) spin trap. *Figure 3* shows the e.s.r. spectrum of the MNP spin adduct of the radical (II)



(II)

The spectrum depicts a 1:1:1 triplet of doublets. The triplet is undoubtedly originated from the nitroxide radical (a_N = 1.45 mT) of MNP and the doublets are generated from H^β splitting (a_H = 0.31 mT). The isothiocarbamido radicals (I) are, however, not trapped by MNP under present condition.

Table 2 Intrinsic viscosities and molecular weights of acrylamide polymers formed by different redox couples

Initiating system	η (ml g^{-1})	$\bar{M}_v$ (× 10^{-5})
Ce(IV)–thiourea[14]	–	0.9
Mn(III)–ethoxyacetic acid[15]	0.5	0.2
Ce(IV)–ethylenediamine tetraacetic acid[16]	133	1.8
Ce(IV)–nitrilotriacetic acid[17]	90	1.1
Ce(IV)–nitrilotripropionic acid[12]	68	0.8
Ce(IV)–iminodiacetic acid[12]	73	0.9

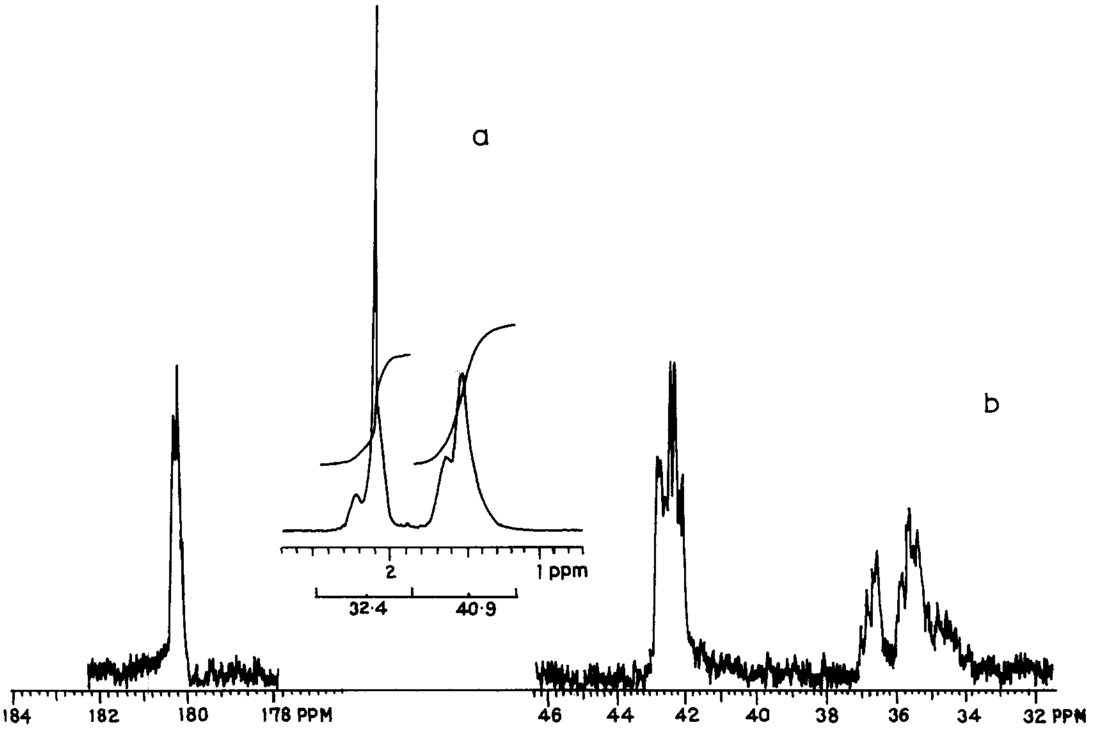


Figure 4 ^{1}H and ^{13}C n.m.r. spectra of thiourea terminated polyacrylamide formed on montmorillonite surfaces: (a) ^{1}H n.m.r. spectrum; (b) ^{13}C n.m.r. spectrum

XRD measurement

Unoriented powder samples of montmorillonite (H^+ and Fe(III) exchanged) before and after polymerisation reaction showed XRD patterns consistent with published results[10]. After the polymerisation reaction, the intensity of peak at $2\theta = 6.25°$ became much lower because of the presence of templates of polymer materials in the interlayer space. On the other hand, intensity of the peak at $2\theta = 9.5–9.8$ is increased due to polymerisation as well as glycerol treatment. Basal spacing of the H^+ and Fe(III) exchanged minerals is increased from 14 to 17 Å due to glycerol treatment for both TU treated and untreated samples. On the other hand, polymerisation increases basal spacing from 14 to 15 Å. Glycerol does not affect basal spacing at this stage. Foregoing results indicate that Fe(III) ions, TU and monomers all are intercalated between layers of the mineral without expanding the same and the locus of the polymerisation reaction is the interlayer spaces of the mineral. The location of Fe(III) ions in the interlayer space eventually retard the termination process, resulting in the higher degree of polymerisation.

^{1}H and ^{13}C n.m.r. spectra of PAM

^{1}H n.m.r. spectrum of PAM is not usually an well resolved spectrum and no special feature is apparent in present spectrum (*Figure 4a*) except that of overlapping of a sharp line with chemical shift of 2.12 ppm near the $-CHCONH_2$ position. This line in all probability represents the hydrogens from the isothiocarbamido end groups of thiourea terminated PAM. The expanded ^{13}C n.m.r. spectrum (*Figure 4b*) showed methylene, methine and carbonyl carbons of head-to-tail polymer of AM. No monomeric acrylamide was seen indicating purity of the polymer sample. The carbonyl carbon (at 180.2 ppm) splittings were small and not as readily interpreted as backbone carbon absorptions. The methine resonance (42.2–43.5 ppm) is a triplet (triad sensitivity) which is further split, showing pentade sensitivity. The low field and high field triplet peaks are assigned to rr (syndiotactic) and mm (isotactic) sequences, respectively. The central peak corresponds to heterotactic sequences (mr + rm). The methylene carbon lines (34–37.4 ppm) fall into three fairly well separated groups with almost all the 20 lines required by hexad sensitivity resolved. The resemblance of the

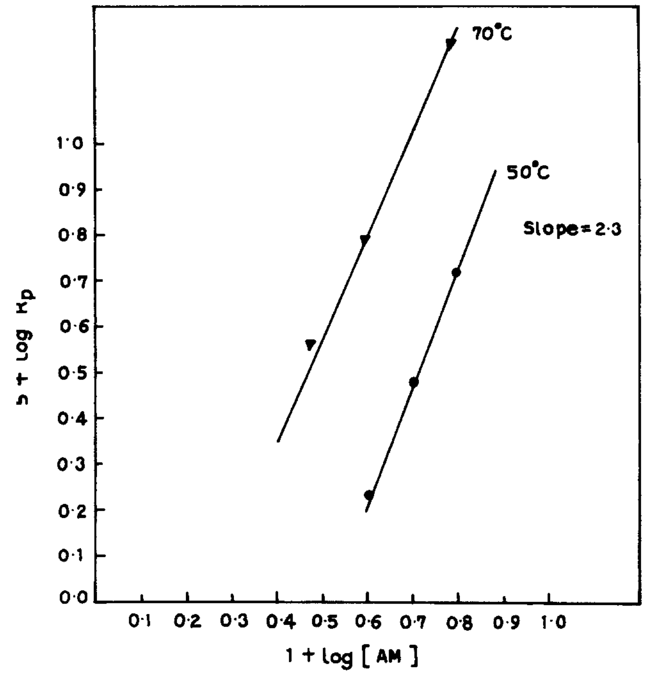


Figure 5 Logarithm plot of R_p *versus* [AM]: [Fe(III)] = 0.0015 mol l^{-1}, [TU] = 0.04 mol l^{-1}

spectrum to those obtained by Lancaster and Coworker suggests that Bernoulli statistics are followed, which is common in vinyl polymers[20].

Kinetics and mechanism. In homogeneous reaction condition (i.e., in the absence of any clay mineral) R_p is decreased with increased Fe(III) ion concentrations (*Table 1*), which is consistent with previous reports on similar redox systems and supports linear termination hypothesis by the metal ions[12,14–17]. The rate dependence on the monomer (M) concentrations could be related to neither a first order nor a second order reaction and the slope of the logarithm plot of R_p *versus* [AM] was found to be 1.45 (not shown in figure). Referring to the literature concerned with other redox systems involving metals as oxidants, the above kinetic behaviour predicts a polymerisation mechanism similar to that reported earlier[16]. The variation of the initial rate of polymerisation as a function of monomer concentration in the presence of montmorillonite is shown in *Figure 5*. Not all the points fell on a linear line. If it is assumed to be linear, the slope could be estimated as about 2.3. (The proposed mechanism, however, predicts an exponent of 2.0, the error in the experimental data may be introduced from the inherent coarseness in following the kinetics of a heterogeneous system.) The significant change in the monomer exponent due to the occurrence of the reaction on the montmorillonite surface indicates that the polymerisation mechanism is greatly affected by the mineral microenvironment. A rate dependence of second order and above on monomer concentration was also observed earlier in heterogeneous and precipitation polymerisation of acrylamide and various interpretations, including 'cage effect' and 'complex theory', were proposed to account for the significant departure from first order kinetics[18,19]. The 'cage effect' suggests that when an initiator decomposes into two radicals, there is a formation of a potential barrier by the surrounding solvent molecules which prevent their immediate diffusion and favours their destruction by mutual recombination. The 'complex theory' is based on the formation of a complex between the initiator and the monomer, the rate of initiation then being determined by the rate of decomposition of the complex. The 'cage effect' seems to be a good conceptual starting point in explaining the high monomer exponent which has been observed in the present system. To examine the dependence of rate on the montmorillonite content and Fe(III) concentrations, the initial rate of polymerisation is plotted as a function of Fe(III) ion concentration (*Figure 6*), R_p is increased with the montmorillonite and Fe(III) contents of the reaction mixture but the slope of logarithm plot varied from 0.25 to 0.40 as a result of raising the reaction temperature from 50 to 70°C. However, if the locus of polymerisation is assumed to be the interlayer space of montmorillonite, above slopes can not be regarded as metal ion exponents because increasing addition of Fe(III)-saturated mineral does not increase Fe(III) ion concentration in the mineral phase but, on the contrary, only

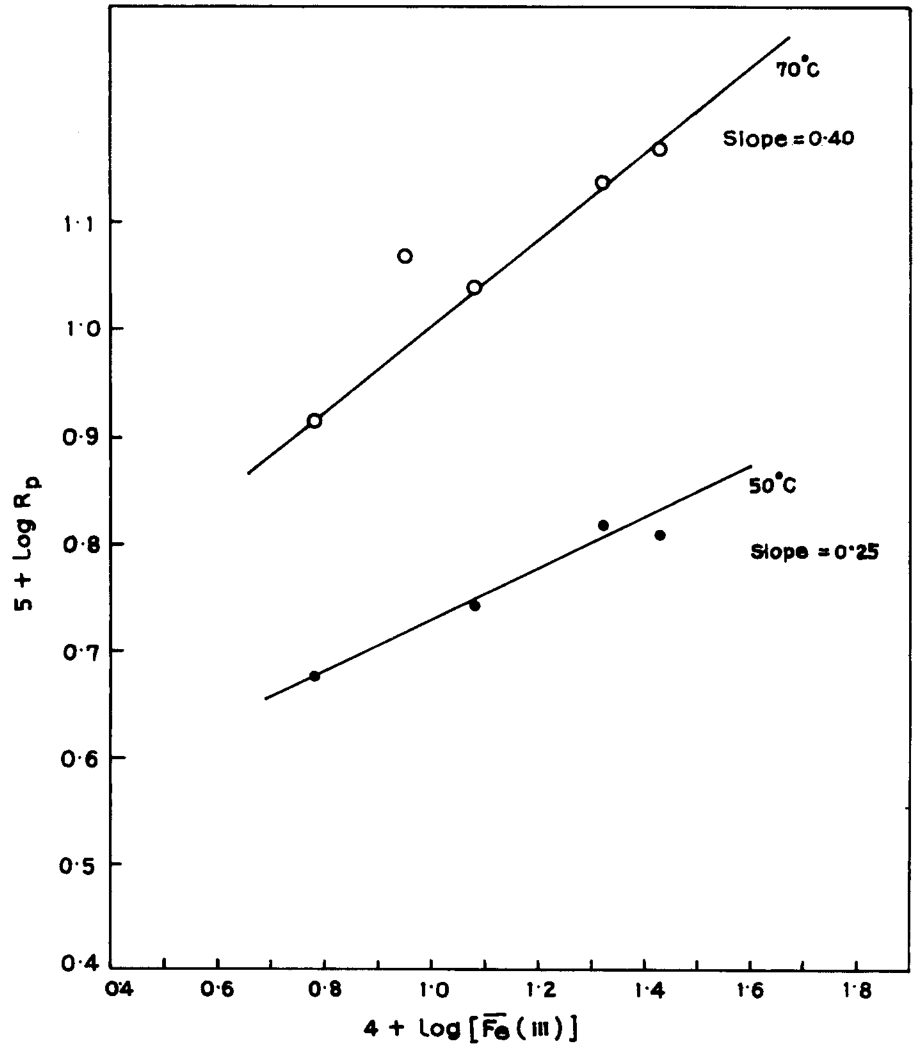


Figure 6 Logarithm plot of R_p *versus* [Fe(III)]: [AM] = 0.4 mol l^{-1}, [TU] = 0.04 mol l^{-1}, [Mo] = 0.5%

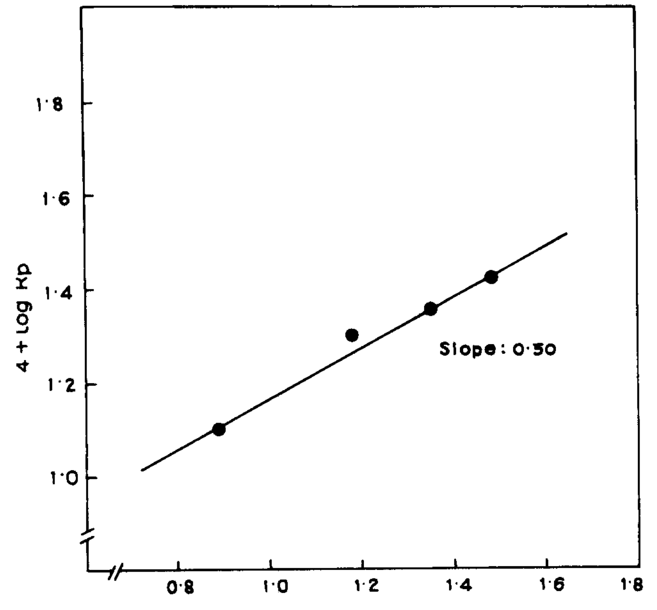


Figure 7 Logarithm plot of R_p *versus* $[\overline{\text{Fe}}(\text{III})]$: $[\text{AM}] = 0.4\ \text{mol l}^{-1}$, $[\text{TU}] = 0.04\ \text{mol l}^{-1}$, $[\text{Mo}] = 0.5\%$ ($[\overline{\text{Fe}}(\text{III})]$ in this figure represents moles of ferric ions in the montmorillonite gel phase)

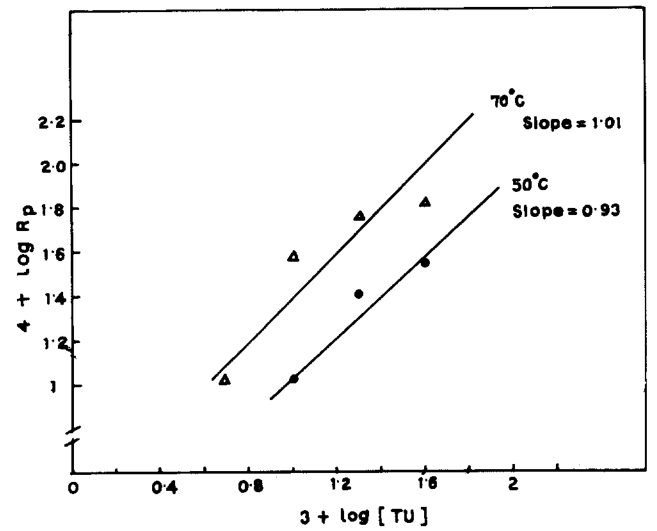


Figure 8 Logarithm plot of R_p *versus* [TU]: $[\overline{\text{Fe}}(\text{III})] = 0.0015\ \text{mol l}^{-1}$, $[\text{AM}] = 0.4\ \text{mol l}^{-1}$, $[\text{Mo}] = 0.5\%$

adds to the total metal ion and adsorbent contents of the reaction mixture. This in turn increases monomer and TU contents of the intercalate position, which result in the high rates of polymer yield. In order to measure the actual metal exponent for the reaction in the mineral phase, R_p values were plotted as a function of Fe(III) ion concentration in the montmorillonite gel. The concentrations of Fe(III) in the montmorillonite gel were varied by adding calculated quantities of HM in the reaction mixture. The slope of such a logarithm plot (*Figure 7*) has been estimated as 0.50 at 50°C. (The concentration of Fe(III) now being moles of interlayer Fe(III) ions per 1000 mL montmorillonite gel; the water content of montmorillonite sample was measured following the method described by Marinsky and co-workers and found to be $10\ \text{ml g}^{-1}$)[21]. *Figure 8* shows the dependence of R_p on TU concentrations. Since the isothiocarbamido primary radicals (I) have strong tendency to dimerise above $0.05\ \text{mol l}^{-1}$, the present study was confined below that concentration only[8]. Again, not all the points fell on a linear line (in the logarithm plot) owing to the heterogeneous reaction mixture. However, the slopes of the average lines drawn through the points at two different temperatures indicate that the reaction is first order with respect to TU concentrations. To rationalise the above experimental results and to predict a possible mechanism for the seemingly complex polymerisation reaction occurring in the mineral microenvironment, the following assumptions are made[12,22].

(1) Intercalated TU reacts fast with the Fe(III) ions of montmorillonite layered spaces to form the reactive TU (isothiocarbamido (I)) radicals via an intermediate complex. The decomposition of the complex is the rate-controlling step.
(2) In the acidic and metal ion exchanged aqueous montmorillonite system, a fraction of the intercalated acrylamide molecules are present near reacting sites as pairs either through hemisalts formation, where two amide molecules share a proton by means of symmetrical hydrogen bond or/and through weak coordination to the exchanged cations[2]. The protonated as well as the complexed amide pairs are at fast equilibrium with unprotonated and free amide molecules, respectively, which are defined by a protonation constant or a formation constant. In view of high monomer exponent, it is certain that it must have resulted in part from the involvement of monomer in the initiation step, where such monomer pairs are entailed.
(3) Since the reactive TU radicals are formed as pairs, assumption of the 'cage effect' seems to be conceptually appropriate. The initiation step involves collision of the 'amide pairs' with caged TU radicals at the wall of the cage and random diffusion of the radicals from the cage and their secondary recombination are less significant in comparison with the rate of dimerisation of caged radicals or their reaction with acrylamide.

Initiation

$$\overline{\text{Fe}}(\text{III}) + \text{TU} \overset{K}{\rightleftharpoons} \overline{\text{Fe}}(\text{III}) \underset{\text{Complex}}{-} \text{TU} \qquad (1)$$

$$\overline{\text{Fe}}(\text{III}) - \text{TU} + \text{TU} \xrightarrow{k_d} \overline{\text{Fe}}(\text{II}) + (2\text{TU}^{\cdot}) + \text{H}^+ \qquad (2)$$

$$(\text{TU}^{\cdot}) + \text{M}_2\text{H}^+ \xrightarrow{k_i} \text{M}_1^{\cdot} + \text{M} + \text{H}^+ \qquad (3)$$

Propagation

$$\text{M}_1^{\cdot} + \text{M} \xrightarrow{k_p} \text{M}_2^{\cdot}$$

$$\text{M}_{n-1}^{\cdot} + \text{M} \xrightarrow{k_p} \text{M}_n^{\cdot} \ldots\text{etc.} \qquad (4)$$

Termination

$$\text{M}_n^{\cdot} + \text{M}_n^{\cdot} \xrightarrow{k_t} \text{M}_n - \text{M}_n \qquad (5)$$

$$(\text{TU}^{\cdot}) + \overline{\text{Fe}}(\text{III}) \xrightarrow{k_t'} \text{TU} + \overline{\text{Fe}}(\text{II}) \qquad (6)$$

$$(2\text{TU}^{\cdot}) \xrightarrow{k_t''} \text{TU} - \text{TU} \qquad (7)$$

(caged species are enclosed in brackets)

Using the above scheme and the pseudo-steady-state assumption, we derive the rate expressions as follows:

$$\frac{-\mathrm{d}[\overline{\mathrm{Fe}}(\mathrm{III})]}{\mathrm{d}t}=\frac{k_{\mathrm{d}}K[\mathrm{TU}]^2[\overline{\mathrm{Fe}}(\mathrm{III})]}{1+K[\mathrm{TU}]} \tag{8}$$

$$R_{\mathrm{p}}=\frac{(k_{\mathrm{d}}k_{\mathrm{i}}KK')^{1/2}k_{\mathrm{p}}[\overline{\mathrm{Fe}}(\mathrm{III})]^{1/2}[\mathrm{TU}][\mathrm{M}]^2}{k_{\mathrm{t}}^{1/2}(k_{\mathrm{i}}K'[\mathrm{M}]^2+k_{\mathrm{i}}KK'[\mathrm{M}]^2[\mathrm{TU}]+k_{\mathrm{t}}'[\overline{\mathrm{Fe}}(\mathrm{III})]+k_{\mathrm{t}}''(1+K[\mathrm{TU}]))^{1/2}} \tag{9}$$

(K' ($= [\mathrm{M_2H^+}]/[\mathrm{M}]^2$) is the apparent protonation constant at a fixed pH (or a formation constant))

If the oxidative termination (step 6) is assumed to be insignificant in comparison with the dimerisation rate of caged radicals, equation (9) reduces to:

$$R_{\mathrm{p}}=\frac{(k_{\mathrm{d}}k_{\mathrm{i}}KK')^{1/2}k_{\mathrm{p}}[\overline{\mathrm{Fe}}(\mathrm{III})]^{1/2}[\mathrm{TU}][\mathrm{M}]^2}{k_{\mathrm{t}}^{1/2}(k_{\mathrm{i}}K'[\mathrm{M}]^2+k_{\mathrm{i}}KK'[\mathrm{M}]^2[\mathrm{TU}]+k_{\mathrm{t}}''(1+K[\mathrm{TU}]))^{1/2}} \tag{10}$$

The interpretation of high kinetic order of the monomer finally hinges on the dominance of a reaction between caged radicals and those of monomers with the radicals at the cage wall. Although the concentrations of the monomer and TU in solution phase were fixed mostly at 0.40 mol $\mathrm{l^{-1}}$ and 0.04 mol $\mathrm{l^{-1}}$ respectively, the concentrations of intercalated species must be much lower, specially due to the presence of water molecules in the interlayer spaces.

Thus, while the concentrations, [M] and [TU], in the montmorillonite gel-phase should be

$$[\mathrm{M}]=L_{\mathrm{o}}^{\mathrm{a}}\theta_{\mathrm{m}}=\frac{L_{\mathrm{o}}^{\mathrm{a}}K_{\mathrm{m}}^{\mathrm{a}}[\mathrm{M}]_{\mathrm{s}}}{1+K_{\mathrm{tu}}^{\mathrm{a}}[\mathrm{TU}]_{\mathrm{s}}+K_{\mathrm{m}}^{\mathrm{a}}[\mathrm{M}]_{\mathrm{s}}} \tag{11}$$

and,

$$[\mathrm{TU}]=L_{\mathrm{o}}^{\mathrm{a}}\theta_{\mathrm{tu}}=\frac{L_{\mathrm{o}}^{\mathrm{a}}K_{\mathrm{tu}}^{\mathrm{a}}[\mathrm{TU}]_{\mathrm{s}}}{1+K_{\mathrm{tu}}^{\mathrm{a}}[\mathrm{TU}]_{\mathrm{s}}+K_{\mathrm{m}}^{\mathrm{a}}[\mathrm{M}]_{\mathrm{s}}} \tag{12}$$

(subscript 's' denotes solution)

($L_{\mathrm{o}}^{\mathrm{a}}$ and θ are the total active sites in unit mass of montmorillonite and the fraction of total sites occupied by each species respectively; $K_{\mathrm{m}}^{\mathrm{a}}$ and $K_{\mathrm{tu}}^{\mathrm{a}}$ are selectivity coefficients)

the denominators of equations (11) and (12) are nearly unity. By appropriate substitution of [M] and [TU] in equation (10) and considering the dominance of the last term of the denominator over others, the equation becomes

$$R_{\mathrm{p}}=\frac{k_{\mathrm{p}}(k_{\mathrm{d}}k_{\mathrm{i}}KK'/k_{\mathrm{t}}k_{\mathrm{t}}'')^{1/2}K_{\mathrm{tu}}^{\mathrm{a}}(K_{\mathrm{m}}^{\mathrm{a}})^2(L_{\mathrm{o}}^{\mathrm{a}})^3[\overline{\mathrm{Fe}}(\mathrm{III})]^{1/2}[\mathrm{TU}]_{\mathrm{s}}[\mathrm{M}]_{\mathrm{s}}^2}{(1+KL_{\mathrm{o}}^{\mathrm{a}}K_{\mathrm{tu}}^{\mathrm{a}}[\mathrm{TU}]_{\mathrm{s}})^{1/2}} \tag{13}$$

(Values of $K_{\mathrm{m}}^{\mathrm{a}}$ (or $K_{\mathrm{tu}}^{\mathrm{a}}$), $L_{\mathrm{o}}^{\mathrm{a}}$ and K are of the order of 10^{-2}, 2 mmol $\mathrm{g^{-1}}$ and 2 l $\mathrm{mol^{-1}}$, respectively[22,23]. Small values of above parameters including that of K', ensure that terms involving quadratic and above concentrations are very small in the present conditions[24,25]).

Further inspection of equation (13) shows that the value of $KL_{\mathrm{o}}^{\mathrm{a}}K_{\mathrm{tu}}^{\mathrm{a}}$ $[\mathrm{TU}]_{\mathrm{s}}$ in the denominator varies from 10^{-5} to 10^{-6} for the variation of aqueous TU concentration from 0.05 to 0.005 mol $\mathrm{l^{-1}}$. This implies that the rate equation under the present condition is reduced to

$$R_{\mathrm{p}}=k_{\mathrm{p}}(k_{\mathrm{d}}k_{\mathrm{i}}KK'/k_{\mathrm{t}}k_{\mathrm{t}}'')^{1/2}K_{\mathrm{tu}}^{\mathrm{a}}(K_{\mathrm{m}}^{\mathrm{a}})^2(L_{\mathrm{o}}^{\mathrm{a}})^3[\overline{\mathrm{Fe}}(\mathrm{III})]^{1/2}[\mathrm{TU}]_{\mathrm{s}}[\mathrm{M}]_{\mathrm{s}}^2 \tag{14}$$

Reviewing the above result, we find that equation (14) could satisfactorily account for the present behaviour of the $\overline{\mathrm{Fe}}$(III)–TU initialised acrylamide polymerisation exhibited in the aqueous montmorillonite layered space.

CONCLUSIONS

Aqueous polymerisation of acrylamide by Fe(III)–thiourea redox couple shows kinetic behaviour and mechanism similar to those of other redox initiated polymerisations of acrylamide. On the other hand, polymerisation initiated by the same redox couple but by loading Fe(III) ions in the interlayer spaces of montmorillonite influences the kinetics as well as the mechanism to a great extent. The latter technique increases the degree of polymerisation and the intrinsic viscosity of the polymers dramatically by decreasing the rate of linear termination process. The method was demonstrated to be a promising technique of achieving high molecular weight polymers for redox initiated reactions, where low molecular weight polymers are often displayed. The maximum values of $\bar{M}_{\mathrm{V}}$ were found to be 2.6×10^5 and 2.5×10^6 in the absence and presence of montmorillonite respectively, while η values increased from 108 to 595 ml $\mathrm{g^{-1}}$ due to the presence of the mineral under identical condition. E.s.r. study confirms that lattice substituted Fe(III) in montmorillonite reacts with thiourea but the reaction failed to initiate polymerisation of acrylamide in water. The locus of the polymerisation was identified by XRD as the interlayer space of the mineral while, the propagating radicals were characterised by spin-trapping technique. The hyperfine splitting parameters a_{N} and a_{H}^{β} for the MNP adduct are 1.45 and 0.31 mT respectively. The polymers, characterised by ^{1}H and ^{13}C n.m.r., were mostly thiourea terminated head-to-tail polymers with mixed tacticities where Bernoulli statistics were followed. The kinetics study showed the monomer, TU and the metal ion exponents to be 2.0, 1.0, and 0.5 respectively, which have been explained by means of a radical mechanism involving 'cage effect' on the initiating TU radical pairs. In view of the presence of acrylamide molecules as hemisalts where two amide molecules share a proton through a symmetrical hydrogen bond in the acidic montmorillonite layered space, the initiation step probably involves collision of caged TU radicals with the monomer pairs at the cage wall.

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