

Interpretation of the chain structures of PMMAs, PANs and PAAMs obtained by using Ce(IV) and KMnO_4 in combination with NTA and DTPA as initiator systems by FTIR spectroscopic analysis

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Abstract

Polyacrylamides (PAAMs), polyacrylonitriles (PANs) and poly(methyl methacrylate)s (PMMAs) were synthesized by using $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and KMnO_4 in combination with nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA), which have strong chelating properties, as redox initiators. Polymerizations were carried out in the aqueous acidic solutions at 25°C and 55°C in the presence of air. The chain structures of the resulting products were studied by Fourier-transform infrared (FTIR) spectroscopic measurements. From the comparison of the spectroscopic results with gravimetric and viscometric data it was concluded that both the differences between the solubility behaviour in aqueous solutions of MMA, AN, AAm and their polymers, and catalyst–activator–monomer combinations were important parameters effecting the polymerization mechanisms, conversions and the structures of the polymers. The FTIR and viscosity results indicated that PAAMs obtained in our experimental conditions formed crosslinked structures with sulphated complexes of Ce(III) and MnSO_4 produced by the redox reactions between catalysts (MnO_4^- and Ce(IV)), NTA and AAm. Further, it was observed that PAN chains were terminated by hydrated and sulphated complexes of Ce(III) while the termination of PMMA radicals took place by primary radicals because PMMAs were formed by emulsion polymerization kinetics. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceric salts (Ce(IV)) and permanganate ($\text{Mn}(\text{VII})\text{O}_4^-$) in combination with different reducing agents were used for the aqueous polymerizations of acrylamide (AAm), acrylonitrile (AN) and methylmethacrylate (MMA) [1–6]. Recently, Hsu et al. and Saraç et al. studied the aqueous polymerization of AAm initiated by Ce(IV)–polyaminocarboxylic acid (PACA) redox systems as the Ce(IV)-mediated decarboxylations of PACAs lead to the formation of a free radical along with various oxidation products [7–15]. Another metal ion which formed stable complexes with PACAs is tetravalent manganese ion, i.e. Mn(IV) and these complexes also govern the generation of primary radicals [1,16].

In our previous study, spectroscopic, conductometric, and gravimetric methods were used to provide some structural definitions for the final products obtained from the aqueous acidic polymerizations of AAm by using Ce(IV)–PACA

redox systems [17]. The experimental observations in that work showed that the stabilities of the primary radical sources depended on the ligand type and concentration of Ce(IV) salts.

It is known that both PACA : Ce(IV) ratios and acidity of the medium can effect the reaction path, the stability of Ce(IV)–PACA complexes and the types of Ce(IV)–ligand complexes. Hence, it is not easy to investigate the oxidation reaction of polyaminocarboxylic acids which are commonly used as chelating agents [13–15]. Further, there was no systematic study concerned with the effects of the various monomer–catalyst–activator combinations, the concentration and type of each constituent in these combinations on the structures of the products synthesized with them. So, the main aim this work was to elucidate the process of aqueous polymerizations of AAm, AN and MMA, with different solubility behaviour, initiated with nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA) in the presence of ceric ammonium nitrate, ceric sulphate and potassium permanganate under acidic conditions; and by using FTIR spectroscopic analysis results and viscosity measurements the effects of catalyst–activator–monomer

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combinations on the polymerization yields and mechanisms, and the chain structures of the resulting polymers were studied.

2. Experimental

The reagents used, AAm, NTA, DTPA, ceric sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), ceric ammonium nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$), KMnO_4 , DMF, benzene, H_2SO_4 and HNO_3 , were from Merck and were used as received. The monomers AN and MMA were also from Merck but distilled under reduced pressure before use. All solutions were prepared in distilled-deionized water.

Polymerizations were carried out under aerated conditions and were shielded from light, except AAm. Polymerization procedures for $\text{Ce}(\text{IV})$ –PACA redox pairs were similar to that reported earlier [18]; but in the case of KMnO_4 , the order of the addition of reagents was slightly different. The first step in the polymerizations of AAm and AN initiated by KMnO_4 –PACA redox pairs was the separation of colloidal manganese dioxide (MnO_2 produced by the reaction between monomer and MnO_4^-). NTA (or DTPA) was added after the formation of brownish-black MnO_2 and polymerization occurred with dissolution of MnO_2 .

The molecular weights of the polymers were determined by viscosity measurements in DMF and benzene at 25°C using

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75}, \quad (1)$$

$$[\eta] = 5.5 \times 10^{-5} \bar{M}_w^{0.76}. \quad (2)$$

Eqs. (1) and (2) were used for PAN and PMMA, respectively [19,20].

FTIR spectroscopy was used to analyse the structures of the polymers and oxidation products using a Mattson 1000 Fourier-transform infrared spectrometer. The test samples were made in the form of pellets with KBr.

3. Results and discussion

3.1. Effects of types and concentrations of catalysts, activators and monomers on conversions and molecular weights

The experimental results summarized in Table 1 can be explained by considering the following:

The conversions of polymerizations initiated with DTPA– $\text{Ce}(\text{IV})$ and DTPA– MnO_2 redox pairs are lower than that of NTA– $\text{Ce}(\text{IV})$ and NTA– MnO_2 . This indicates that the stability of the DTPA– $\text{M}(\text{IV})$ complexes are higher than that of NTA– $\text{M}(\text{IV})$ complexes.

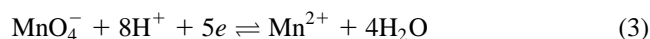
There are some differences between the solubility behaviour in aqueous solutions of MMA, AN and their polymers. AN has a larger solubility in water than MMA. PAN cannot dissolve in its own monomer while MMA behave like a

solvent for PMMA. These differences can also be observed by comparing the conversions and molecular weights of PANs and PMMAs obtained with $\text{Ce}(\text{IV})$ –NTA and $\text{Ce}(\text{IV})$ –DTPA redox systems at two temperatures, 25°C and 55°C, in this work. (Sets 1, 2, 6 and 7 in Table 1). For example, the lowest AN concentration, which was necessary to initiate the polymerization process and obtain PAN chains was 0.60 mol l^{-1} (the experimental conditions used were $[\text{PACA}] = 2 \times 10^{-2} \text{ mol l}^{-1}$; $[\text{Ce}(\text{IV})] = 3 \times 10^{-2} \text{ mol l}^{-1}$ and $[\text{HNO}_3] = [\text{H}_2\text{SO}_4] = 0.75 \text{ mol l}^{-1}$). In contrast PMMA chains could be formed by 0.1 mol l^{-1} MMA concentration. Further, although catalyst and activator concentrations were the same in the cases of both MMA and AN, molecular weights of the PANs synthesized with approximately four times concentrated solutions (1.50 and 0.38 mol l^{-1} for AN and MMA, respectively) were ten times lower than those of PMMAs.

It is known that AN and MMA polymerization systems in aqueous solutions are heterogeneous. As to the results on heterogeneous polymerizations in the literature, terminations can occur in both aqueous and precipitated phase. Before precipitation, oligomeric short chains are terminated by either metal ions and primary radicals or oligomeric radicals [21,22]. Hence, we can say that PAN chains are terminated by $\text{Ce}(\text{IV})$ ions, $\text{Ce}(\text{IV})$ –sulphate complexes and primary radicals produced by PACA (unimolecular termination); while MMA polymerizations proceed in heterogeneous phase following emulsion polymerization kinetics (mutual termination) because NTA and DTPA behave like emulsifying agents.

Another important point observed is the fall in the conversion rate at higher monomer concentrations, i.e. 0.72 and 2.50 mol l^{-1} for MMA and AN, respectively. This is probably because of the excess monomer acting as good and bad solvents for PMMA and PAN, respectively (as the solubilities of PMMA and PAN differ from each other).

The comparison of the data given in Table 1 (Sets 1, 3, and 5) with that in Refs. [10,13] shows that the performance of $\text{Ce}(\text{IV})$ –PACA pairs is better than that of MnO_2 –PACA, in the cases of both AAm and AN. The depression of the conversions depend on the catalyst, activator and monomer types (Sets 1 and 2) and might be because of the following factors: (a) The concentration of the primary radical sources, i.e. NTA and DTPA might decrease because of the side reactions between PACAs and KMnO_4 ; (b) The standard potentials of KMnO_4 and $\text{Ce}(\text{IV})$ sulphate in H_2SO_4 solution were calculated to be 1.52 and 1.44 V , respectively [23]. The reduction of MnO_4^- in acid solutions can be represented by



In contrast, if the reaction media contain some organic substances such as AAm, AN, NTA and DTPA, reacting with potassium permanganate ($\text{MnO}_4^- + 4\text{H} + 3e \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$; $E^0 = 1.69 \text{ V}$), colloidal MnO_2 is formed.

Table 1
Effects of temperature, monomer concentration and, initiator, activator and monomer type on the conversion and molecular weight^a

Set number	Initiator–activator–acid combinations	Temperature (°C)	Monomer type	Concentration (mol l ⁻¹)	Conversion after 1 h, %	\bar{M}_v
1	Ce(IV)–NTA	25	AN	0.60	65	2150
	Ce(IV)–NTA			1.50	78	5950
	Ce(IV)–NTA			2.50	24	9200
	Ce(IV)–DTPA			0.60	64	2400
	Ce(IV)–DTPA–H ₂ SO ₄			2.50	24	7350
2	Ce(IV)–NTA	55	AN	0.60	52	2550
	Ce(IV)–NTA			2.50	30	10 200
	Ce(IV)–DTPA			0.60	36	6400
	Ce(IV)–DTPA			1.50	63	12 500
	Ce(IV)–DTPA–H ₂ SO ₄			2.50	22	21 000
3	MnO ₂ –NTA	25	AAM	0.20	—	—
	MnO ₂ –NTA			0.40	72	—
	MnO ₂ –NTA			0.60	85	—
	MnO ₂ –DTPA			0.40	28	—
	MnO ₂ –DTPA–H ₂ SO ₄			0.60	75	—
4	MnO ₂ –NTA–H ₂ SO ₄	55	AAM	0.20	54	—
5	MnO ₂ –NTA	25	AN	0.40	—	—
	MnO ₂ –NTA			1.00	5	10 400
	MnO ₂ –NTA			1.50	14	17 900
	MnO ₂ –NTA			2.50	7	33 500
	MnO ₂ –DTPA			1.00	—	—
	MnO ₂ –DTPA–H ₂ SO ₄			2.50	3	100 000
6	Ce(IV)–NTA	25	MMA	0.10	26	—
	Ce(IV)–NTA			0.38	71	52 100
	Ce(IV)–DTPA			0.38	12	47 100
	Ce(IV)–DTPA–HNO ₃			0.72	4	—
7	Ce(IV)–NTA	55	MMA	0.10	28	23 000
	Ce(IV)–NTA			0.39	67	74 800
	Ce(IV)–DTPA–HNO ₃			0.39	33	13 700
8	Ce(IV)–NTA–H ₂ SO ₄	25	MMA	0.38	34	20 800

^a [Ce(NH₄)₂(NO₃)₆] = [Ce(SO₄)₂·4H₂O] = [KMnO₄] = 3 × 10⁻² mol l⁻¹; [NTA] = [DTPA] = 2 × 10⁻² mol l⁻¹; [HNO₃] = [H₂SO₄] = 0.75 mol l⁻¹.

In our experimental conditions, the manganese dioxide produced by the reaction between AAM (or AN) and MnO₄⁻ reacts with NTA (or DTPA) to produce Mn(IV)–PACA complexes generating active free radicals. Contrarily, the inhibition effect of the reaction MnO₂ + 4H⁺ + 2e⁻ ⇌ Mn²⁺ + 2H₂O (*E*⁰ = 1.23 V), having high standard potential prevents the formation of Mn³⁺ ions, which are highly reactive in the production of primary free radicals and so the conversions are lower than that of Ce(IV)–PACA systems.

The polymerization behaviour of AN and AAM in the aqueous solutions are apparently different from each other (Sets 3 and 5 in Table 1), PAAm is soluble in water while the polymer of AN cannot dissolve in either water or its own monomer. Hence, the aqueous AN system is a complex and heterogeneous one. This heterogeneity leads to the increase in various byproducts, water-soluble short chain PANs

terminated by metal ions or primary radicals and other side reactions which consume the monomer, activator and catalyst. Consequently, we can infer that these are the main reasons effecting the low conversion observed in the AN polymerizations.

It is known that both extensive protonation of NTA and sulphate complexes of Ce(IV) in H₂SO₄ solution decrease the reductive ability of NTA [24]. Further, Malinina et al. have observed that NTA formed 1 : 1 (NTA : Ce(IV)) complexes in sulphate media where Ce(IV) is strongly sulphato complexed and 2 : 1 complexes in nitrate media where Ce(IV) is not as strongly nitrato complexed [25]. These findings in the literature are equivalent to our experimental results observed in MMA polymerizations (Sets 6 and 8 in Table 1) because decrease in the conversion means decrease in the reactivity of the complexing agent.

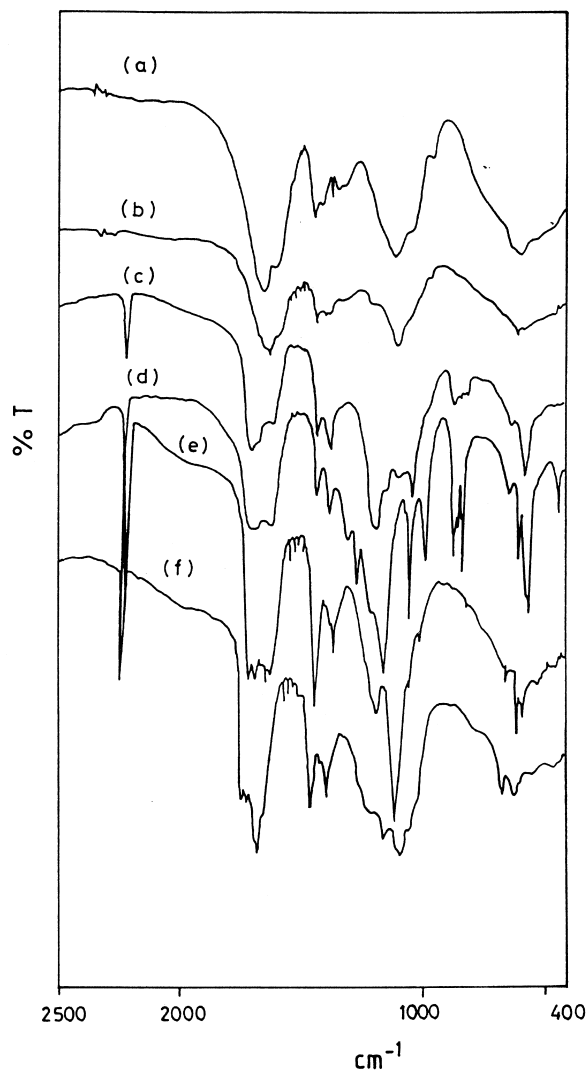


Fig. 1. FT-IR spectra of the polymers synthesized with the following conditions: (a) NTA–AAm–Ce(IV), H_2SO_4 , $[\text{AAm}] = 0.40 \text{ mol l}^{-1}$, $T = 55^\circ\text{C}$; (b) NTA–AAm– MnO_4^- , H_2SO_4 , $[\text{AAm}] = 0.40 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$; (c) NTA–AN–Ce(IV), H_2SO_4 , $[\text{AN}] = 0.60 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$; (d) NTA–AN–Ce(IV), H_2SO_4 , $[\text{AN}] = 1.50 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$; (e) NTA–AN–Ce(IV), H_2SO_4 (purified sample), $[\text{AN}] = 2.50 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$; (f) the same with (e) but unpurified. The other parameters of the polymerizations are given in Table 1.

3.2. Chain structures of the resulting polymers

Figs. 1–3 show the FTIR spectra of the polymers given in Table 1. In this section of the work, we will try to explain the spectroscopic results on the chain structures of these polymers synthesized in aqueous acidic media, by means of both gravimetric and viscometric results (presented in Section 3.1) and literature results related with these initiator systems and monomers.

Figs. 1 and 2 show the FTIR spectra of AAm and AN polymers initiated with NTA–Ce(IV) and NTA– KMnO_4 redox pairs while the FTIR results of PMMAs synthesized with $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ –NTA and $\text{Ce}(\text{SO}_4)_2$ –NTA redox pairs are illustrated in Fig. 3.

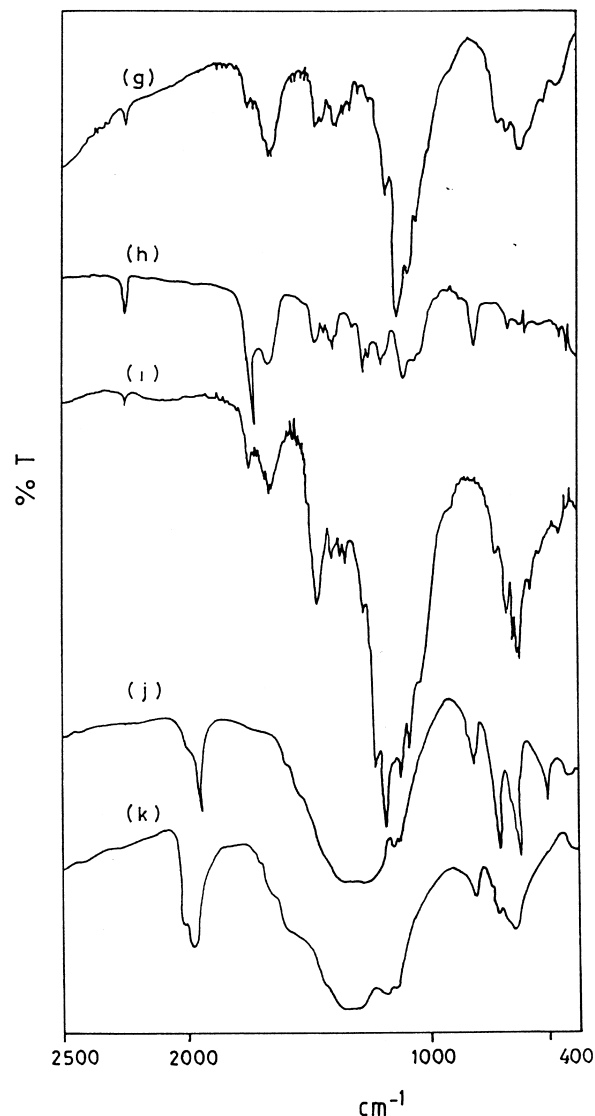


Fig. 2. FT-IR spectra of the polymers synthesized with the following conditions: (g) NTA–AN– MnO_4^- , H_2SO_4 , $[\text{AN}] = 2.50 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$; (h) the same with (g) but purified; (i) NTA–AN–Ce(IV), H_2SO_4 , $[\text{AN}] = 2.50 \text{ mol l}^{-1}$, $T = 55^\circ\text{C}$; (j) $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$; (k) $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The other parameters of the polymerizations are given in Table 1.

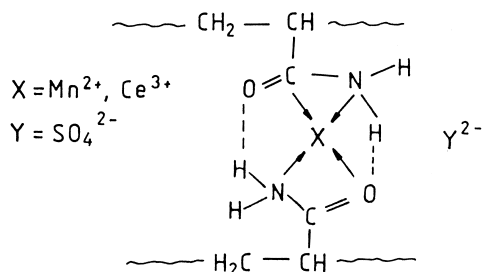
The discussions on the spectroscopic results of the polymers given in Table 1 are summarized as follows:

FTIR spectra of the polymers initiated with DTPA-oxidation agent redox pairs were not determined.

The appearance of the absorption bands characteristic of covalent and ionic sulphate groups (450 – 750 , 1050 – 1230 and 1350 – 1500 cm^{-1}) together with the specific peaks of PAAm at 1660 cm^{-1} ($\text{C}=\text{O}$ stretching), 1620 cm^{-1} ($-\text{NH}$ bending) and 1300 – 1500 cm^{-1} ($-\text{CH}$ bending and $\text{C}-\text{N}$ stretching) indicates the presence of the sulphate group in the polymers (Spectra 1 and 2 in Fig. 1). These absorption bands can lead to the following conclusions that:

1. Amide groups interact with MnSO_4 and Ce(III)-SO_4

complexes produced by the redox reactions between PACAs and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (or MnO_4^-), by the complex formation mechanism as shown in the following possible structure



2. PAAms obtained in this work (Table 1, Set 3) and in Ref. [13] (conditions identical to that in this work) are insoluble in water but swell. This is in agreement with the suggestion for crosslinking structures.
3. Palit and Konar showed that sulphate ion was oxidized by MnO_2 to produce the sulphate ion radical [26]. Narita and Machida found one cerium atom per PAAm molecule prepared by using Ce(IV) as initiator. One possible termination mechanism suggested by them is the formation of a complex between cerium and PAAm [27]. Hence, it can be said that $\cdot\text{OSO}_3^-$ and Ce(III)- SO_4 complexes play an important role in the initiation and termination processes, in our polymerization conditions.

The spectra (c), (d), (f) and (i) in Figs. 1 and 2 show the FTIR results of PANs synthesized with Ce(IV)-NTA redox initiators while (g) in Fig. 2 belongs to PAN polymerized by using the MnO_2 -NTA redox pair. All the peaks in these spectra reflect the various interactions between catalyst, activator, oxidation and reduction products generated with the reactions between them and, polymer chains, polymeric radicals and oligomeric radicals, except the peak at about 2250 cm^{-1} , corresponding to the $-\text{C}\equiv\text{N}$ group. This is the main peak indicating the presence of PAN in the reaction products. The spectra of PANs initiated by using $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ -NTA redox system, in the aqueous acidic solutions containing 0.60 (c), 1.50 (d) and 2.50 mol l^{-1} (f) AN show the characteristic absorption bands of Ce(III) sulphate (in the $400\text{--}1500 \text{ cm}^{-1}$ region). In Fig. 2(j) and (k) the FTIR spectra of $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ are shown. In addition, the strong absorption bands relating to ionic sulphate group and the water molecule coordinated with metal ions (spectra (e) and (h) in Figs. 1 and 2, respectively) become thinner and weaker after the purification of the polymers initiated by using Ce(IV) and MnO_4^- in combination with NTA. Hence, it can be said that:

1. The main part of the products obtained with 0.60 and 1.50 mol l^{-1} AN is the oligomeric chains terminated by the hydrated and sulphated complexes of Ce(III). Both the weakness of the absorption bands, relating to the $-\text{C}\equiv\text{N}$ group, at 2250 cm^{-1} and the low molecular

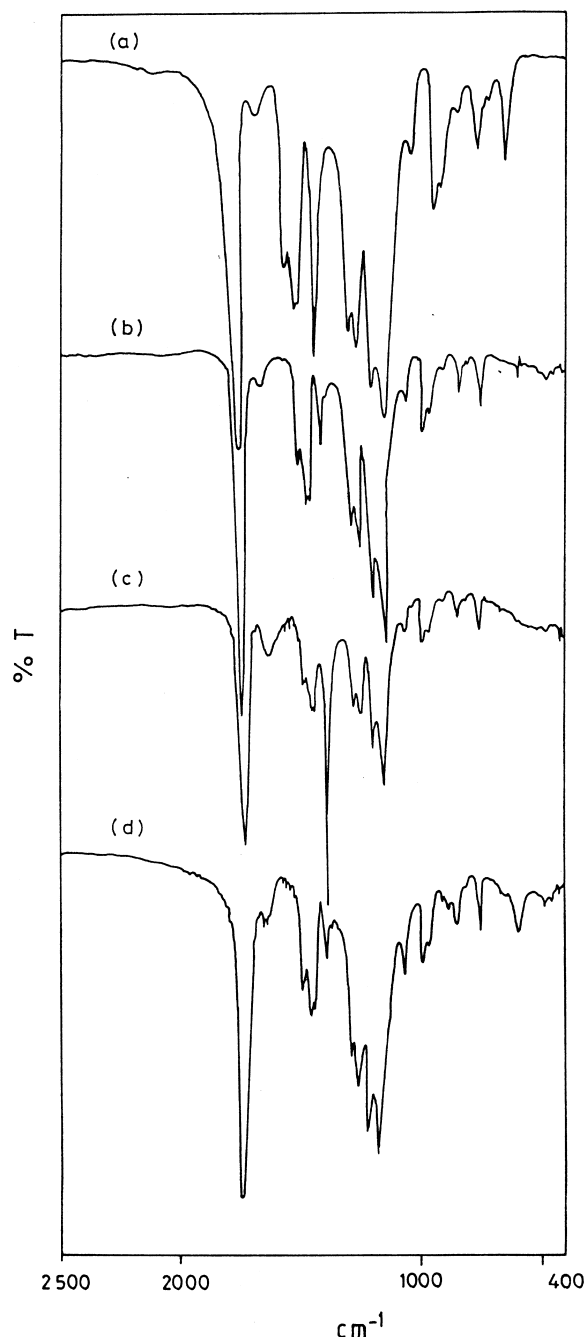


Fig. 3. FT-IR spectra of the polymers synthesized with the following conditions: (a) NTA-MMA-Ce(IV), HNO_3 , $[\text{MMA}] = 0.38 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$; (b) the same with (a) but purified; (c) insoluble part of (a), after reprecipitation; (d) NTA-MMA-Ce(IV), H_2SO_4 , $[\text{MMA}] = 0.38 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$. The other parameters of the polymerizations are given in Table 1.

weight of the polymers support the linear termination process (Set 1 in Table 1, Fig. 1(c) and (d), discussed in Section 3.1).

2. Sulphato complexes of Ce(III) and MnSO_4 produced by the reactions between NTA and, $\text{Ce}(\text{SO}_4)_2$ and MnO_2 generating free radicals form complexes with the nitrile groups of PAN.

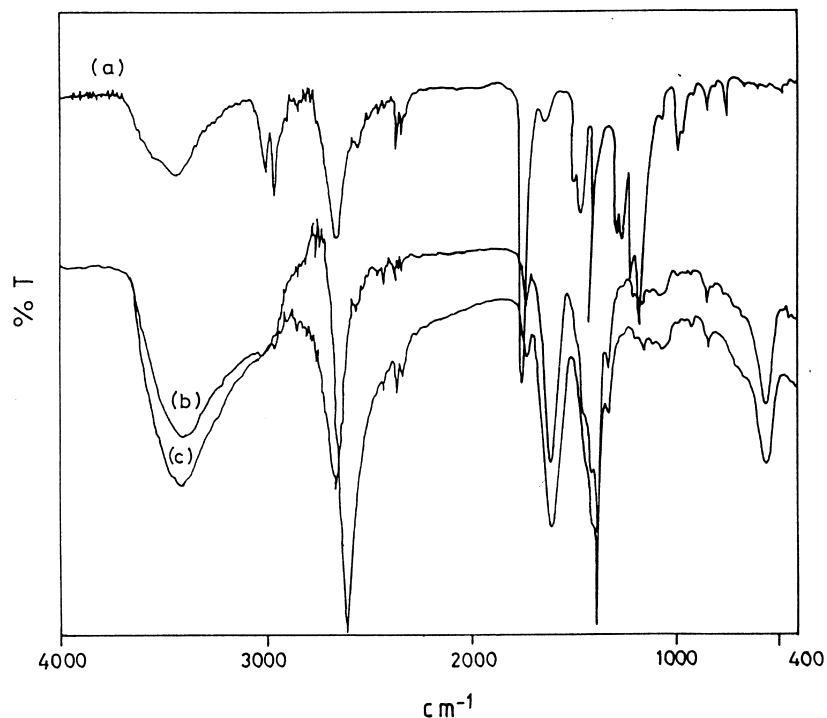


Fig. 4. FT-IR spectra of the samples synthesized with three different concentrations of cerium ammonium nitrate. Conditions: $[NTA] = 2 \times 10^{-2} \text{ mol l}^{-1}$, $[MMA] = 0.10 \text{ mol l}^{-1}$, $[HNO_3] = 0.75 \text{ mol l}^{-1}$, $T = 25^\circ\text{C}$, $[Ce(NH_4)_2(NO_3)_6]$ and percent conversion: (a) $3 \times 10^{-2} \text{ mol l}^{-1}$, 26%, (b) $6 \times 10^{-2} \text{ mol l}^{-1}$, 58%, (c) $9 \times 10^{-3} \text{ mol l}^{-1}$, 47%.

The comparison of these results with that in the literature indicates that the mechanisms of the redox polymerizations is dependent largely on experimental conditions.

There are essentially no differences between the FTIR spectra of PMMAs synthesized by using $Ce(NH_4)_2(NO_3)_6$ -NTA (Spectra (a)–(c) in Fig. 3) and $Ce(SO_4)_2 \cdot 4H_2O$ -NTA (Spectrum (d) in Fig. 3) redox pairs, except the sharp NO_3^- peak at 1385 cm^{-1} and the small absorption band at about 600 cm^{-1} indicating the presence of sulphate group. Palit et al. found that PMMAs synthesized with $EDTA-MnO_4^-$ and MnO_4^- in dilute H_2SO_4 initiator systems contained carboxyl and hydroxyl end groups generated from the oxidation of PACA and water, respectively [28,29]. In addition, end group studies of PMMAs initiated with ceric–thiourea redox pair showed that the linear terminations took place by ligand transfer, which would appear as polymer end group [30].

As to both FTIR spectra (Fig. 3) and the molecular weights of PMMAs (Table 1) obtained in this work, there are two possible termination process: (a) the termination of polymer radicals by primary radicals because PMMA chains form by the emulsion polymerization kinetics (Section 3.1), in our experimental conditions. (b) termination of polymer radicals by ligand transfer. The observations of other workers also support the conclusion that the PMMA radicals produced in aqueous solutions are not terminated by metal ions [31,32].

One of the purposes of this work was to synthesize the short PMMA chains having functional end groups. Hence,

the catalyst concentration was increased by two and three times while $[MMA]$ was decreased four times similar to the one used in the other experiments (Spectra (b) and (c) in Fig. 4). The FTIR spectra of the insoluble products obtained in this conditions revealed the characteristic absorption bands of amine salts ($-NH$ stretching in the $3000\text{--}2700 \text{ cm}^{-1}$ region), carboxylate group of the amino acids in the zwitterion form ($^+NH_3 - \overset{|}{\underset{|}{C}} - \overset{||}{\underset{||}{C}}O_2^-$; at $1610\text{--}1550 \text{ cm}^{-1}$ and near 1400 cm^{-1}), nitrate group (at 1385 cm^{-1}), hydroxyl containing complexes of Ce(III) (at about 600 cm^{-1}) and carbonyl group of MMA ($C=O$ stretching of ester group; 1730 cm^{-1}). Consequently, we can say that these high catalyst concentrations caused some complex oxidation reactions between catalyst, activator and monomer, instead of producing short PMMA chains initiated and terminated by NTA.

References

- [1] Palit SR, Konar RS. *J Polym Sci* 1962;58:85.
- [2] Samal RK, Nayak MC, Suryanarayana GV, Panda G, Das DP. *J Polym Sci, Polym Chem Ed* 1981;19:2759.
- [3] Samal RK, Nayak MC, Panda G, Suryanarayana GV, Das DP. *J Polym Sci, Polym Chem Ed* 1982;20:53.
- [4] Gupta KC, Verma M, Behari K. *Macromolecules* 1946;19:548.
- [5] Bajpai UDN, Ahi A. *J Appl Polym Sci* 1990;40:359.
- [6] Özeroğlu C, Güneş O, Saraç AS, Mustafaev MI. *J Appl Polym Sci* 1996;60:759.

- [7] Hsu W-C, Kuo J-F, Chen C-Y. *J Polym Sci, Part A: Polym Chem* 1992;30:2459.
- [8] Hsu W-C, Kuo J-F, Chen C-Y. *J Polym Sci, Part A: Polym Chem* 1993;31:267.
- [9] Hsu W-C, Kuo J-F, Chen C-Y. *J Polym Sci, Part A: Polym Chem* 1993;31:3213.
- [10] Hsu W-C, Chen C-Y, Kuo J-F, Wu EM. *Polymer* 1994;35(4):849.
- [11] Saraç AS, Erbil C, Soydan AB. *J Appl Polym Sci* 1992;44:877.
- [12] Erbil C, Cin C, Soydan AB, Saraç AS. *J Appl Polym Sci* 1993;47:1643.
- [13] Hanna SB, Hessley RK. *Inorg Nucl Chem Lett* 1971;7:83.
- [14] Hanna SB, Carroll WR, Attiga SA, Webb WH. *Z Naturforsch B* 1975;30:409.
- [15] Hanna SB, Moehlenkamp ME. *J Org Chem* 1983;48:826.
- [16] Mottola HA, Harrison CR. *Talanta* 1971;18:683.
- [17] Saraç AS, Erbil C, Durap F. *Polym Int* 1996;40:179.
- [18] Erbil C, Ustamehmetoğlu B, Uzelli G, Saraç AS. *Eur Polym J* 1994;30:149.
- [19] Onyon PF. *J Polym Sci* 1956;22:13.
- [20] Cantow HJ, Schulz GV. *Ibid* 1954;1:365.
- [21] Fitch RM, Prenosil MB, Spick KJ. *J Polym Sci* 1969;27:95.
- [22] Kreuter J. *J Polym Sci, Polym Lett Ed* 1982;20:543.
- [23] Bassett J, Denney RC, Jeffery GH, Mendham J. *Vogel's Textbook of Quantitative Inorganic Analysis*. 4. New York: Longman Inc, 1978.
- [24] Hanna SB, Hessley R, Webb WH, Carroll WR. *Z Anal Chem* 1971;255:30.
- [25] Petschurova NI, Marthynenko LI, Spitzin VI, Malinina EA. *Z Anorg Allgem Chem* 1971;380:202.
- [26] Palit SR, Konar RS. *J Polym Sci* 1962;57:609.
- [27] Narita H, Machida S. *Macromol Chem* 1966;97:209.
- [28] Ghosh P, Mukherjee AR, Palit SR. *J Polym Sci A* 1964;2:2817.
- [29] Mitra R, Mukherjee AR, Palit SR. *Indian J Chem* 1965;3:49.
- [30] Pramanick D, Chatterjee AK. *J Polym Sci, Polym Chem Edn* 1982;20:1203.
- [31] Dainton FS, Seaman PH. *J Polym Sci* 1959;39:279.
- [32] Atkinson B, Cotton GR. *Trans Faraday Soc* 1950;46:976.