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PREPARATION, CHARACTERIZATION AND THERMAL STABILITY OF POLY[2-(DIMETHYLAMINO)ETHYL ACRYLATE]

Polymer complexes of 2-(dimethylamino)ethyl acrylate with some transition metal chlorides

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Abstract

Poly[2-(dimethylamino)ethyl acrylate] (PDAEA) and polymer complexes of 2-(dimethylamino)ethyl acrylate (DAEA) with nickel(II), copper(II), iron(III) and cobalt(II) chlorides were prepared and characterized by means of IR, electronic spectra and elemental analysis. The thermal stability of the homopolymer was compared with those of the polymer complexes, and the order of stability was given. The activation energies of the polymer complexes were calculated.

Keywords: poly[2-(dimethylamino)ethyl acrylate], polymer complexes

Introduction

Polymer complexes have been the subject of a great deal of interest in the past decade [1–4]. Their structures and thermal stabilities have been of particular interest [5–7]. 2-(Dimethylamino)ethyl acrylate was recently used successfully in the preparation of some synthetic polymer gels [8]. The objective of the present work was to investigate the complexation reactions of DAEA with some transition metal chlorides and to characterize the resulting polymer complexes with different methods. The thermal stabilities of the homopolymer and of the polymer complexes were also investigated. The activation energies of degradation of the polymer complexes were calculated by using the Arrhenius equation.

Experimental

Materials

2-(Dimethylamino)ethyl acrylate (Merck grade) was degassed, twice distilled on a vacuum line, dried over calcium hydride and kept below 18°C. Other chemical reagents were of analytical grade (Merck).

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Preparation of polymer complexes

Poly[2-(dimethylamino)ethyl acrylate] (PDAEA) was prepared by homopolymerization of DAEA for 8 h at 100°C in a water bath, with 0.1% (w/v) $K_2S_2O_8$ as initiator [9]. The polymer was precipitated by addition to absolute ethanol. Polymer complexes of DAEA with copper(II), nickel(II), iron(III) and cobalt(II) chlorides were prepared by dissolving equimolecular amounts of DAEA and the metal salts in the presence of 0.1% (w/v) $K_2S_2O_8$ as initiator in deionized water. The mixture was refluxed for 8 h and the resulting polymer complexes were precipitated by addition to absolute ethanol. The polymer complexes were filtered off, washed with ethanol, and dried in a vacuum oven at 45°C for several days. The contents of cobalt(II), nickel(II) or copper(II) in the polymer complexes were determined by complexometric titration with ethylenediaminetetracetic acid (EDTA) after decomposition with concentrated nitric acid. The iron(III) content was determined spectrophotometrically [10].

Characterization of the polymer complexes

Infrared spectroscopy

IR spectra were recorded with a Perkin-Elmer 883 spectrophotometer. Polymeric samples were examined in KBr or as thin films cast on sodium chloride plates.

Visible-ultraviolet spectroscopy

Polymer samples were dissolved in dilute nitric acid, and measurements were made with a Varian 634 spectrophotometer.

Elemental analysis

Carbon and hydrogen contents were determined by the Microanalytical Unit of Cairo University.

Thermal methods of analysis

Thermogravimetry (TG)

TG measurements were made with a Dupont 950 thermobalance. 10 mg samples were heated at 10 deg·min^{-1} in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped and measured 10 mm× 5 mm×2.5 mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. The initial rates of degradation of the homopolymer and polymer complexes were investigated by means of TG at different intervals. Activation energies were obtained by application of the Arrhenius equation.

Results and discussion

Characterization of the polymer complexes

The polymer complexes obtained are intensely coloured and air-stable. The IR spectrum of PDAEA exhibits a strong absorption band at 1750 cm^{-1}, which is assigned as $\gamma_{C=O}$ of the ester group. The absorption band at 1260 cm^{-1} is assigned as γ_{C-N}, while the γ_{C-O} stretching vibration appears at 1070 cm^{-1}. The IR spectra of the polymer complexes display shifts of some bands of the characteristic modes. The γ_{C-N} stretching vibration appears at 1280 cm^{-1}, i.e. a shift of about 20 cm^{-1}, indicating involvement of the nitrogen atom in the coordination. The band due to the γ_{C-O} stretching vibration was found at 1050 cm^{-1}, i.e. a shift of about 20 cm^{-1}, suggesting participation in complex formation. Also, there is a broad absorption band at 3300 cm^{-1}, due to the water molecule [11, 12]. On the other hand, there is not significant change in the position of the carbonyl absorption band because of coordination.

The electronic spectrum of the DAEA-$CuCl_2$ polymer complex is characterized by a broad band with maxima at 12300–12800 cm^{-1}, resulting from several overlapping bands. This band could be assigned to the $^2E_{2g} \rightarrow {}^2T_{2g}$ transition, which suggests an octahedral configuration [13].

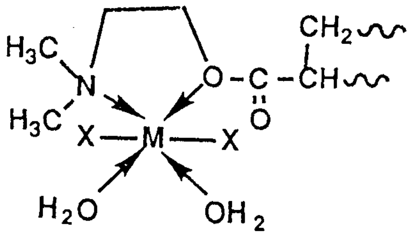
Table 1 Elemental analysis of PDAEA and the polymer complexes DAEA-$CuCl_2$, DAEA-$NiCl_2$, DAEA-$FeCl_3$ and DAEA-$CoCl_2$

Polymer complex	Calculated/Found %			
	C	H	*M*	MO*
PDAEA	58.7/59.6	9.1/9.0	–	–
DAEA-$NiCl_2$	27.2/27.5	5.5/5.3	18.9/19.0	24.2/24.5
DAEA-$CuCl_2$	26.8/27.0	5.4/5.5	20.3/20.5	25.2/25.0
DAEA-$FeCl_3$	27.5/27.3	5.6/5.4	18.3/18.5	52.2/52.4
DAEA-$CoCl_2$	27.2/27.0	5.5/5.6	19.1/19.0	25.0/25.5

* Residual mass percentage of the polymer complexes at 800°C

The electronic spectrum of the DAEA-$NiCl_2$ polymer complex shows two main absorption bands, at 11764 and 13986 cm^{-1}, which are generally observed in high-spin octahedral Ni(II) polymer complexes and are assignable to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions, respectively [14]. The electronic spectrum of the DAEA-$CoCl_2$ polymer complex exhibits the main absorption band at 19417 cm^{-1}, which is observed in high-spin octahedral Co(II) polymer complexes and can probably be assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(p)$ transition. In the case of the DAEA-FeCl$_3$ polymer complex, a broad band is observed with a maximum at 18000–18500 cm^{-1}. This band usually appears in high-spin octahedral Fe(III) polymer complexes and can be assigned to the $^6A_{1g} \rightarrow {}^4T_{2g}$ transition [15, 16].

From the IR, electronic spectra and elemental analysis data presented in Table 1, DAEA is suggested to react with NiCl$_2$, CuCl$_2$, FeCl$_3$ or CoCl$_2$ in 1:1 molar ratio, and the structure postulated for the polymer complexes can be depicted schematically as follows:



X = Cl

M = Co(II), Cu(II), Ni(II) or Fe(III)

Thermal analysis

TG curves of PDAEA and of the DAEA-metal chloride complexes are shown in Fig. 1. It is clear that the polymer complexes are thermally more stable than the PDAEA homopolymer. This is similar to the results obtained by Diab *et al.* [17–19] for some polymer complexes. However, this behaviour may be ascribed to the formation of a 5-membered chelation ring in the polymer complexes. The stabilities of the DAEA polymer complexes increase in the sequence DAEA-FeCl$_3$ > DAEA-CoCl$_2$ > DAEA-CuCl$_2$ > DAEA-NiCl$_2$ > PDAEA. PDAEA degrades in three stages. The first starts at about 60°C with a loss in mass of about 10%, the second stage at about 120°C, with a loss in mass of about 25%, and the third stage at about 240°C, with a loss in mass of 40%. The thermal degradation of the polymer complexes also proceeds in three stages. The first decomposition region begins at 70–90°C, with a loss in mass of about 12%, and it is probably due to the loss of water molecules from the coordinated structures. This corresponds with the theoretical values for loss of the coordinated water molecules, which are 11.5–11.8% depending on the metal ions; this confirms the suggested structure of the polymer complexes. The second region begins a 130–140°C and ends at 250–300°C, with a loss in mass of 20–27%. The third decomposition region follows the second region, and ends at about 500°C. Table 1 lists the mass percentages of the residues for each polymer complex at 800°C. The residual substance can be regarded as metal oxides. The results are in good agreement with those calculated from the metal contents obtained by using EDTA titration.

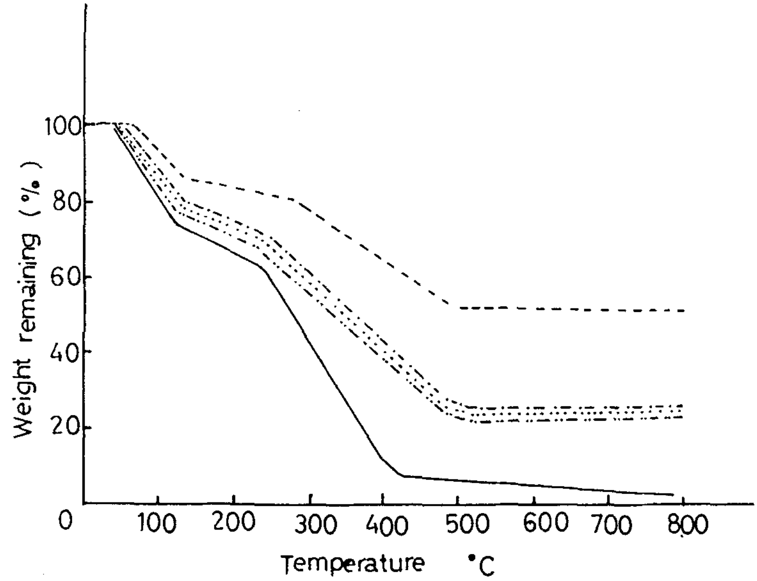


Fig. 1 TG curves of PDAEA and the polymer complexes of DAEA with $CuCl_2$, $NiCl_2$, $CoCl_2$ and $FeCl_3$. (—) PDAEA, (---) DAEA-$FeCl_3$, (-·-·-) DAEA-$CoCl_2$, (·····) DAEA-$CuCl_2$, and (-··-) DAEA-$NiCl_2$

Table 2 Activation energies of thermal degradaton of PDAEA and the polymer complexes of DAEA with $CuCl_2$,$NiCl_2$,$FeCl_3$ and $CoCl_2$

Polymer complex	E_a/kJ·mol^{-1}
PDAEA	24.9
DAEA-$CuCl_2$	36.6
DAEA-$NiCl_2$	32.7
DAEA-$FeCl_3$	53.2
DAEA-$CoCl_2$	44.3

The degradation rate constants of the homopolymer and the polymer complexes were determined from the TG curves in the initial stages of the decomposition, which were calculated from the correlations of the percentage loss in mass as a function of time at different temperatures. The higher decomposition

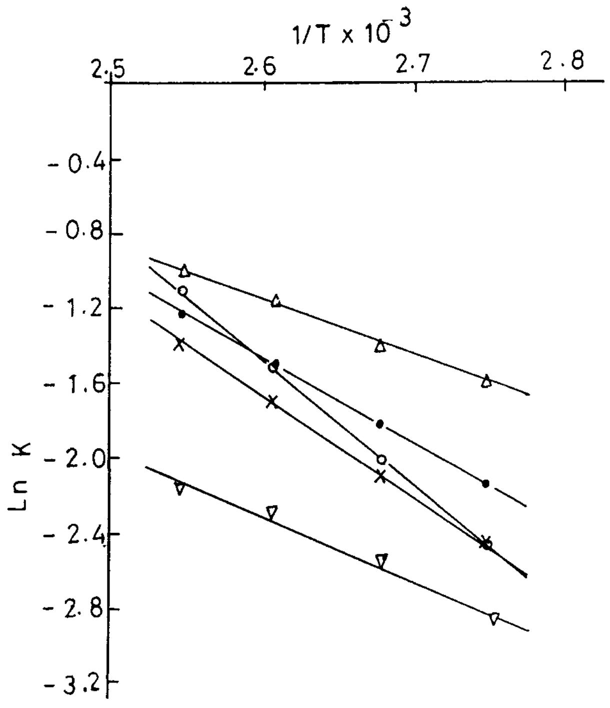


Fig. 2 Arrhenius plots of the thermal degradation rate constants for PDAEA and the polymer complexes of DAEA with $NiCl_2$, $CuCl_2$ $CoCl_2$ and $FeCl_3$. (Δ) PDAEA, (o) DAEA-$CuCl_2$, (•) DAEA-$FeCl_3$, (x) DAEA-$CoCl_2$ and (∇) DAEA-$NiCl_2$

rates for the Ni(II), Cu(II) and Co(II) polymer complexes are probably caused by oxidation of the polymer because of the catalytic action of these ions (Fig. 1) [20]. Table 2 indicates the effective activation energies of thermal degradation of PDAEA and the polymer complexes. The energies were determined from the temperature dependence of the rate of degradation, as shown in Fig. 2. The activation energies are in the same sequence as the stabilities of the homopolymer and the polymer complexes.

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Zusammenfassung — Es wurden Poly(2-dimethyl-aminoethylacrylat) Homopolymer, PDAEA und Polymerkomplexe von 2-Dimethylaminoethylacrylat (DAEA) mit Nickel(II)-, Kupfer(II)-, Eisen(III)- und Kobalt(II)-chloriden hergestellt und mittels IR, Elektronenspektren und Elementaranalyse untersucht. Die thermische Stabilität des Homopolymers wurde mit der der Polymerkomplexe verglichen und eine Stabilitätsreihenfolge erstellt. Weiterhin wurden die Aktivierungsenergien für die Polymerkomplexe berechnet.