Polymer Bulletin 1, 509-515 (1979)

Polymer Bulletin

Inorganic Polymers

I. Synthesis and Properties of Some Polyaminopyridinium Molybdates

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SUMMARY

For the first time, the polymolybdates of organic bases have been synthesized $(BH)_4Mo_8O_{26}$ (B = 2-aminopyridine, 3-aminopyridine and 4-aminopyridine). These compounds have been characterized using X-ray and infrared spectroscopy. The energies of thermal decomposition have been determined by differential calorimetry.

On the other hand, the molecular weights of these new compounds in DMSO solution have been measured by vapour pressure osmometry and viscometry, obtaining results in agreement with the structures, as well as with the activation energies corresponding to the thermal decomposition, calculated from the TGA curves.

INTRODUCTION

Most commercial polymers are long-chain molecules with carbon atoms in their backbone. New families of polymers with backbones of atoms other than carbon are yielding materials with unusual characteristics.

In this paper we report the synthesis, characterization and some properties of several polymolybdates of organic bases (n-aminopyridine) studied by thermogravimetry, differential scanning calorimetry, vapour pressure osmometry and viscometry.

EXPERIMENTAL

Synthesis. The synthesis of the different polymolybdates of n-aminopyridinium was made by making the molybdenum oxide, MoO_3, to react with the organic base (n-aminopyridine), in distilled water, so that their molar relation was always unity. In this way an excess of organic base is obtained, which prevents non-reaction of part of the molybdenum oxide which would make impure the obtained products. We make the mixture react in a flow back and with a strong agitation during five hours (ROMAN 1976).

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0170-0839/79/0001/0509/$01.40

The obtained products were washed successively with ethyl alcohol, diethyl ether and distilled water and dried under an air current during three hours.

All the reagents used in the synthesis of the different polymolybdates were from Merck (p.a.).

The different polymolybdates appear in a polycrystalline, pale yellow coloured form, insoluble in water, benzene, chloroform and other common organic solvents, but somewhat soluble in DMSO at 400 K.

In order to simplify the nomenclature, the polymolybdates of 2, 3 and 4-aminopyridinium are named as K, L and M, respectively.

Analysis. The analysis of molybdenum content of the different polymolybdates has been made by gravimetry and thermogravimetric analysis. The C, H and N contents were analyzed by microanalysis. The obtained results are shown in table 1.

TABLE 1
Analytical date for polymolybdates of n-aminopyridinium

	% MoO_3		% C		% H		% N	
	calc.	found[a]	calc.	found	calc.	found	calc.	found
K	73.62	73.82	15.36	15.20	1.79	1.89	7.16	6.98
L	73.62	73.67	15.36	15.40	1.79	1.90	7.16	7.28
M	73.62	73.81	15.36	15.29	1.79	1.85	7.16	7.24

a) thermogravimetric method

Thermogravimetric and calorimetric measurements
A Perkin-Elmer TGS-1 thermobalance with a UU1 temperature programmer from the same firm was used. All experiments were carried out at a rate of heating of 5°per minute and in dry nitrogen atmosphere (TELLO et al. 1975).

Calorimetric measurements were made by differential calorimetry using a Perkin-Elmer DSC-18 calorimeter, with samples ranging from 8 to 15 mg., and with a rate of heating of 8° per minute. The heats of decomposition were obtained from the calorimetric curves by measurements of the areas with planimeter.

Diffractogrammes. A Phillips PW-1100 automatic X-ray diffractometer was used. The radiation was from Cu K_α filtered with nickel ($\lambda = 0.15418$ nm). The sweeping rate was 1° per minute. The different polymolybdates of n-aminopyridinium, as well as the products of the thermal decomposition were characterized by their X-ray diffractogrammes, as it can be seen in table 2.

Infrared spectra. The infrared spectra were obtained with a Perkin-Elmer 621 in KBr using product concentrations about 3 per cent in weight. The characteristic frequencies of vibration in which the different polymolybdates absorbed are given in table 3 with their corresponding assignements. Previously, the IR spectra of the different organic bases and their chlorohydrates

TABLE 2
Diffractogrammes of polymolybdates of n-aminopyridinium.

K		L		M	
d(Å)	I/I_o	d(Å)	I/I_o	d(Å)	I/I_o
10.82	100	10.96	77	10.60	100
9.62	35	9.60	100	9.98	30
7.72	25	5.46	11	5.87	14
6.63	6	5.30	26	5.00	9
6.14	7	4.28	8	4.17	3
4.78	13	3.81	40	3.97	4
4.48	9	3.64	64	3.70	4
4.13	6	3.49	27	3.59	5
3.92	10	3.21	30	3.53	4
3.67	15	3.02	58	3.35	4
3.29	23	2.76	22	3.32	6
2.99	13	2.40	12	3.03	5

TABLE 3
Characteristic frequencies of vibration (in cm^{-1}) for different polymolybdates of n-aminopyridinium.

Assignem.	K	L	M
Mo-O vibration	948(F) 610(m) 938(F) 563(a,F) 900(F) 465(m) 868(F) 340(f) 700(a,f) 305(f)	940(F) 690(a,f) 930(F) 670(f) 898(F) 430(f) 877(F) 360(f) 840(a,F) 305(f) 775(f)	940(F) 368(f) 900(F) 505(m) 870(F) 462(f) 798(F) 340(f) 720(a,f) 308(m) 690(a,F)
C-H deform.	1234(f) 758(F) 1160(f) 640(md) 990(m)	1268(f) 1030(md) 1175(md) 818(F) 1125(md) 560(F)	1190(F) 580(a,F) 922(f) 540(f) 834(f)
C=C N=N stretch. and N-H deformat.	1640(f) 1610(f) 1525(m) 1469(f)	1625(f) 1385(m) 1598(f) 1338(f) 1550(F) 1475(f)	1640(F) 1390(f) 1578(f) 1560(f) 1534(F)
$N-H^+$ stretch.	3190(a,f)	3210(m) 3170(m) 3110(d)	3180(a,F) 2960(f) 2655(m)

F: very strong; f: strong; m: medium; d: weak and a: broad were determined.

Vapour pressure osmometry and viscometry. Molecular weights of the different polymolybdates of n-aminopyridinium were determined in a Knauer model 1974 vapour pressure osmometer. A universal probe which had previously been calibrated with dibenzyle and naphtalene in DMSO at 403 K (KATIME and AGUILAR 1978).

Intrinsic viscosities were measured in an Ubbelohde modified viscometer in DMSO at 403 K. The value of $[\eta]$ was obtained by ploting η_{sp}/c and $\ln \eta_r/c$ against concentration.

DISCUSSION

These compounds were formulated, in previous papers (TELLO et al. 1977, ROMAN 1976, TELLO et al.1975) as tetramolybdates $(BH)_2Mo_4O_{13}$, since all the investigations were carried out on polycristalline samples being represented by the most simple formula. Recent studies, using X-ray technique on a monocrystal of a compound similar to the polymolybdate of n-aminopyridinium, the polymolybdate of 3-ethylpyridinium allowed us the determination of the real structure, corresponding to the octomolybdate one (ROMAN).

As it is shown in table 3, there are no strong bands between 800 and 830 cm^{-1} and, on the other hand, intense bands appear in the 850-960 cm^{-1} regions. This seems to indicate the existence of octahedrons MoO_6 (GATEHOUSE and LEVERETT 1971, GATEHOUSE and LEVERETT 1970) instead of tetrahedrons MoO_4, in the coordination of the molybdenum. As it can be seen in figure 1, these structures may consist in groups of eight octahedrons, probably joined all together by a common edge. Each conjunct of these eight octahedrons is joined by the cation of organic base, which in this case is the n-aminopyridine (n = 2, 3 and 4). The proton of the nitrogen in the heterocycle keeps joined the eight octahedrons, because of electrostatic interactions. So, the molecular weight of the different polymolybdates must be in terms of the proton acidity. In the references, the va

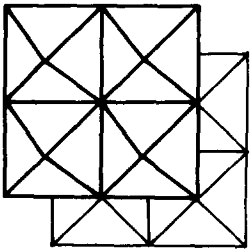

Figure 1.- A view normal of an infinite chain of MoO_6 octahedra where two of the basic units of eight edge-shared octahedra are shown

lues of pK_a are given for these organic bases (PERRIN 1965), and they are found in the following order: 3-aminopyridine > 2-aminopyridine > 4-aminopyridine. This means that the 3-aminopyridine proton is more easily ionizable, so that it will be farther from the organic base and it will stabilize less the structure of the compound. According to this, it is probably that the molecular weight, which can be a measure of the stability, will follow the same order, as it actually happens.

In figure 2, the curves of thermal decomposition for these three polymolybdates are shown. In each of them, three steps of decomposition are observed. A hypothetical pathway of decomposition is proposed for each of this compounds:

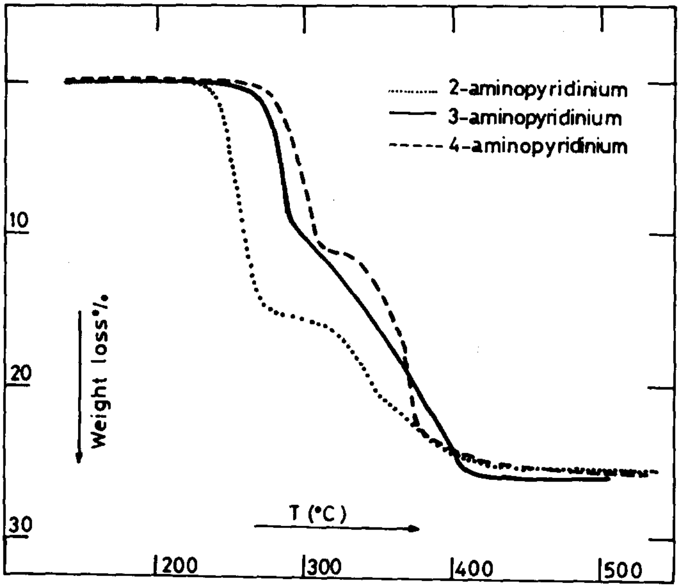

Figure 2. Plots of thermal decomposition (TGA) of the three organic polymolybdates.

Poly(2-aminopyridinium molybdate):

$$(BH)_4Mo_8O_{26} \xrightarrow{495-550\ K} 8MoO_3.2B + 2B + 2\ H_2O$$

$$8\ MoO_3.2B \xrightarrow{577-623\ K} 8\ MoO_3.B + B$$

$$8\ MoO_3.B \xrightarrow{623-704\ K} 8\ MoO_3 + B$$

Poly(3-aminopyridinium molybdate):

$$(BH)_4.Mo_8O_{26} \xrightarrow{504-562\ K} 8MoO_3.3B + B + 2\ H_2O$$

$$8\ MoO_3.3B \xrightarrow{562-628\ K} 8\ MoO_3.\frac{8}{5}B + \frac{7}{5}B$$

$$8\ MoO_3.\frac{8}{5}B \xrightarrow{628-691\ K} 8\ MoO_3 + \frac{8}{5}B$$

Poly(4-aminopyridinium molybdate):

$$(BH)_4Mo_8O_{26} \xrightarrow{531-591\ K} 8\ MoO_3.\frac{5}{2}B + \frac{3}{2}B + 2H_2O$$

$$8\ MoO_3.\frac{5}{2}B \xrightarrow{591-658\ K} 8\ MoO_3.\frac{1}{2}B + 2B$$

$$8\ MoO_3.\frac{1}{2}B \xrightarrow{658-691\ K} 8\ MoO_3 + \frac{1}{2}B$$

Of these three steps, the corresponding decomposition heats of the first one where obtained by DSC measurements. The obtained results are shown in table 4.

TABLE 4

Number average molecular weights, $\overline{M}_n$, intrinsic viscosity, enthalpy, temperature interval of decomposition of first step and activation energy for the polymolybdates de n-aminopyridinium.

Compound	$\overline{M}_n$x10^{-3}	$[\eta]$ (ml·g^{-1})	enthal. (kJ/mol)	ΔT/K first st.	E_a (kJ/mol)
K	13.0±0.3	7.1	75.5	498-596	16.16
L	5.5±0.2	3.5	79.5	528-615	10.81
M	15.6±0.4	8.3	85.0	535-632	15.98

If the activation energies, E_a, are calculated from the decomposition curves using the Satava's method (SATAVA 1971), we find that the poly(3-aminopyridinium molybdate) is the more inestable of them. If we represent pK_a against activation energy, figure 3, we find a relationship between these two parameters and, it seems to confirm the fact that the acidity of the nitrogen proton plays an important role in the stability of these compounds. In the same figure we have represented the dependence of molecular weight on pK_a and we have observed that it follows a similar habit to the previous one.

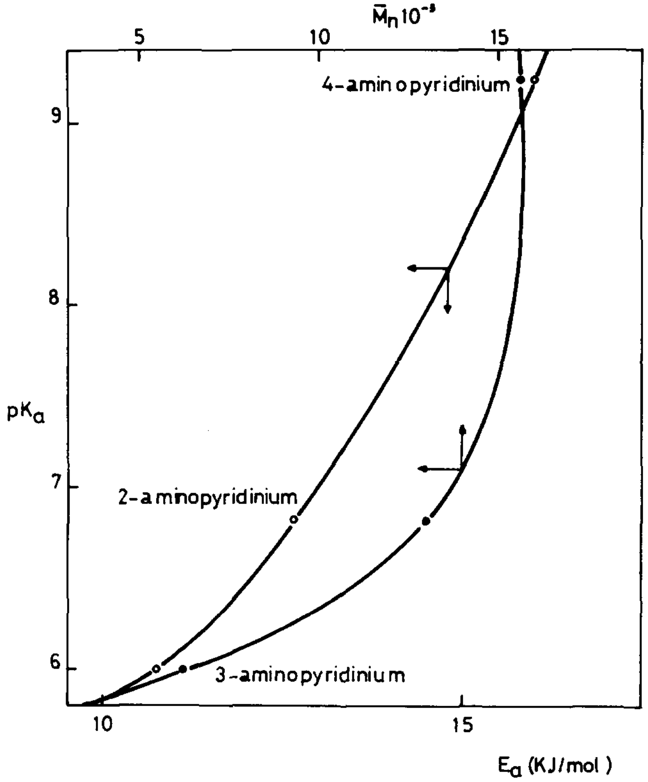

Figure 3. pK$_a$ and number average molecular weights against activation energy.

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Received April 9, 1979