Thermochimica Acta, 170 (1990) 155–166
Elsevier Science Publishers B.V., Amsterdam

THERMAL DECOMPOSITION OF A BENTONITE–POLYACRYLAMIDE COMPLEX

ILONA TÓTH, JÁNOS SZÉPVÖLGYI *, EMMA JAKAB, PIROSKA SZABÓ
and TAMÁS SZÉKELY

Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi ut 45 (Hungary)

(Received 7 March 1990)

ABSTRACT

The thermal decomposition of complexes produced from bentonite and a linear polyacrylamide (PAM) was investigated by using thermogravimetry–mass spectrometry (TG–MS). Data obtained for the polymer degradation supported the model proposed by Leung et al. Thermal behaviour of bentonite–PAM complexes was mainly determined by PAM degradation below 580 °C. Above this temperature decomposition of bentonite proved to be the decisive process. Measurements revealed the formation of strong bonding between the constituents of the complexes.

INTRODUCTION

Many layer silicates are able to adsorb polymers and form intercalation compounds [1]. For example, a linear polyacrylamide (PAM), when applied in a dilute aqueous solution, is adsorbed via its numerous functional groups onto clay. The adsorption is practically irreversible because simultaneous detachment of all polymer segments from the silicate surface is unlikely.

Schamp and Huylebroeck [2] investigated the adsorption of PAM on different clay minerals, such as kaolinite, montmorillonite and illite containing Na^+, Ca^{2+} and H^+ as exchangeable cations. The Na-montmorillonite which had been peptized, whereby its surface accessibility was enhanced, attracted much more polymer than the other minerals.

The clay–polymer complexes are usually characterized by their adsorption isotherms and kinetics. In addition, thermoanalytical methods may also generate valuable information on clay minerals [3] and polymers [4] as well as on their interactions.

---

* Author to whom correspondence should be addressed.

During the thermal degradation of montmorillonite, the anhydride was produced between 150 ° C and 250 ° C. Further dehydration occurred in the range 450–700 ° C. From 1000 ° C to 1150 ° C there was a spinel-type phase, while above 1150 ° C mullite was formed [3].

Tutas et al. [4] investigated the thermal decomposition of PAM by dynamic thermogravimetric (TG) and differential thermogravimetric (DTG) techniques. Three DTG peaks were detected at 110 ° C, 330 ° C and 400 ° C with mass losses of 10%, 17% and 56%, respectively.

A state-of-the-art study on PAM degradation has been published by Leung et al. [5]. On the basis of differential scanning calorimetric (DSC), TGA, GC–MS, FTIR and solid state NMR studies they proposed the following decomposition mechanism. In the temperature range 220–335 ° C imidization takes place, accompanied by release of NH_3; reactions of secondary importance are the formation of nitrile (release of H_2O) and of imine (release of H_2O and NH_3). Shortly after formation, imide groups are transformed to nitrile and isocyanide groups (release of CO_2). Above 335 ° C degradation of imide groups to nitrile is completed, along with the decomposition of amide groups and the breakdown of the polymer backbone into long chain hydrocarbons.

The present work is aimed at studying the thermal decomposition of bentonite–PAM complexes, as compared to the behaviour of PAM and bentonite separately. Thermogravimetry–mass spectrometry (TG–MS) was applied as the experimental technique.

EXPERIMENTAL

Materials

The bentonite was a product of Erbslöh Co. (F.R.G.). After having been activated by wet milling in the presence of 5% Na_2CO_3 the sample had the following chemical composition (dry basis) as determined by AAS analysis: SiO_2 56.0, Al_2O_3 20.6, Fe_2O_3 4.7, MgO 3.4, CaO 2.0, Na_2O 3.0 and K_2O 1.4%. Montmorillonite (75%), illite (15%) and quartz (5%) were present as the main crystallographic phases. The methylene blue capacity of the sample was equal to 125 mequiv per 100 g.

The PAM sample was prepared by the radical polymerization of technical grade acrylamide (American Cyanamid Co.) in an aqueous solution in a nitrogen atmosphere with azobisisobutyronitrile as catalyst. Molecular mass was calculated from the viscosity measurements of aqueous solutions (at 25 ° C) by the formula: $[\eta] = KM^a$, with $K = 6.31 \times 10^{-3}$ and $a = 0.8$ for $[\eta]$ in $cm^3\ g^{-1}$ (where η is the intrinsic viscosity and M is the molecular mass). The average molecular mass of the polymer was found to be 8×10^6.

In order to study the influence of sodium ions present in the bentonite–PAM complexes on the thermal behaviour of PAM, a PAM–Na_2CO_3 mixture containing 28% of Na_2CO_3 was prepared. This polymer-to-Na_2CO_3 ratio is equal to one of the actual ratios in the bentonite–PAM complexes studied in this work.

The complexes were produced by mixing aqueous bentonite suspensions with polymer solutions in appropriate proportions. The most remarkable property of the complexes formed is their rheopexy. The flow resistance of the aqueous gel subjected to a steady-state shear becomes higher with increasing time up to the degradation of the polymer.

After drying at room temperature, xerogels were formed containing 4.8%, 7.5%, 8.3% and 11.1% of PAM, respectively. The xerogels can take up 30–50 times their mass of water.

Measurement and data processing

The TG–MS system consists of a Perkin–Elmer thermobalance (TGS-2), a Balzers quadrupole mass spectrometer (QMG-511) and a DEC PDP-11 minicomputer. A detailed description of the hardware and data processing has already been published [6].

A standard heating rate of $20\,^\circ C\ min^{-1}$ was applied. The sample size varied from 5 to 6 mg. A high purity argon atmosphere with a gas flow rate of $140\ cm^3$ (STP) min^{-1} was maintained. DTG curves were generated numerically from the TG data. MS intensity curves were recorded from $m/z = 2$ to 144 in intervals of $5\,^\circ C$ with an electron impact ionization energy of 70 eV.

Factors limiting possibilities of interpretation are as follows.

(i) Compounds with boiling points above $180\,^\circ C$ cannot be detected with the mass spectrometer.

(ii) Identification of the individual ions is difficult owing to the formation of similar mass units from more than one compound; comparison of the intensity profiles and the intensity ratios of several fragments, however, made it possible to specify the most probable decomposition products. The intensity of mass number 17 is automatically reduced by the m/z intensity originating from H_2O, so $m/z = 17$ really belongs to the NH_3 molecule. Similar subtraction takes place in the case of CO ($m/z = 28$), where the corresponding $m/z = 28$ intensity due to CO_2 must be taken into account.

(iii) Actual amounts of components contributing to the mass losses are not known exactly, so the mass spectrometric intensities are given in arbitrary units. Nevertheless, the different intensity signals generated by the same fragment within a given series of measurements can be compared quantitatively.

RESULTS AND DISCUSSION

Bentonite

The TG curve of bentonite resembles the usual TG run for montmorillonites [3]. Decomposition took place in two ranges with mass losses of 1% and 9%, respectively (Table 1).

The adsorbed water left the interlayer space at 110 ° C. No further water removal was observed up to 200 ° C, which also proved the dominance of Na montmorillonite in the sample. However, a smaller water peak at about 200 ° C indicated the presence of some di- and trivalent cations in the interlayer space as well.

From 300–800 ° C water was released in two steps, in accordance with our previous TG–MS measurements on Na and H montmorillonites. The first peak was detected at 530 ° C, and the second peak at 620 ° C. Two CO_2 peaks could be distinguished. A small peak observed at 300 ° C may be assigned to degradation of the Al complexes present in the sample. Another intense CO_2 peak at 700 ° C resulted from carbonate decomposition.

Polyacrylamide

Three thermal degradation ranges were detected for PAM (Fig. 1). The total mass loss amounted to 85%.

The MS measurements were interpreted partly on the basis of simple fragments of well defined origin ($m/z = 17$, 18, 44), partly in terms of fragments characteristic of certain decomposition products ($m/z = 27$, 28, 43, 53 and 54). Assignments of the of MS peaks is summarized in Table 2.

The MS intensity curves (Figs. 2 and 3) support the degradation mechanism proposed by Leung et al. [5]. A broad water peak was detected at 20–220 ° C. The quantity of water bound by adsorptive forces depends on the conditions of drying. Vacuum dried samples may contain as much as 15% of water in hydrogen bonds [7]. After heating the sample to 200 ° C the

TABLE 1

Thermal decomposition of bentonite sample

TG data			MS data		
Region	Temperature range (° C)	Mass loss (%)	m/z	Assignment	Temperature (° C)
I	20–220	1	18	H_2O	110, (220)
II	300–800	9	18 44	H_2O CO_2	530, 620 (300), 700

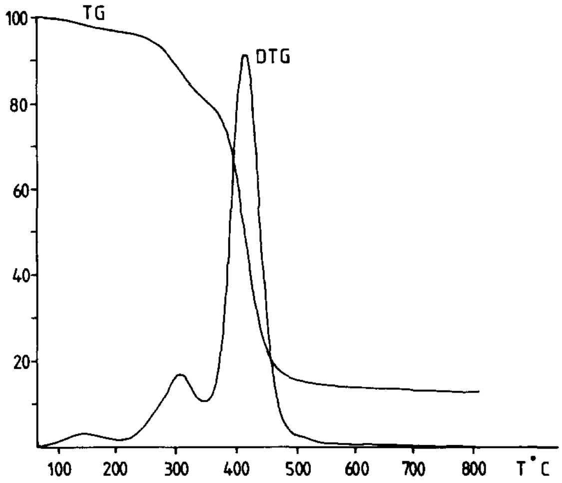

Fig. 1. TG and DTG curves for polyacrylamide; TG full scale 100%; DTG full scale 0.0166% s^{-1}.

polymeric residue did not contain nitrile groups, i.e. water released below 200 ° C was bound by secondary forces [8].

The mass loss of 19% in the second region originates from the transformation of amide groups to imides and imines and, to a small extent, to nitriles (release of H_2O and NH_3; Fig. 2). Simultaneous release of CO and NH_3 at ca. 310 ° C relates to the formation of aliphatic compounds, in accordance with Leung's model [5]. From 340–500 ° C the PAM sample decomposed in

TABLE 2

Thermal decomposition of PAM sample

TG data			MS data		
Region	Temperature range (° C)	Mass loss (%)	*m/z*	Assignment	Temperature (° C)
I	20–220	3	18	H_2O	150
II	220–340	19	17	NH_3	310
			18	H_2O	320
			28	CO	280
III	340–500	63	17	NH_3	410
			18	H_2O	400
			27	HCN	430, 480
			28	CO	410
			43	C_2H_5N	420
			44	CO_2	400
			53	C_3H_3N	440
			54	C_4H_6	420

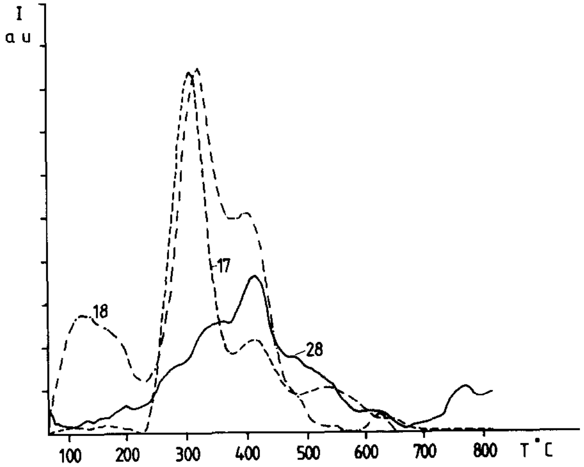

Fig. 2. MS intensity curves (1) for PAM (for assignments see Table 2).

a complex way (Figs. 2 and 3). At lower temperatures nitriles were formed from the amide and imide groups. Above 400 ° C the final breakdown of the polymer backbone, accompanied by charring processes (release of CO, CO_2, NH_3, HCN, C_2H_5N, C_3H_3N, C_4H_6,...) was taking place.

Polyacrylamide–Na_2CO_3 mixture

Na_2CO_3 affected the decomposition of PAM considerably. All characteristic products, excluding HCN, were released from the PAM–Na_2CO_3 mixture at temperatures ca. 20–70 ° C lower than for release from the polymer itself (Table 3). The lower water desorption temperature may be

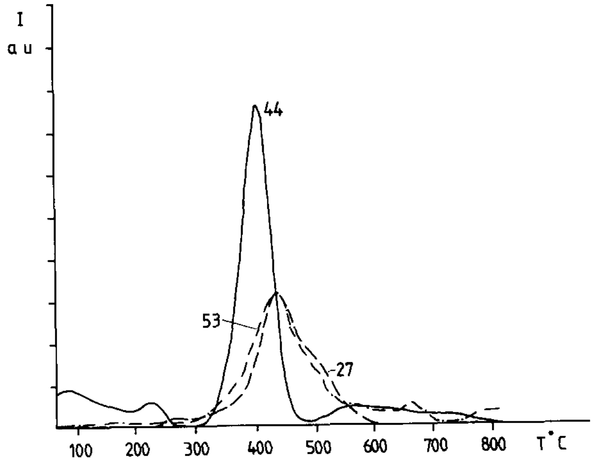

Fig. 3. MS intensity curves (2) for PAM (for assignments see Table 2).

TABLE 3

Thermal decomposition of PAM–Na_2CO_3 mixture

TG data			MS data		
Region	Temperature range (°C)	Mass loss (%)	m/z	Assignment	Temperature (°C)
I	20–200	4	18	H_2O	130
II	200–290	11	17	NH_3	250
			18	H_2O	260
			44	CO_2	230
III	290–550	38	17	NH_3	(330)
			18	H_2O	330, 520
			27	HCN	420, (480)
			44	CO_2	330, (400)
IV	550–850	33	18	H_2O	580
			28	CO	790
			44	CO_2	670

explained by a decrease in the number of intermolecular hydrogen bonds between the polymer chains in the presence of sodium ions. At the same time, Na^+ ions catalyse splitting off reactions of the side groups from the polymer chain. However, the breakdown of the polymer backbone is not influenced by Na^+ ions, as can be seen from the similar temperatures of HCN formation in the presence and absence of Na^+ ions (Tables 2 and 3).

Further decomposition, leading to the release of CO, was detected at 790 °C. Some CO_2 is soon formed from the Na_2CO_3 at this temperature [9], and is transformed into CO in the presence of carbon due to the catalytic effect of the platinum sample holder.

Bentonite–polyacrylamide complex

TG–MS curves of a dried bentonite–PAM complex of 7.5% polymer content are shown in Figs. 4–6. A total mass loss of 19% was measured and four degradation ranges were distinguished (Table 4). Below 580 °C decomposition of PAM was the dominant reaction; however, the bentonite also contributed to the changes by releasing water at 180 and 500 °C. Above 500 °C dehydroxylation of bentonite and formation of CO_2 from carbonates were occurring, just as in the case of bentonite alone.

Below 500 °C all gaseous products were relased from the complex at temperatures 20–90 °C higher compared with those for PAM. Because the decomposition reactions are kinetically controlled below 500 °C and under the given experimental conditions resistance against heat and mass transfer is negligible, the foregoing phenomena relate to the formation of strong bonding between the polymer and the bentonite.

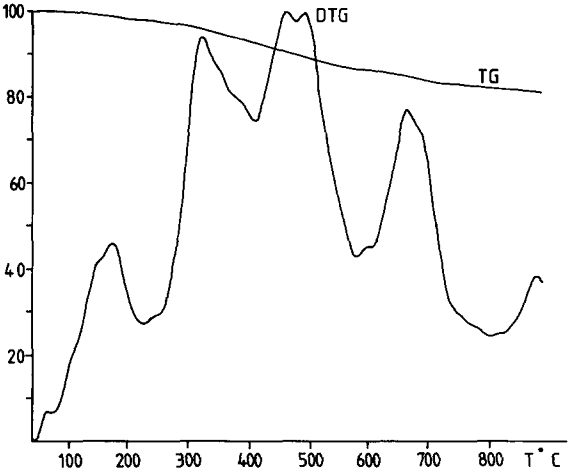

Fig. 4. TG and DTG curves for the bentonite–PAM complex of 7.5% PAM content: TG full scale 100%; DTG full scale 0.0145% s^{-1}.

While the effect of Na^+ ions in the PAM–Na_2CO_3 mixture was to give lower decomposition temperature, in the case of bentonite–PAM complexes this influence was not observed. Comparison of temperatures at which the same fragments were released from the PAM–Na_2CO_3 mixture and from the complex of 7.5% PAM content revealed that Na^+ ions are predominantly connected to the bentonite in the complex.

HCN, a typical product from the breakdown of the polymer backbone, was detected as a peak with a shoulder in the case of PAM (Fig. 3). In

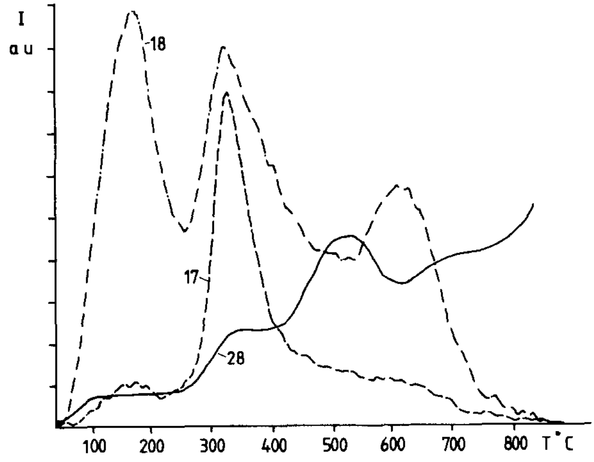

Fig. 5. MS intensity curves (I) for the bentonite–PAM complex of 7.5% PAM content (for assignments see Table 4).

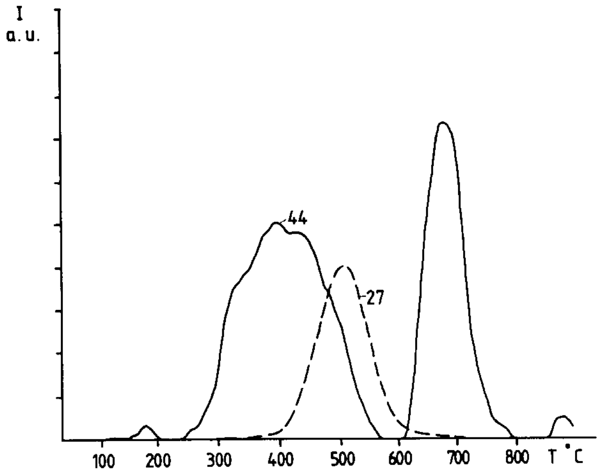

Fig. 6. MS intensity curves (2) for the bentonite–PAM complex of 7.5% PAM content (for assignments see Table 4).

contrast, the bentonite–PAM complex produced a uniform and symmetrical HCN peak (Fig. 6).

The TG–MS data of three bentonite–PAM complexes are summarized in Table 5. Some differences were observed in the decomposition temperatures of similar fragments measured against the PAM content, without, however, any marked trends. The mass losses measured in the range 20–850 °C were smaller than the calculated values that were determined by considering the TG data of the constituents and the composition of the complexes (Table 6).

TABLE 4

Thermal decomposition of bentonite–PAM complex of 7.5% PAM content

TG data			MS data		
Region	Temperature range (°C)	Mass loss (%)	*m/z*	Assignment	Temperature (°C)
I	20–220	2	18	H_2O	170
II	220–400	5	17	NH_3	330
			18	H_2O	330
			28	CO	330
			44	CO_2	330, 390
III	400–580	6	18	H_2O	(500)
			27	HCN	500
			28	CO	500
			44	CO_2	440
IV	580–850	4	18	H_2O	610
			44	CO_2	690

TABLE 5

Thermal decomposition of different bentonite–PAM complexes

Sample PAM (%)	TG data			MS data		
	Range	Temperature range (°C)	Mass loss (%)	m/z	Assignment	Temperature (°C)
4.8	I	20–220	2.0	18	H_2O	140
8.3			2.1	18	H_2O	150
11.1			2.2	18	H_2O	170
4.8	II	220–400	2.3	17	NH_3	330
				18	H_2O	330
				28	CO	300
				44	CO_2	300
8.3			3.5	17	NH_3	340
				18	H_2O	340
				28	CO	320
				44	CO_2	350
11.1			4.6	17	NH_3	340
				18	H_2O	330
				28	CO	330
				44	CO_2	350
4.8	III	400–580	3.7	18	H_2O	460
				27	HCN	490
				28	CO	490
				44	CO_2	450
8.3			4.0	18	H_2O	460
				27	HCN	480
				28	CO	480
				44	CO_2	440
11.1			5.5	18	H_2O	(460)
				27	HCN	540
				28	CO	480
				44	CO_2	440
4.8	IV	580–850	4.8	18	H_2O	600
				44	CO_2	650
8.3			4.8	18	H_2O	600
				44	CO_2	660
11.1			4.6	18	H_2O	600
				44	CO_2	670

TABLE 6

Measured and calculated mass losses for the complexes in the range 20–850 °C

PAM content (%)	Mass loss (%)		Measured/ calculated ratio
	Calculated	Measured	
4.8	13.6	12.8	0.94
8.3	16.2	14.4	0.88
11.1	18.3	16.9	0.93

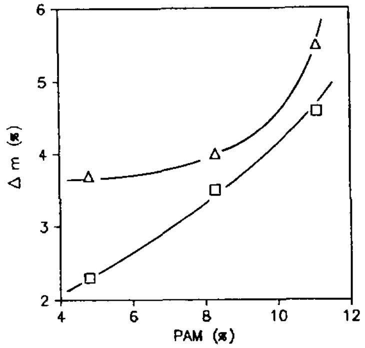

Fig. 7. Mass losses of bentonite–PAM complexes as a function of PAM content: □, 220–400 ° C; △, 400–580 ° C.

These figures also demonstrate the existence of strong bonding in the complexes.

Below 220 and above 580 ° C, mass losses were virtually independent of the PAM content. In between, mass losses increased with rising PAM concentration. From 220 ° C to 400 ° C the mass loss was directly proportional to the PAM content throughout the whole concentration range, while from 400–580 ° C a parabolic type curve could be fitted to the measured data (Fig. 7).

The MS intensities as plotted against the PAM content exhibited similar tendencies (Fig. 8). In both temperature ranges the change of intensities was ‘accelerated’ by raising the polymer content. At least two sets of differently bound PAM molecules could exist in the complex. PAM partly formed intercalation compounds and partly was adsorbed on the surface of the particles. The ratio of the latter group, which degraded more easily due to thermal effects, to the intercalated PAM molecules rose with increasing PAM content.

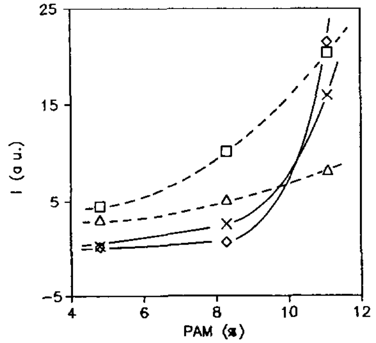

Fig. 8. MS intensity curves for the bentonite–PAM complexes as a function of PAM content: □, 300–330 ° C, $m/z = 28$; △, 300–350 ° C, $m/z = 44$; ◇, 480–540 ° C, $m/z = 27$; ×, 480–490 ° C, $m/z = 28$.

CONCLUSIONS

The bentonite sample revealed the usual TG behaviour of sodium montmortillonites. However, on the basis of water relase, the presence of di- and/or trivalent cations is also probable.

Results on PAM decomposition supported the degradation mechanism proposed by Leung et al. Below 340 ° C amide groups were mainly transformed to imides and imines, while at higher temperatures complex decomposition of the polymer was observed.

In the PAM–Na_2CO_3 mixture, all characteristic decomposition products of PAM were released at temperatures 20–70 ° C lower than those without Na_2CO_3. This can be attributed to the catalytic effect of Na^+ ions.

For the bentonite–PAM complexes, degradation of PAM was the dominant reaction below 580 ° C, but some water was released from the bentonite as well. All typical volatile products were detected at temperatures 20–90 ° C higher than those for the pure polymer. This phenomenon, along with the observed dependence of MS intensities on the PAM content, is evidence for the formation of strong bonds between the polymer and bentonite.

The proportion of PAM not present as an intercalation compound in the complex was increased by raising the polymer content. Probably there is an optimum PAM content in the range 4.8–8.3% which is able to penetrate the interlayer space. However, further optimization work is necessary in this field.

REFERENCES

1 B.K.G. Theng, Clay and Clay Miner., 30 (1) (1982) 10.
2 N. Schamp and J. Huylebroeck, J. Polym. Sci., Polym. Symp., 42 (1973) 553.
3 A.C.D. Newman, Chemistry of Clays and Clay Minerals, Mineralogical Society Monograph No. 6, Wiley–Interscience, New York, 1987, p. 319.
4 M. Tutas, M. Saglam, M. Yüksel and C. Güler, Thermochim. Acta, 111 (1987) 121.
5 W.M. Leung, D.E. Axelson and J.D. van Dyke, J. Polym. Sci., 25 (1987) 1825.
6 G. Várhegyi, M.J. Antal, T. Székely, F. Till and E. Jakab, Energy Fuels, 2 (1988) 267.
7 S. Sawant and H. Moravetz, J. Polym. Sci., Polym. Lett. Ed., 20 (1982) 385.
8 L.M. Minsk, C. Kotlarchik and G.N. Meyer, J. Polym. Sci. Polym. Chem. Ed., 12 (1974) 133.
9 R. Scarlat, D. Fatu and E. Segal, Thermochim. Acta, 72 (1984) 377.