Eur. Polym. J. Vol. 34, No. 5/6, pp. 733–737, 1998

Printed in Great Britain
0014-3057/98 $19.00 + 0.00

PII: S0014-3057(97)00189-4

THERMAL BEHAVIOUR OF SOME CATIONIC POLYELECTROLYTES AND POLYELECTROLYTE COMPLEXES

STELA DRAGAN,[1]* I. DRANCA,[2] LUMINITA GHIMICI,[1] MARIANA CRISTEA,[1] GH. FUNDUIANU[1] and T. LUPASCU[2]

[1]"Petru Poni" Institute of Macromolecular Chemistry, 6600 Iasi, Romania and [2]Institute of Chemistry, 2028 Chisinau, Republic of Moldova

(Received 22 December 1996; accepted in final form 18 March 1997)

Abstract—Thermogravimetric and differential thermal analysis were developed on some cationic polymers, different both by the content of the quaternary ammonium salt groups in the main chain and by the content and type of polyfunctional amines, as well as on some polyelectrolyte complexes (PECs), when the cationic component was one of the above cationic polymers and the anionic component was poly(acrylic acid) sodium salt (PANa). The polycation with the lowest content in the quaternary ammonium salt groups had the highest thermal stability. The electrostatic interactions between the oppositely charged polyions in PECs induced a greater thermal stability of their structure compared with the starting polycations. The thermal behaviour of the PECs was compared with that of the physical mixtures of the corresponding complementary polymers taken in the same mass ratio as in PECs. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Thermal degradation is frequently used in the study of polymers both from the theoretical [1] and practical point of view [2–4]. Thermogravimetric analysis supplies information on the relative thermal stability of polymers and also helps in the selection of materials with the best properties for specific uses. However, the classification of polymers according to their thermal stability is very hazardous due to the high number of reactions which take place at high temperatures.

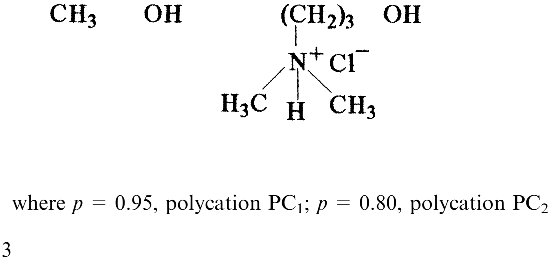
Study of the thermal stability of the cationic polyelectrolytes could give some information on the possibility of using them as films, coatings, adhesives, etc. The available studies in this field are very scarce [5]. Also, information on the thermal stability of PECs is very limited [6, 7].

The aim of this paper is the study of the thermal properties of some cationic polyelectrolytes and of the influence of the cationic component structure on the thermal stability of some PECs when the anionic component was poly(acrylic acid) sodium salt (PANa). The thermal behaviour of the PECs was followed by comparison with the physical mixtures between PANa and the corresponding cationic polymers taken in the same molar ratio as in the PEC.

EXPERIMENTAL

Materials

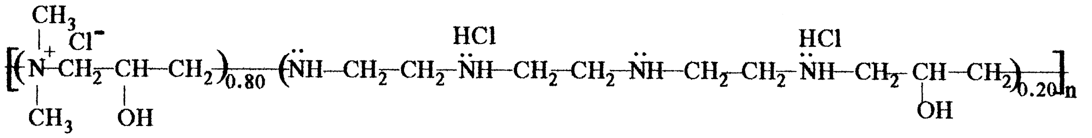
The cationic polyelectrolytes with *N*-*N*-dimethyl-2-hydroxypropylenammonium chloride units in the main chain were synthesized by condensative polymerization of epichlorohydrin with dimethylamine and a polyfunctional amine such as *N*-*N*-dimethyl-1,3-diaminopropane (DMDAP) or triethylenetetramine (TETA), according to the method previously described [8]. Samples were carefully purified against distilled water and then recovered by atomization. The cationic polymer samples were kept for days in vacuum on P_2O_5, at room temperature. The intrinsic viscosities of these polymers, determined in 1 M NaCl aqueous solution at 25°C, were as follows: 0.420 dl/g for PC_1; 0.355 dl/g for PC_2 and 0.422 dl/g for PC_3. Their structures are presented in Scheme 1.



where $p = 0.95$, polycation PC_1; $p = 0.80$, polycation PC_2

---

*To whom all correspondence should be addressed.



$$\left[\left(\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}Cl^- -CH_2-\underset{OH}{CH}-CH_2\right)_{0.80}\left(\ddot{N}H-CH_2-CH_2-\overset{HCl}{\ddot{N}H}-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-\overset{HCl}{\ddot{N}H}-CH_2-\underset{OH}{CH}-CH_2\right)_{0.20}\right]_n$$

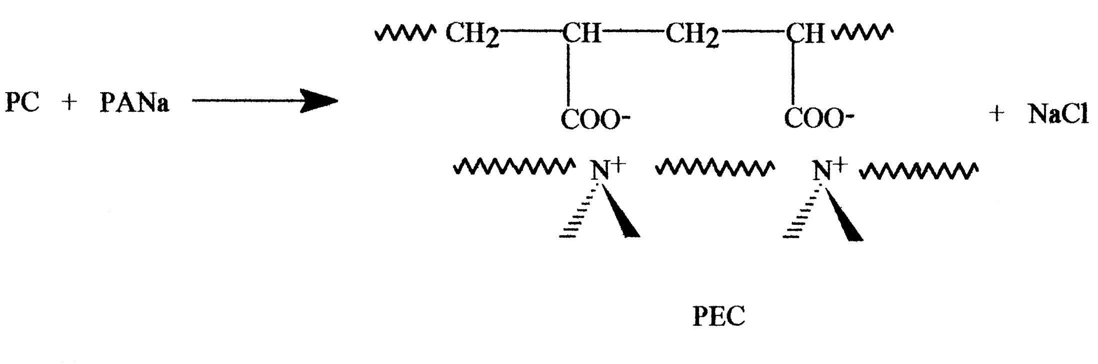
polycation PC_3

Scheme 1

In Scheme 1 the ideal structure units were presented; the polyfunctional amines taken into account have the functionalities 4 (DMDAP) and 10 (TETA), respectively. Consequently, at the tertiary and secondary amine groups, branching could take place, this possibility being higher in the case of a greater content of amine.

Poly(acrylic acid) was converted to the sodium salt by use of aqueous sodium hydroxide. After two purifications with a water/acetone system, the sodium salt was recovered from aqueous solution by atomizing. The molecular weight of the sodium salt of poly(acrylic acid) (PANa), in 2N NaOH aqueous solution at 25°C was 51,400.

The PECs were prepared and purified according to the method previously described [9]. The aqueous solution of polyanion, with a concentration of 10^{-2} unit mol/l, was slowly dropped into the aqueous solution of polycation having a concentration of 10^{-3} unit mol/l, under magnetic stirring, at room temperature, the final unit [PA]:[PC] molar ratio being 1:1. The mixing was continued for 2 hr, then the precipitates were removed by filtration. The precipitates were washed for a long time with distilled water until there were no Cl^- ions in the washing water and finally with acetone. When the PEC was a coacervate, the complex-rich phase was first treated with acetone, then with water until the absence of Cl^- ions in the washing water and finally again with acetone. PECs were dried at 50°C in vacuum for about 48 hr. Only stoichiometric complexes, checked by elemental analysis (absence of the Cl and Na), were used in this work. The formation of the PECs is schematically presented in Scheme 2.



when $PC = PC_1 \rightarrow PEC_1$; $PC = PC_2 \rightarrow PEC_2$; $PC = PC_3 \rightarrow PEC_3$.

Scheme 2

Thermal characterization techniques

Thermogravimetry (TG) was performed with MOM, Budapest Thermal Analyzer, in air at a heating rate of 5°C/min, sample weight 50 mg, the reference material α-Al_2O_3, the sensitivity being for TG 50 mg, DTG 500 V (1/10) and DTA 100 V (1/5).

RESULTS AND DISCUSSION

The first polymer thermally analysed in this work was PANa (Fig. 1). The TG, DTG and DTA curves suggest that thermal decomposition of PANa took place in three stages: dehydration in the range 100–200°C, when the mass loss was about 5%, a strong exothermic effect with a maximum of 480°C, assigned to decomposition of the organic part, and an endothermic effect with a maximum at 810°C that reflects the decomposition of Na_2CO_3.

The TG, DTG and DTA curves for the PC_2 and PC_3 and also for PEC_1 and PEC_3, are presented in Figs 2, 3 and 4.

Table 1 includes the degradation stages and the mass loss for the mentioned polymers.

The polycations taken into account in Figs 2–4 differ by the nature and the functionality of the polyfunctional amine used in their synthesis, but they have the same molar content of polyfunctional amine. The TG curves indicate a higher thermal stability of PC_3, compared with PC_2. This is because the branches in the case of polymer PC_2 are formed by quaternization of the side tertiary amine groups, but in the case of PC_3, the branching reaction leads mainly to formation of the tertiary amine groups. The higher content in the quaternary ammonium salt groups and also the presence of these groups in the side chain lead to a lower thermal stability of PC_2 compared with PC_3. This different behaviour is also proved by the DTA curves (Fig. 4, curves 1 and 3) that show a shift of the maximum of the exothermic stages to higher temperatures. Compared with PC_1 characterized by

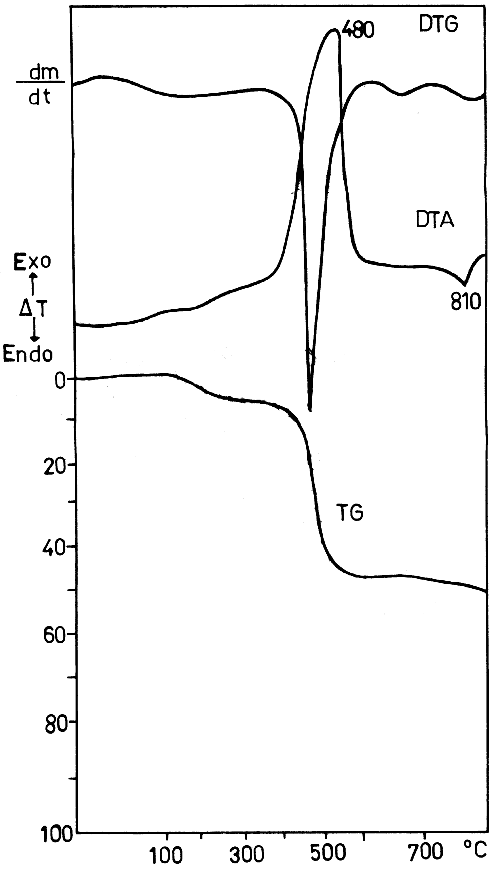


Fig. 1. TG, DTG and DTA curves for PANa.

an endothermic stage with a maximum at 160°C and two exothermic stages with maxima at 500 and 550°C, assigned to thermal degradation of the tertiary amine, a lower thermal stability of PC_2 is evident. PC_2 can reach about the same content in the quaternary ammonium salt groups as PC_1 by branching due to quaternization of the side tertiary amine groups. This means that at about the same content of quaternary ammonium salt groups the polymer with the higher content of the ammonium salt group in the side chain degrades faster than the other one. For the polycations studied in this work, the following order of thermal stability was suggested: $PC_3 > PC_1 > PC_2$.

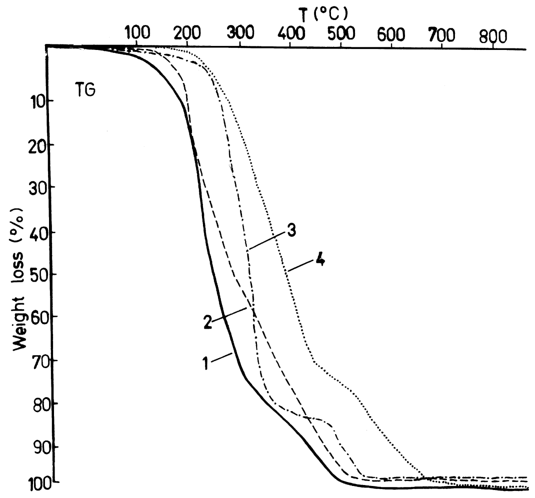


Fig. 2. Thermogravimetric analysis in air of polycations and their polyelectrolyte complexes: (1) PC_2; (2) PEC_1; (3) PC_3; (4) PEC_4.

Another aspect pursued in this study was the influence of the complexation of the above mentioned polycations with PANa on their thermal stability. The TG curves for PEC_1 and PEC_3 (Fig. 2, curves 2 and 4) indicate that the complexes degrade at higher temperatures than the corresponding polycations, for the same heating rate. This is also suggested by the larger area of the maximum of the exothermic stage in the DTA curves (Fig. 4, curves 2 and 4). The higher the thermal stability of the polycation, the greater the thermal stability of the corresponding PEC. According to Scheme 2,

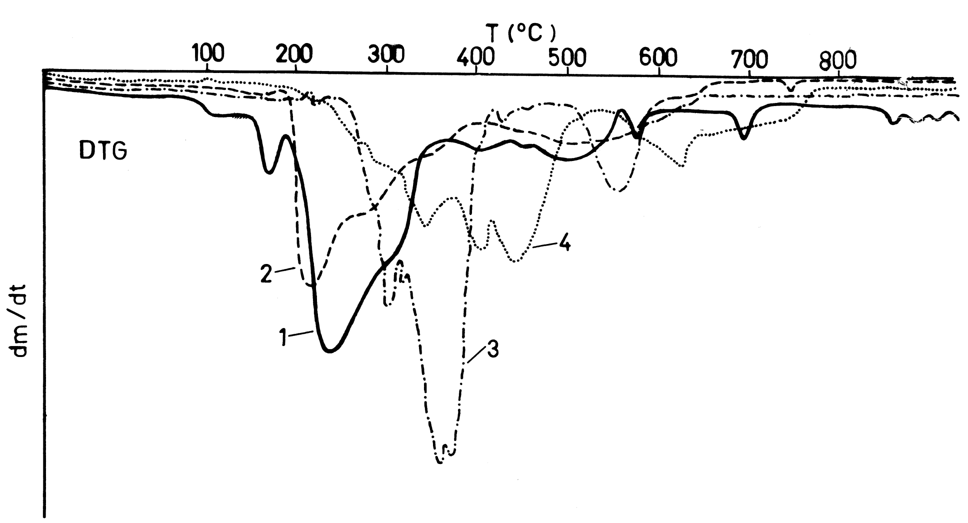


Fig. 3. Derivative thermogravimetry (DTG) of polycations and their polyelectrolyte complexes: (1) PC_2; (2) PEC_1; (3) PC_3; (4) PEC_3.

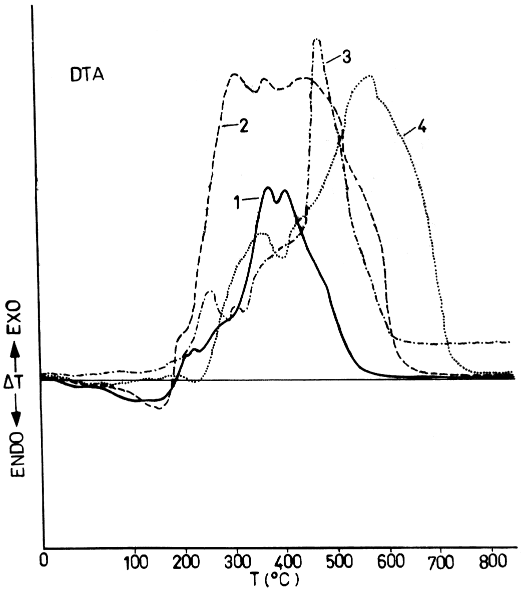


Fig. 4. Differential thermal analysis curves of polycations and their polyelectrolyte complexes: (1) PC_2; (2) PEC_1; (3) PC_3; (4) PEC_3.

the formation of the PECs taken into account in this work takes place by electrostatic interactions between the polycation and polyanion. The higher thermal stability of the PECs compared to the corresponding PCs is also a proof of their structure, according to Scheme 2. The electrostatic interactions between the oppositely charged polyions result in a great thermal stability of their structure.

The thermal behaviour of the PECs was also compared with that of the 1:1 physical mixtures of the corresponding complementary polymers. Figure 5 includes the TG, DTG and DTA curves for the 1:1 physical mixture between PC_2 and PANa.

As can be seen from Fig. 5, the thermal stability of the 1:1 physical mixture PC_2/PANa is superior to the corresponding complex (PEC_2) and also much higher than that of the polycation taken alone (Fig. 2) after the first exothermic stage, assigned to thermal destruction of the quaternary ammonium salt groups. The same behaviour was observed for the other physical mixtures (PC_1/PANa and PC_3/PANa). It seems that the presence of PANa close to these polycations induces an increase in their thermal stability that is even higher than that of the corresponding complexes. A similar situation was emphasized in the case of the physical mixture 1:1 between chitosan and carboxymethylcellulose sodium salt [7].

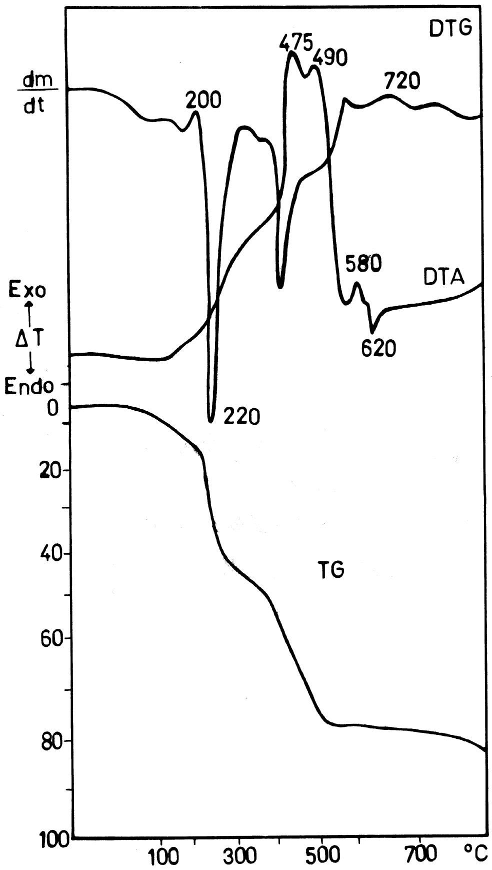


Fig. 5. TG, DTG and DA curves for the 1:1 physical mixture of PC_2 and PANa.

Table 1. Some thermogravimetric data for cationic polyelectrolytes and polyelectrolyte complexes

Sample	Characteristics of DTA curves	Beginning	T(°C) Maximum	End	Mass loss Δm(%)
PC_2	1-*endo*	65	—	190	11.0
	2-*exo*	190	—	355	66.5
	3-*exo*	355	430, 470	605	22.5
PEC_1	1-*endo*	140	165	215	17.0
	2-*exo*	215	390	420	60.5
	3-*exo*	420	450, 505	640	22.5
PC_3	1-*endo*	80	—	170	3.0
	2-*exo*	170	260	305	31.0
	3-*exo*	305	320	445	52.0
	4-*exo*	445	530	640	14.0
PEC_3	1-*endo*	170	220	330	18.5
	2-*exo*	330	370	410	19.0
	3-*exo*	410	—	505	41.0
	4-*exo*	505	595	700	21.5

CONCLUSION

The thermal stability of the polycations taken into account in this work could be proof of their structure because it depends both on the density and the position of the quaternary ammonium salt groups vis-à-vis the backbone. The polycation with the lowest content of quaternary ammonium salt groups had the highest thermal stability (PC_3).

Study of the thermal behaviour of the PECs obtained by interaction between a polycation with quaternary ammonium salt groups in the main chain and PANa emphasized a higher stability of the PECs compared to the starting polycations. The electrostatic interactions between the oppositely charged polyions, according to Scheme 2, bring about a great thermal stability of their structure. The 1:1 physical mixtures between PANa and any polycation showed a higher thermal stability than the corresponding PECs. This is also proof of the PEC structure, that means the absence of the low molecular weight salts in these products.

REFERENCES

1. Vasile, C., Calugaru, E. M., Stoleru, A., Sabliovschi, M. and Mihai, E., *Thermal Behaviour of Polymers*. Romanian Academy, 1980.
2. Cascaval, C. N., *Eur. Polym. J.*, 1994, **30,** 969.
3. Cascaval, C. N. and Neagu, V., *Polym. Degrad. Stab.*, 1994, **45,** 423.
4. Cascaval, C. N., Hurduc, N. and Poinescu, Ig, *J. Thermal Anal.*, 1988, **34,** 311.
5. Prasad, B. B., Easo, S. and Kumar, A., *Polym. J.*, 1994, **26,** 251.
6. Kubota, N. and Kikuki, Y., *Makromol. Chem.*, 1992, **193,** 559.
7. Argüelles-Monal, W., Garciga, M. and Peniche-Covas, C., *Polym. Bull.*, 1990, **23,** 307.
8. Dragan, S. and Ghimici, L., *Makromol. Chem.*, 1991, **192,** 199.
9. Dragan, S., Cristea, M., Luca, C. and Simionescu, B. C., *J. Polym. Sci. Part A: Polym. Chem.*, 1996, **34,** 3485.