ELSEVIER

Thermochimica Acta 385 (2002) 153–162

thermochimica acta

www.elsevier.com/locate/tca

Aspects of polyesterurethane interaction with metallic ions II. Synthesis and thermal behavior of polyurethane interaction products with manganese and copper ions

Gabriela Moroi*, Constantin Ciobanu

Institute of Macromolecular Chemistry "Petru Poni", Aleea Grigore Ghica Vodă 41A, 6600 Iaşi, Romania

Received 8 June 2001; received in revised form 16 August 2001; accepted 17 August 2001

Abstract

The objective of this study was to investigate the effects of some transition metal ions on the thermal behavior of polyurethane materials. The interaction products of a segmented polyesterurethane prepared from 4,4′-diphenylmethane diisocyanate, poly(ethylene-co-diethylene adipate)diol and ethylene glycol, with manganese and copper ions were synthesized and their thermal decomposition was studied in comparison to that of the original polyurethane by using thermogravimetric analysis. The activation energy of the thermal degradation was evaluated by Coats–Redfern and Levi–Reich methods. It was revealed that the thermal decomposition of the polyurethane is affected by the presence of both metallic ions and that each ion has a specific influence on the process. By modification with manganese and copper ions, changes in the degradation mechanism of the polyurethane are induced. It was found that manganese ions have a catalytic effect on the overall decomposition process, whereas copper ions reduce the initial thermal stability of the polyurethane and catalyze the final stage of its decomposition, but enhance the thermal stability of the intermediate products. In general, the influence of metallic ions on the thermal behavior of the polyurethane becomes more significant as their proportion increases.

Keywords: Polyesterurethane; Thermal behavior; Manganese ions; Copper ions; Thermogravimetry

---

1. Introduction

Studies of the interaction between metallic ions and polymers with coordinating groups, among which are the polyurethanes, resulting in macromolecule-metal complexes (metallopolymers), has received considerable attention during the last decades [1–4]. This intense interest is caused by the great variety of new products that is obtained, having a wide range of interesting properties and potential applications in many diverse fields such as catalysis, conduction, medicine, electronics. Some polymer-metal complexes may serve as models for bioinorganic systems such as metalloenzymes [5–16]. Conversely, the metallic ions which are present in polymers as residual catalysts, additives or contaminants [17–24] can influence the processing and induce pronounced changes in the performances of the final product [25,26]. Among the polymer properties that can be affected by the presence of metallic ions are the thermal properties [27–30]. Therefore, it is useful to investigate the modifications induced by the metallic ions in the thermal behavior of polyurethanes, which are a very important

---

[*] Corresponding author. Fax: +40-32-211299.
E-mail address: gmoroi@icmpp.tuiasi.ro (G. Moroi).

0040-6031/02/$ – see front matter
PII: S0040-6031(01)00713-4

class of polymers due to their applications as elastomers, rigid and flexible foams, elastomeric fibers, adhesives, surface coatings, membranes and medical implants. In the present work, we have studied the effect of two transition metal ions, namely, manganese and copper on the thermal behavior of a segmented polyurethane obtained from 4,4′-diphenylmethane diisocyanate, a copolyester and ethylene glycol. The thermal decomposition of the polyesterurethane interaction products with metallic ions in comparison with that of the original polyurethane was investigated by using thermogravimetric analysis.

2. Experimental

The polyesterurethane (PU) was obtained by the polyaddition reaction of 4,4′-diphenylmethane diisocyanate (MDI), poly(ethylene-co-diethylene adipate)-diol (PEDA) and ethylene glycol (EG) as chain extender, in dimethylformamide (DMF) with urethane group concentration of 3.26×10^{-3} mol/g.

The polyurethane interaction products (IP) with manganese and copper ions (IP-Mg and IP-Cu, respectively) were synthesized from PU and metallic ions as chlorides, $MnCl_2{\cdot}4H_2O$ and $CuCl_2{\cdot}2H_2O$, respectively. For every ion species, a series of three interaction products were prepared by using different molar ratios of urethane groups in the polymer chains to metallic ions (180:1, 36:1 and 12:1). The interaction of the polymer with the inorganic salt was effected by the following procedure. In a vigorously stirred solution of PU in DMF, a solution of metallic chloride in DMF was dropwise added at 20 °C. The reaction system was maintained under continuous stirring at 20 °C for 1 h and then it was allowed to stand at room temperature for 2 days. The resulting viscous solution was cast on polished Teflon plates at atmosphere pressure, cured at 110 °C for 65 min and then allowed to cool slowly to ambient temperature. Further, drying was carried out under vacuum, until the solvent was removed, as indicated by constant weight. Homogeneous films with thickness below 100 μm were thus obtained. Before being analyzed, the films were thoroughly wiped with ethanol for the complete removal of the superficial layer formed by the salt unretained in the polymeric matrix. These were dried at room temperature. In the same conditions as for the interaction products, a reference sample from PU without inorganic salt was prepared. The surface of both PU and IP films was smooth and continuous. While the PU film was almost colorless, the IP films developed colors that were characteristic for each series (yellow-brown for IP-Mn and greenish yellow-brown for IP-Cu) and more intense as the metal content increased. The color of IP films was taken as evidence for complex formation by the interaction of the polar groups of PU with the metallic ions. In contrast to PU film, the IP films exhibited good adherence to glass substrates.

3. Analysis

The metal content of IP was determined by atomic absorption spectrometry using a Perkin Elmer AA800 spectrometer.

The thermal decomposition of IP-Mn, IP-Cu and PU was monitored with a TGA V5.1A DuPont 2000 thermal analyzer. The thermogravimetric experiments were carried out in a dynamic nitrogen atmosphere, with an average heating rate of 9 K min^{-1} to 950 °C. The sample mass was 10 mg. The thermoanalytical (TG and DTG) curves were simultaneously recorded. In order to obtain comparable data, the thermal analyses were performed with the same conditions for all samples.

4. Results and discussion

The results of quantitative analysis of the metal in IP are presented in Table 1. All IP contain lower quantities of metal than those added in the initial systems. It can be assumed that many polar groups of PU are not involved in the interaction because they are inaccessible, presumably due to the conformations adopted by the macromolecules in solution during preparation. In both series, the metal content of IP is higher as the amount of ions in the corresponding initial systems is larger. This cooperative binding pattern could tentatively be rationalized in terms of the conformational changes of the polymer chains induced by the coordination process [31]. The accentuating interaction is more pronounced in IP-Mn series than in the IP-Cu series, which supports the assumption

Table 1
Results of elemental analysis

Composition	Symbol	Molar ratio U/MI[a]		Metal content (wt.%)	
		Initial	Final	Added	Retained
PU/$MnCl_2{\cdot}4H_2O$	1Mn	180.2:1	358.1:1	0.10	0.05
PU/$MnCl_2{\cdot}4H_2O$	2Mn	36:1	44.4:1	0.49	0.40
PU/$MnCl_2{\cdot}4H_2O$	3Mn	12:1	13.8:1	1.44	1.26
PU/$CuCl_2{\cdot}2H_2O$	1Cu	180:1	213.3:1	0.11	0.10
PU/$CuCl_2{\cdot}2H_2O$	2Cu	36:1	71.1:1	0.57	0.29
PU/$CuCl_2{\cdot}2H_2O$	3Cu	12:1	50.1:1	1.67	0.41

[a] Urethane group/metallic ions.

that under the conditions adopted, the affinity of PU towards manganese ions is higher than that towards copper ions.

The thermal decomposition of polyurethanes is, in general, a complex process [32–36]. The thermal degradation of PU, IP-Mn and IP-Cu proceeds in two consecutive, well-defined stages, the first stage being the main one (Figs. 1–4). For PU, the main stage consists of several partially overlapped steps, four of them corresponding to distinct peaks on the DTG curve. The steps of the process might tentatively be assigned as follows: steps I and II—mainly to the decomposition of EG and MDI, respectively, steps III and IV—mostly to the decomposition of PEDA [37–40] and step V (the final stage)—to the decomposition of the products formed by the secondary reactions of MDI [39–41]. This proposed assignment of the steps seems to be substantiated by the match between, respectively, the mass losses (8% in step I, 45% in steps II and V and 46.5% in steps III and IV) and PU composition (7% EG, 42% MDI and 51% PEDA).

Both IP-Mn and IP-Cu show, as compared to PU, lower initial temperatures of decomposition (which seems to indicate that both metallic ions promote the scission of the urethane linkage [42–44]) and lower temperature ranges of the process (Tables 2 and 3). For IP-Mn the mass losses in the main stage are higher, while those in the final stage are lower than the corresponding mass loss for PU. In general, the mass losses for IP-Cu as compared to the corresponding one

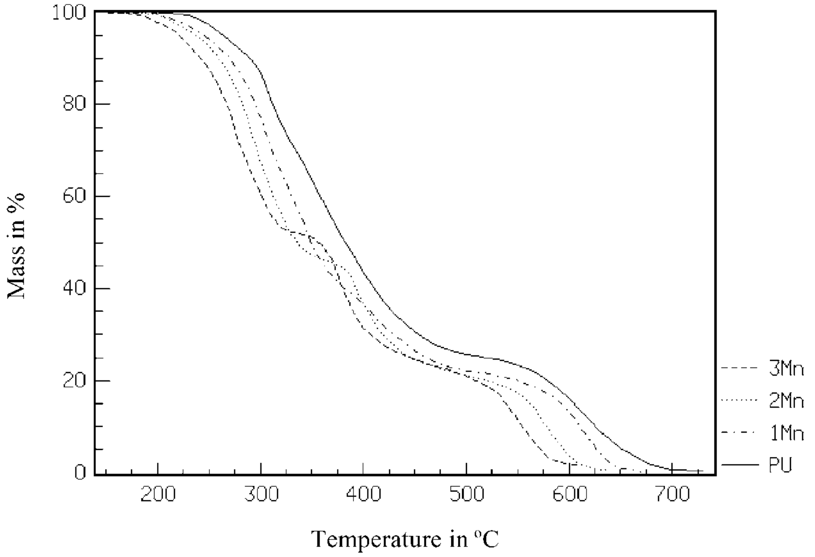

Fig. 1. TG curves of PU and IP-Mn.

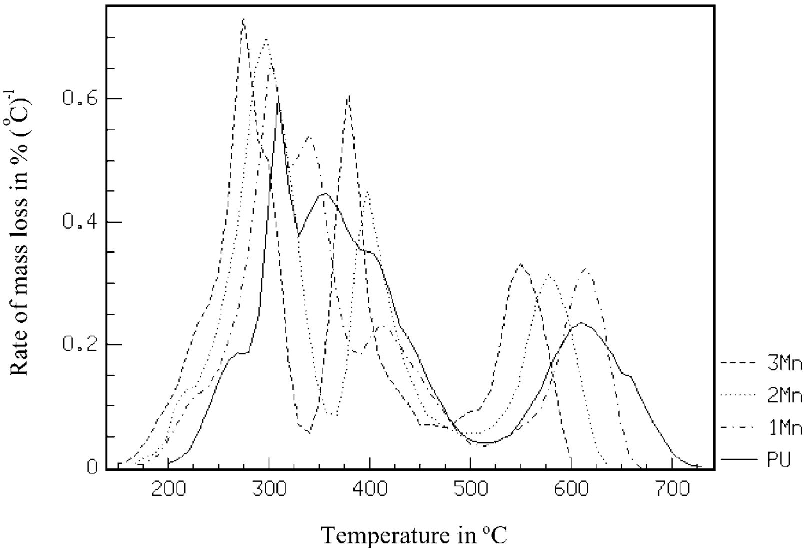

Fig. 2. DTG curves of PU and IP-Mn.

for PU are lower in step II (as well as in the whole main stage) and higher in step V. The accumulated mass losses of steps II and V are similar for IP-Cu and PU. For IP-Cu, the mass losses in step IV are somewhat comparable with the accumulated mass losses of steps III and IV for PU.

For all IP-Mn the TG curves are placed below the TG curve of PU over the entire temperature range of the process and are more sinuous (Fig. 1). IP-Mn exhibit higher maximum volatilization rates than those for PU in all the decomposition steps, except step I (Fig. 2). For all IP-Mn, the highest rate of the process is in step II, as for PU. The maximum rates of mass loss of all the decomposition steps progressively shift towards lower temperatures as the manganese content increases. The main stage tends to separate into two

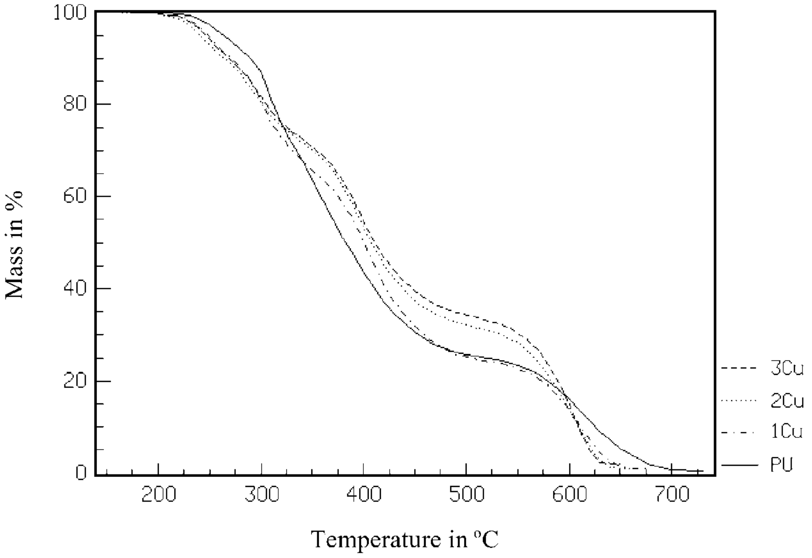

Fig. 3. TG curves of PU and IP-Cu.

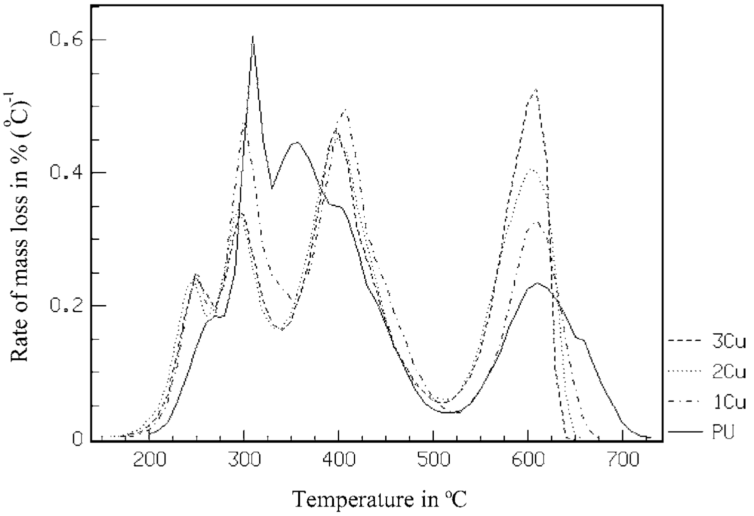

Fig. 4. DTG curves of PU and IP-Cu.

Table 2
Results of thermogravimetric analysis[a]

Sample	Temperature range (°C)				
	First stage				Second stage (step V)
	Step I	Step II	Step III	Step IV	
PU	202–281 (269)	281–331 (310)	331–394 (358)	394–516 (403)	516–728 (610)
1Mn	177–244 (227)	244–323 (304)	323–388 (340)	388–511 (412)	511–670 (614)
2Mn	168 →[b]	→ → (297)	→ 362	362–497 (398)	497–638 (579)
3Mn	153 →[b]	→ → (275)	→ 338	338–470 (378)	470–610 (549)
1Cu	178–267 (250)	267–352 (301)	–	352–515 (407)	515–676 (609)
2Cu	165–263 (246)	263–335 (294)	–	335–511 (400)	511–650 (602)
3Cu	173–267 (251)	267–339 (297)	–	339–507 (398)	507–640 (609)

[a] In parentheses are the temperatures at the maximum rate of mass loss.

[b] Steps I–III are strongly overlapped.

Table 3
Results of thermogravimetric analysis

Sample	Mass losses (%)						
	First stage					Second stage (step V)	Total
	Step I	Step II	Step III	Step IV	Total		
PU	8.0	20.6	25.5	20.8	74.9	24.6	99.5
1Mn	4.9	31.2	25.1	17.1	78.3	21.2	99.5
2Mn	←	53.8[a]	→	24.9	78.7	20.7	99.4
3Mn	←	48.1[a]	→	28.7	76.8	21.5	98.3
1Cu	9.2	25.4	–	41.1	75.7	23.5	99.2
2Cu	9.7	17.6	–	41.2	68.5	30.5	99.0
3Cu	9.7	17.7	–	38.9	66.3	31.9	98.2

[a] Accumulated mass losses for steps I–III.

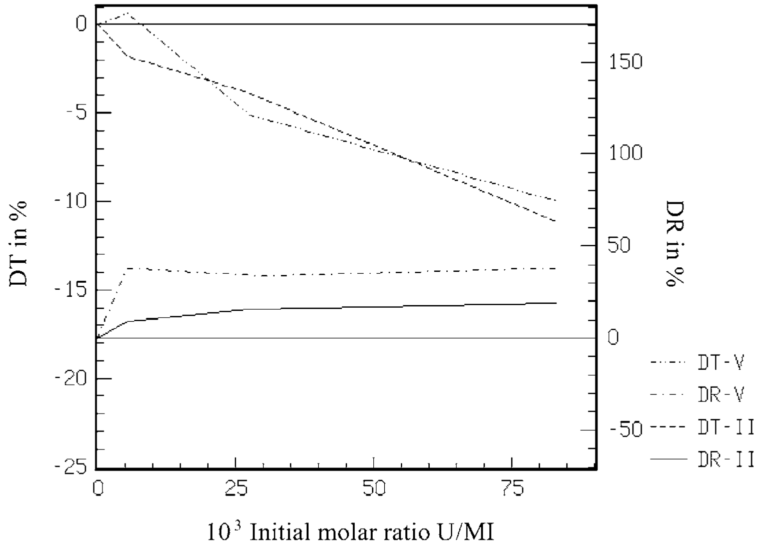

Fig. 5. *DR–DT* diagram for IP-Mn.

substages, the first of these being formed by the combination of steps I–III.

The TG curves of IP-Cu are more convoluted than the TG curve of PU (Fig. 3). The mass losses for IP-Cu are higher than that corresponding for PU below 320 and above 600 °C, whereas within the temperature range 320–600 °C are lower than that for PU. As compared to PU, a major difference in the decomposition of all IP-Cu consists of the absence of step III (Fig. 4). For IP-Cu, the decrease of the maximum rate of volatilization of step II, as well as the increase of the maximum rates of steps I, IV and V, also take place. The maximum rate of the process is either in step IV or in step V.

Figs. 5 and 6 present the effect of metallic ions on the maximum rate of mass loss (R) in steps II and V of

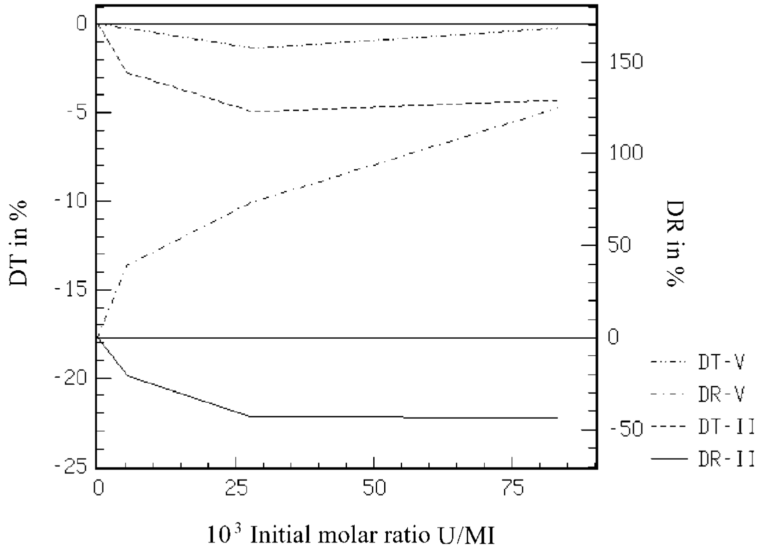

Fig. 6. *DR–DT* diagram for IP-Cu.

the thermal decomposition of PU and the corresponding temperature (T). The percentage differences $DR = (R_{\mathrm{IP}} - R_{\mathrm{PU}}) \times 100/R_{\mathrm{PU}}$ and $DT = (T_{\mathrm{IP}} - T_{\mathrm{PU}}) \times 100/T_{\mathrm{PU}}$ are plotted as a function of the initial molar ratio metallic ions/urethane groups (U/MI).

All IP-Mn show in steps II and V higher maximum volatilization rates and lower corresponding temperatures than those of PU (Fig. 5). It is noted that manganese ions have a catalytic effect on both steps, which is more substantial in step V than in step II.

As compared to PU, all IP-Cu exhibit in step II lower maximum rates of mass loss and lower corresponding temperatures (Fig. 6). The decrease in rate is more significant than the temperature decrease, which suggests that the overall effect of copper ions consists of the inhibition of the processes occurring. In step V, the maximum volatilization rate increases dramatically with increasing copper content, whereas the corresponding temperature remains almost unchanged, irrespectively of metal amount.

Since every series of IP exhibits a characteristic pattern of simultaneous variation of the two maximum rates of mass loss and of the corresponding temperatures with increasing initial molar ratio metallic ions/urethane groups, the *DR–DT* diagrams can be considered as a simple way of fingerprinting the thermal decomposition behavior.

The temperatures at which the mass losses of 10–50% take place are presented in Table 4. For IP-Mn, the temperatures at 10–50% mass losses are lower than those corresponding to PU. For IP-Cu, the mass losses of 10–20% occur at lower temperatures, while those of 30–50% take place, in general, at higher temperatures than those for PU. The mass losses of 10–50% occur for all IP-Cu at higher temperatures than those corresponding to IP-Mn.

Table 4
Temperatures at 10–50% mass losses

Sample	Temperature (°C) at mass loss (%) of				
	10	20	30	40	50
PU	290	312	335	358	382
1Mn	270	295	311	331	350
2Mn	260	283	298	313	336
3Mn	242	268	283	301	357
1Cu	272	302	331	374	401
2Cu	265	301	351	385	408
3Cu	269	305	354	388	411

Table 5
Values of activation energy for the thermal decomposition process

Sample	$E_{\mathrm{a,CR}}$ (kJ/mol)	
	Steps I–III	Steps I–II
PU	103	122
1Mn	93	–
2Mn	94	–
3Mn	90	–
1Cu	–	120
2Cu	–	107
3Cu	–	116

In order to compare the thermal behavior of the studied products, the modification of the activation energy of the degradation process for IP in comparison with PU was also investigated, by both Coats–Redfern and Levi–Reich methods [45,46]. The former method was used to calculate the value of the activation energy, whereas the latter gave the change of the activation energy during degradation as a function of the fractional extent of reaction α. The methods were applied for steps I–III for IP-Mn and steps I–II for IP-Cu.

The values of the activation energy ($E_{\mathrm{a,CR}}$) are presented in Table 5. It is noted that both IP-Mn and IP-Cu display lower activation energies than those corresponding to PU. The shape of the activation energy vs. α curves of IP-Mn is less convoluted than that of PU, which means that changes in the degradation pathway take place (Fig. 7). As compared to the activation energy of PU, the activation energies of IP-Mn show a more abrupt original decrease and reach the minimum value at lower conversions, indicating a more rapid loss of the light degradation compounds. Throughout the conversion range, the values of the activation energy for IP-Mn are lower than that corresponding to PU.

The presence of copper ions imparts a somewhat different degradation route, as shown by the more sinuous activation energy vs. α curves of IP-Cu as compared to that of PU (Fig. 8). In comparison with the activation energy for PU, the corresponding activation energies for IP-Cu are lower at the onset of the process, which is an indication that copper ions accelerate the loss of the volatile compounds. Within the conversion range 0.1–0.2 these become super-ior, which seems to confirm the formation of more ther-

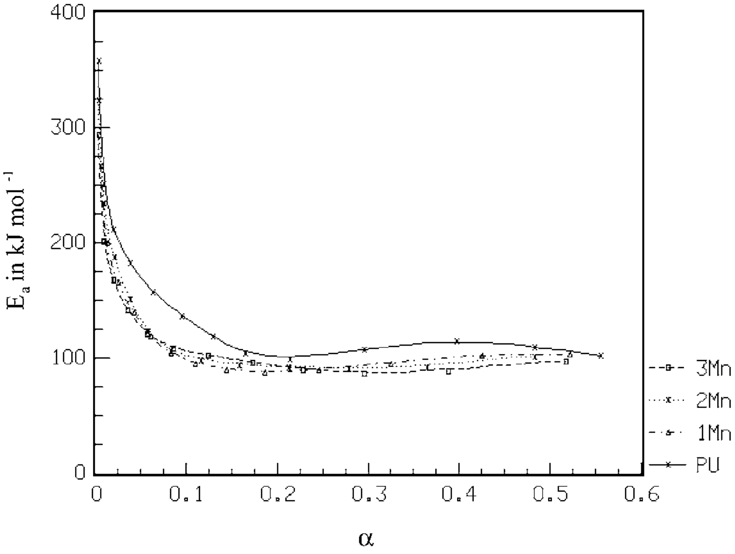

Fig. 7. Dependence of activation energy on fractional extent of reaction for PU and IP-Mn.

mally stable intermediate decomposition products than those of PU.

According to the changes induced by the two metallic ions in the thermogravimetric data and in the activation energy of PU decomposition and taking into consideration the above proposed assignment of the PU decomposition steps, the following effects of the ions on the processes involved in the PU decomposition can be assumed. Manganese ions promote the scission of the urethane linkage, the decomposition of EG, MDI (thus, hindering to some extent the occurrence of its secondary reactions) and PEDA, as well as the decomposition of the products of MDI secondary reactions. Copper ions promote the scission

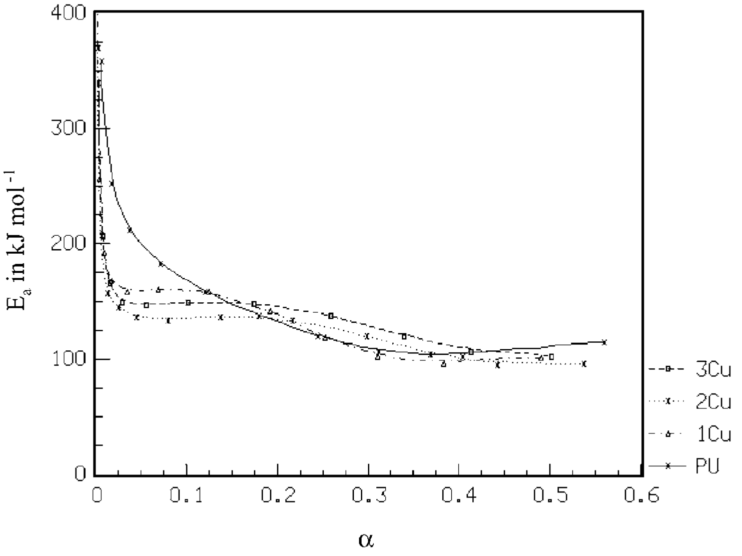

Fig. 8. Dependence of activation energy on fractional extent of reaction for PU and IP-Cu.

of the urethane linkage and the decomposition of EG, but partially impede the decomposition of MDI (thus, favoring its secondary reactions) and retard the decomposition of PEDA (which takes place in a single step having the temperature at the maximum volatilization rate close to that of the final step of PEDA decomposition in PU). They catalyze the decomposition of the structures formed by MDI secondary reactions.

5. Conclusions

In order to study the modifications induced by the presence of some transition metal ions in the thermal behavior of a segmented PU, polyurethane interaction products with manganese and copper ions were synthesized.

The amounts of metallic ions retained by the polyurethane depend on the conformational state of the interacting polymer chains. The polyurethane affinity for manganese ions seems to be higher than for copper ions.

In investigating the influence of manganese and copper ions on the polyurethane thermal behavior, the distinct effects of the two transition metal ions on thermal decomposition were revealed. It is shown that manganese ions have a catalytic effect on the entire decomposition process. Copper ions reduce the initial thermal stability of the polyurethane and have a catalytic effect on the processes that take place in the final stage of decomposition. In contrast, they enhance the thermal stability of the intermediate decomposition products. The two metallic ions change the degradation mechanism of the polyurethane. In general, the effect (catalytic or inhibiting) of manganese and copper ions on the steps of the polyurethane thermal decomposition process is increasingly pronounced as their content is higher.

Acknowledgements

The authors gratefully acknowledge the support of Professor Xiaozu Han of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences for the metal content measurements.

References

[1] F. Ciardelli, E. Tsuchida, D. Wöhrle (Eds.), Macromolecule Metal Complexes, Springer, Heidelberg, 1995.

[2] J.E. Sheats, C.E. Carraher Jr., C.U. Pittman Jr. (Eds.), Metal-containing Polymeric Systems, Plenum Press, New York, 1985.

[3] A.D. Pomogailo, I.E. Uflyand, Macromolecule Metal Chelates, Nauka, Moscow, 1991.

[4] A. Eisenberg (Ed.), Ions in Polymers, Advances in Chemical Series 187, American Chemical Society, Washington, DC, 1980.

[5] N.M. Sawy, F.Al. Sagheer, Eur. Polym. J. 37 (2001) 161.

[6] C.L. Fraser, A.P. Smith, J. Polym. Sci., Part A 38 (Suppl.) (2000) 4704.

[7] Yu.V. Savel'ev, Ukr. Khim. Zh. 66 (2000) 43.

[8] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dhal, J. Polym. Sci., Polym. Chem. 35 (1997) 1809.

[9] G. Yu, H. Chen, X. Zhang, Z. Jiang, B. Huang, J. Polym. Sci., Polym. Chem. 34 (1996) 2237.

[10] D.C. Sherrington, H.-G. Tang, Macromol. Symp. 80 (1994) 193.

[11] D. Wöhrle, G. Schulz-Ekloff, Adv. Mater. 6 (1994) 875.

[12] J.C.W. Chien, B.M. Gong, X. Mu, Y. Yang, J. Polym. Sci., Part A 28 (1990) 1999.

[13] P.S. Hammond, J.S. Forster, J. Appl. Polym. Sci. 43 (1991) 1925.

[14] K. Masao, E. Tsuchida, J. Polym. Sci., Macromol. Rev. 16 (1981) 397.

[15] E. Tsuchida, H. Nishide, Advances in Polymer Science, Vol. 24, Springer, Berlin, 1977.

[16] K. Zhang, G. Sudesh Kumar, D.K. Neckers, J. Polym. Sci., Polym. Chem. 23 (1985) 1213.

[17] S. Ying, C. Huang, X. Wan, Chinese Patent 1 257 083 (2000).

[18] H.-J. Laas, O. Wilmes, H.-U. Meier-Westhues, M. Ullrich, K. Fisher, U. Freudenberg, German Patent 19 929 064 (2000).

[19] T. Hideaki, K. Kiyoaki, T. Masahiko, Japanese Patent 09 851 (2001).

[20] H. Nakamura, K. Sunouchi, S. Terada, Japanese Patent 06 444 (2001).

[21] A. Arlt, S. Chakrabarti, M. Kreyenschmidt, D. Rodewald, German Patent 19 928 676 (2000).

[22] Z. Sakaki, S. Yamazaki, K. Suzuki, S. Tamura, T. Izukawa, Japanese Patent 09 12 706 (1997).

[23] C.M. Sungail, K.R. Riddle, Canadian Patent 2 154 622 (1996).

[24] M. Watanabe, T. Kato, M. Suzuki, Y. Amaike, T. Hirai, Jpn. J. Appl. Phys. 38 (1999) L872.

[25] B. Valenti, E. Bianchi, A. Tealdi, S. Russo, A. Ciferri, Macromolecules 9 (1976) 117.

[26] L. Seibles, J. Polym. Sci., Part A 28 (1990) 2179.

[27] G. Moroi, C. Ciobanu, E. Costea, N. Bilba, I. Palamaru, Thermochim. Acta 291 (1997) 95.

[28] G. Moroi, C. Ciobanu, N. Bilba, M. Palamaru, V. Condratov, Int. J. Polym. Mater. 39 (1998) 141.

[29] G. Moroi, C. Ciobanu, N. Bilba, M. Palamaru, Polym. Degrad. Stab. 65 (1999) 253.

[30] G. Moroi, D. Bilba, N. Bilba, Polym. Degrad. Stab. 72 (2001) 525.
[31] T. Takagishi, S. Okuda, N. Kuroki, H. Kozuka, J. Polym. Sci., Part A 23 (1985) 2112.
[32] N. Grassie, M. Zulfiqar, M.I. Guy, Eur. Polym. J. 30 (1994) 925.
[33] K. Tamaraselvy, K. Venkatarao, O. Kothandaraman, J. Polym. Sci., Part A 28 (1990) 2679.
[34] R.P. Lattimer, M.J. Polce, C. Wesdemiotis, J. Anal. Appl. Pyrolysis 48 (1998) 1.
[35] A. Ballistreri, S. Foti, P. Maravigna, G. Montaudo, E. Scamporrino, J. Appl. Polym. Sci. 26 (1981) 2781.
[36] J.S. Petrovic, Z. Zavargo, J.H. Flynn, W.J. Macknight, J. Appl. Polym. Sci. 51 (1994) 1087.
[37] S.-L. Huang, J.-Y. Lai, J. Appl. Polym. Sci. 64 (1997) 1235.
[38] W.J. Kauffman, J. Polym. Sci., Polym. Chem. Ed. 12 (1974) 1735.
[39] N. Grassie, M. Zulfiqar, M.I. Guy, J. Polym. Sci., Polym. Chem. Ed. 18 (1980) 265.
[40] N. Grassie, M. Zulfiqar, J. Polym. Sci., Polym. Chem. Ed. 16 (1978) 1563.
[41] G.W. Miller, J.H. Saunders, J. Polym. Sci., Part A-1 8 (1970) 1923.
[42] R. Arun Prasath, S. Nanjundan, Eur. Polym. J. 35 (1999) 1939.
[43] K. Matsunaga, K. Ogawa, M. Tajima, H. Okuma, Mater. Technol. 18 (2001) 385.
[44] H. Matsuda, J. Polym. Sci., Polym. Chem. Ed. 12 (1974) 2419.
[45] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[46] L. Reich, D.W. Levi, Makromol. Chem. 66 (1963) 102.