ON THE THERMAL BEHAVIOUR OF SOME POLYIMIDE MEMBRANES

EugeniaTotu[1], E. Segal[2] and A. K. Covington[3]

[1]Department of Analytical Chemistry, Faculty of Industrial Chemistry, University Politehnica Bucharest, 1–4 Polizu Str., Bucharest
[2]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest
13 Bd. Republicii, Bucharest, Romania
[3]Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne
NE2 7RU, England

Abstract

The authors present their results concerning the influence of the nature and amount of plasticizer on the thermal stability of some polyimide membranes. A non-isothermal kinetic investigation of some thermal decomposition workable steps was performed too.

Introduction

The polymeric membranes used for ion-selective devices have to exhibit a glass transition point, T_g, close to the room temperature. The T_g value of initial polymer is lowered by adding various plasticizers in the polymeric matrix. The influence of the nature and proportion of the used plasticizer in polymeric matrix on the glass transition point could be followed by thermal analysis (DSC, TG). Thus, it is possible to choose an optimum plasticizer for a given polymeric matrix. In this investigation, the influence of some plasticizers as: diethylene glycol dibenzoate (DGD) and dimethyl phthalate (DMP) on the properties of a polyimide solution was followed. Adding these substances to a polyimide solution results in flexible polymeric membranes, transparent when using DGD and opaque when using DMP. The efficiency of the plasticization was followed by help of thermal analysis on polyimide plastified membranes *vs.* non plastified polymer. There was also carried out a kinetic investigation on the thermal decomposition of the polyimide precursor.

Experimental

In this work two polyimide varietie were used as follows: commercial pre-imidized polyimide (Aldrich) and synthesized by us polyimide. The plasticizers used were two compounds compatible with the polyimide: diethylene glycol dibenzoate (DGD) and dimethyl phthalate (DMP), both purchased from Aldrich. The thermal analysis curves were recorded by help of a Perkin Elmer 7 Series Thermal Analyzer as well as with a derivatograph, at various heating rates: 1.25, 2.5, 5, 10 and 20 K min^{-1}, in the temperature range 25–1000°C.

For some samples, when it was not possible to obtain an accurate value for T_g from the DSC data either thermomechanical analysis (TMA) was performed or heat capacity data (C_p) vs. temperature curves were used. The experiments were performed by help of Perkin Elmer 7 Series Thermal Analyzer. The values of the glass transition point, T_g, of the investigated samples were graphically determined from the obtained curves, by drawing in on the curves the two tangents and calculating the T_g at the midpoint as indicated in the Fig. 1.
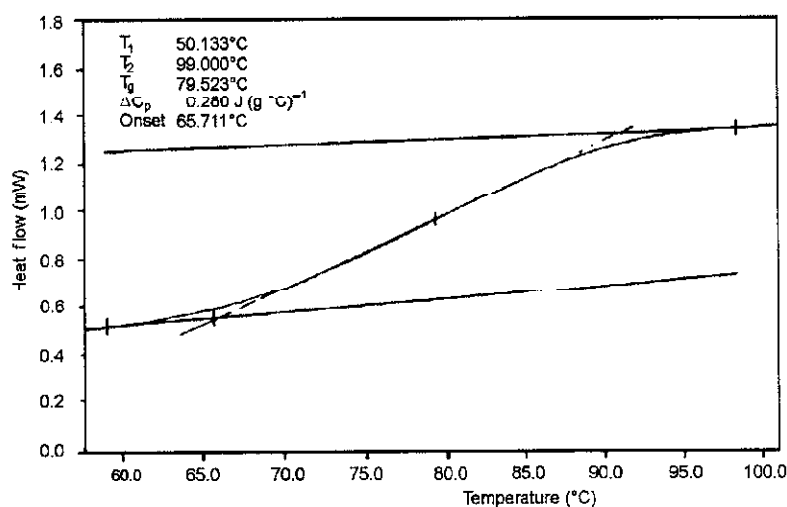

Fig. 1 The determination of T_g using a graphic procedure

The values of kinetic parameters were obtained from the derivatographic data using three integral methods: Coats-Redfern [1], Flyn-Wall [2] and Coats-Redfern modified [3], by help of a Versatil [4] program for automatic processing of data. This program also allows to simulate the thermogravimetric curve in (α, T°C) coordinates on the basis of the obtained kinetic parameters using the method Coats-Redfern, as well as to place the experimental points on it in the same coordinates.

Results and discussion

In Table 1 the variation of the initial decomposition temperature of the plasti-
fied polyimide with DGD or DMP is recorded.

Table 1 The initial decomposition temperature of the polyimide plastified with diethylene glycol
dibenzoate (DGD) and dimethyl phthalate (DMP)

Plasticizer/%	Initial decomposition temperature/ °C plasticizer	
	DGD	DMP
10	310	380
20	295	360
40	215	370
60	205	350

When compared to the polyimide without plasticizer, the initial decomposi-
tion temperature presented a lower value for the compositions containing DGD.
If DMP is used as plasticizer, the value of this temperature is not essentially
modified with respect to 398°C which is characteristic for initial polyimide.

The polymeric films obtained by help of DGD were flexible, transparent, ho-
mogeneous and without obvious microstructure superficial defects. When using
DMP, up to 15% polymer in composition (15 phr) we also obtained transparent,
flexible and mechanical resistant membranes. From a concentration of 15 phr on,
the membranes became opaque, with a poor mechanical resistance, in such a way
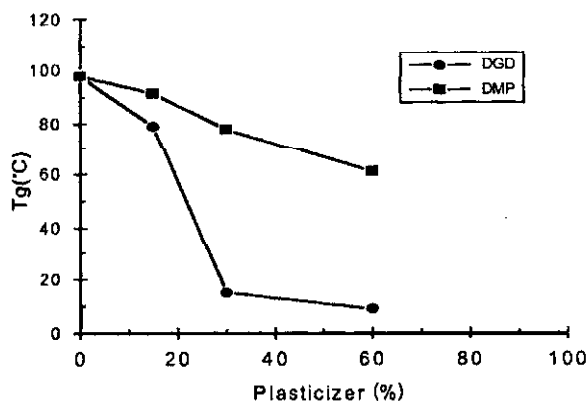that at 25 phr the samples are completely opaque and brittle.

Fig. 2 Variation of T_g values for different concentrations of plasticizer

The decrease of T_g value with the quantity of DGD or DMP in membrane composition is presented in Fig. 2. It could be observed that while the variation of the content in DGD plasticizer affects dramatically the T_g value, the DMP plasticizer presents a small effect on T_g value starting from a 15 phr polymer concentration.

The membranes based on polyimide polymeric matrix plastified with DGD, exhibit T_g values within 10–90°C temperature range. Suitable ion-selective membranes could be obtained from compositions with T_g value between 9 and 15°C. For the compositions with 40 and 60% content in DGD the T_g value was determined by thermomechanical analysis (TMA) or from the change of the heat capacity with the temperature.

The results concerning the behaviour of the membranes obtained using a mixture of the two plasticizers are presented in Fig. 3. The two plasticizers, DGD and DMP, were added in 60% total quantity in composition. It was noticed that DMP addition results in a lower effect of plasticization. The plasticizer DMP could be incorporated up to 20 phr in membrane composition when using it in mixture with DGD, unlike of a 15 phr DMP maximum content in polymeric matrix when using it alone.
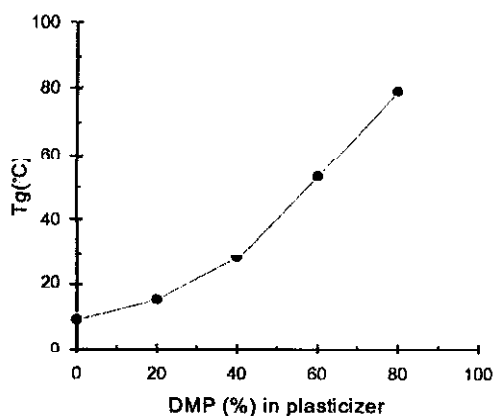

Fig. 3 Values of T_g for various compositions of polyimide with DMP/DGD plasticizers mixture. The whole quantity of plasticizer for all compositions is 60%

The selective membrane based on polyimide decomposes up to 700°C. At higher temperatures the thermogravimetric curve obtained in the temperature range at heating rate 10 K min^{-1} in nitrogen atmosphere levels – Fig. 4.

The experimental results proved that DGD can act as plasticizer for polyimide, the membranes obtained by its use being suitable for ion-selective electrodes. The system polyimide/DMP present a lower compatibility, thus reducing the chances of this compound to be used as plasticizer.

The thermogravimetric curve of the synthesized polyimide precursor was obtained by thermal analysis run in nitrogen purge gas – flow rate 50 cm^3 min^{-1}.
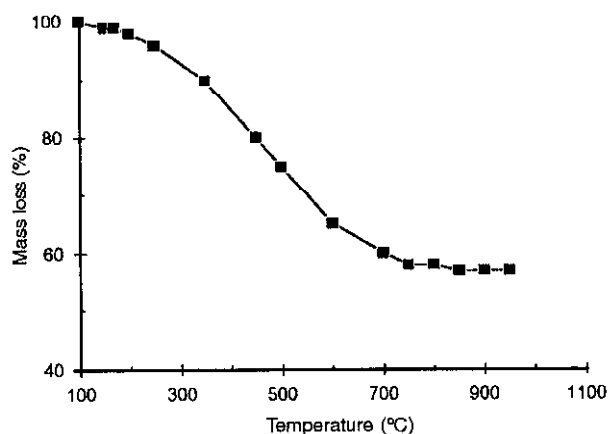
Fig. 4 Thermogravimetric curve obtained for a polyimide polymeric matrix: heating rate
10 K min⁻¹, nitrogen atmosphere

The thermal degradation of polymer started slowly. Between 25 and 103°C a small increase in mass, of approximately 0.50%, due to water adsorption, can be recorded. After heating to 500°C residual sample was black in color. The mass changes at various temperatures are listed in Table 2.

In the temperature range 120–290°C at a small heating rate, 5 K min⁻¹, the DTG analysis put in evidence a single step. Starting with 650°C the identification of decomposition steps becomes difficult due to their important overlapping. In Table 3 the values of the nonisothermal kinetic parameters determined for the kinetically workable steps are listed.

The first step of water release (step I) is due to adsorbed water loss. Taking into account the mass loss, it was shown that for each monomer unit there were lost 1.5 water molecules during the second step of adsorbed water release (step II). This value shows that there is an important amount of adsorbed water by the polymer in its whole.

There were also performed density determinations on the polymer by help of a gradient calibrated column using a mixture of hexanol and tetrachlormethane. The solvents were chosen in such way to be able to avoid the swallow of polymer samples. The density obtained in this way was 1.41 g cm⁻³. From the bulk density of the polymer, the molecular mass of the repeat unit (M=394 g) and the calculated Van der Waals volume of the polymer molecules (obtained by adding the volume increments of each atom depending on its direct surroundings) the packing coefficient K (the part of the volume which is occupied) was determined. The obtained value was 0.68. Hence 32% of polyimide matrix consists of not occupied volume, in other words 32% is free volume, accessible to an important amount of water.

Table 2 Mass change of initial polyimide (20–1000°C); sample mass 3.174 mg; heating rate
5 K min⁻¹

Temperature range/°C	Mass change/mg	Assigned process
25–103	+0.017	adsorption H_2O
105–120	–0.019	adsorbed H_2O loss (step I)
120–290	–0.035	H_2O loss; cyclisation (step II)
307–396	–0.037	CO; CO_2 loss (step III)
396–640	–1.165	CO; CO_2; H_2 loss (step IV)

Table 3 Values of kinetic parameters for the kinetically workable steps of the thermal
decomposition of synthesized polyimide precursor, at a heating rate of 2 K min⁻¹

Step	method	Kinetic parameters			
		reaction order	activation energy/ kJ mol⁻¹	preexponential factor A/s^{-1}	correlation coefficient r
	Coats-Redfern	1.30	64.7	$7.5 \cdot 10^7$	0.9992
I	Flynn-Wall	1.30	66.7	$1.8 \cdot 10^8$	0.9993
	Modified Coats-Redfern	1.10	64.5	$7.1 \cdot 10^7$	0.9995
	Coats-Redfern	1.5	57.5	$1.6 \cdot 10^3$	0.9983
II	Flynn-Wall	1.4	60.2	$6.0 \cdot 10^3$	0.9987
	Modified Coats-Redfern	1.5	59.1	$2.9 \cdot 10^3$	0.9982
	Coats-Redfern	0.8	152.3	$7.7 \cdot 10^{13}$	0.9981
III	Flynn-Wall	0.8	152.3	$7.7 \cdot 10^{13}$	0.9983
	Modified Coats-Redfern	0.7	149.3	$3.6 \cdot 10^{13}$	0.9983
	Coats-Redfern	0.8	89.6	$9.1 \cdot 10^2$	0.9939
IV	Flynn-Wall	0.8	97.0	$5.9 \cdot 10^3$	0.9955
	Modified Coats-Redfern	0.8	92.8	$1.8 \cdot 10^3$	0.9936

The thermogravimetric curve (TG) recorded for the commercial preimidized polyimide at a heating rate of 2.0 K min⁻¹, exhibits also three decomposition steps similarly with those observed for the thermal decomposition of the synthesized polyimide precursor. The first step was attributed to the elimination of ad-

sorbed water (step V), while the second step represents the water loss as result of cyclodehydration reaction (step VI). The third step of mass decrease was assigned to the loss of volatile components which occurs due to the thermal degradation of the polyimide formed during the cyclodehydration process (step VII).

In Table 4 the calculated values of the activation energy as well as of the preexponential factor for the thermal decomposition of the commercial preimidized polyimide are presented.

The inspection of Tables 3 and 4 shows a satisfactory agreement among the values of the nonisothermal kinetic parameters obtained by help of the three applied integral methods.

In Figs 5 and 6 the simulated thermogravimetric curves in coordinates (α, $T^\circ C$) for steps (II) and (IV) are presented. It is easy to observe that the experimental points are practically placed on the calculated curves, conferring in this way consistency to the obtained results.

From the inspection of Table 2, one can notice a reaction order which equals 2 for the step VII. This could be assigned to the participation of two reactant units at the decomposition. Regarding the values of the preexponential factor for the steps (II) and (IV), these are much lower than the value calculated by help of the transition state theory for a real reaction order equal to unity. The reaction order of 0.8 for the steps (III) and (IV), as well as the reaction orders of 1.3 and 1.4 for the steps (I), (II), (V) and (VI) respectively, also correspond in fact to an apparent reaction order value which equals one.

Table 4 Values of the kinetic parameters obtained for the thermal decomposition of the commercial preimidized polyimide, at a heating rate of 2 K min^{-1}

| Step	Kinetic parameters				
	method	reaction order	activation energy/ kJ mol^{-1}	preexponential factor A/s^{-1}	correlation coefficient r
V	Coats-Redfern	1.4	89.2	$9.5\cdot10^{11}$	0.9955
	Flynn-Wall	1.4	90.1	$1.3\cdot10^{12}$	0.9960
	Modified Coats-Redfern	1.3	84.9	$1.9\cdot10^{11}$	0.9954
VI	Coats-Redfern	1.4	77.9	$2.5\cdot10^{6}$	0.9953
	Flynn-Wall	1.4	80.9	$7.3\cdot10^{6}$	0.9960
	Modified Coats-Redfern	1.3	78.2	$2.8\cdot10^{6}$	0.9953
VII	Coats-Redfern	2	250.2	$2.6\cdot10^{16}$	0.9924
	Flynn-Wall	2	248.6	$1.9\cdot10^{16}$	0.9931
	Modified Coats-Redfern	1.9	252.9	$4.5\cdot10^{16}$	0.9920
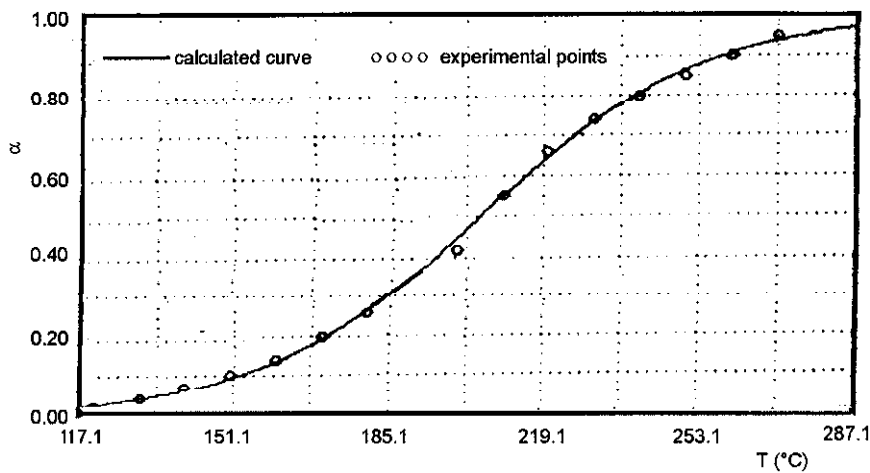
Fig. 5 The simulated curve obtained for step II of the thermal decomposition of the synthesized polyimide precursor
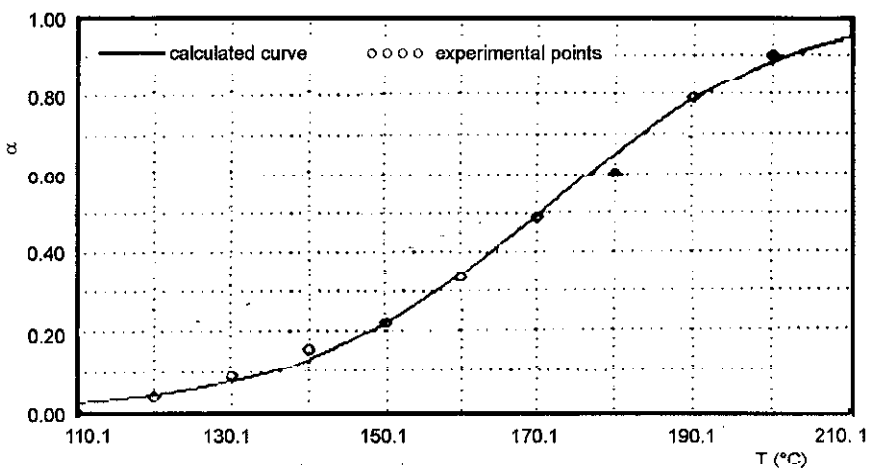

Fig. 6 The simulated curve obtained for step VI of the thermal decomposition of the commercial preimidized polyimide

Conclusions

The investigation of the thermal stability of some polyimide membranes with various compositions, showed the influence both of the nature of the used plasticizer and of the used quantity of plasticizer. Thus, the polyimide which is a vitreous material in the temperature range commonly used for ion-selective membranes determinations, could be transformed in a polymer with a glass transition

point below 20°C. It was noticed that when using DGD as plasticizer it occurs a significant decrease of the initial decomposition temperature as well as of the glass transition temperature. When using DMP as plasticizer, it was not observed a favorable decrease of T_g. The membranes containing different amounts of DGD as plasticizer presented T_g values between 10 and 90°C. Suitable ion-selective membranes were obtained from the compositions with a T_g value between 9 and 15°C. The addition of 60% DGD as plasticizer in the membrane composition resulted in a polymeric matrix characterized by $T_g=9$°C. The low value of the glass transition temperature offers the opportunity to use this polymeric matrix as base for ion-selective membranes.

The nonisothermal kinetic investigation of the workable steps showed a quite satisfactory agreement between the values of the kinetic parameters obtained by help of three integral methods.

References

1 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
2 J. H. Flynn and L. A. Wall, J. Res. Nat. Bul. Stand., 70A (1966) 487.
3 E. Urbanovici and E. Segal, Thermochim. Acta, 80 (1984) 379.
4 N. Dragoe and E. Segal, Thermochim. Acta, 185 (1991) 129.