

Synthesis and thermal properties of polyamide 6 (A)-polyimide (B) block copolymers of ABA type

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Summary

Polyimides (PI) having different molecular weights were prepared by condensation of oxydiphthalic anhydride with 9,9-bis-(4-aminophenyl)fluorene in nitrobenzene solution at 180°C. These polyimides carried two amino chain ends which allowed us to fix polycaprolactam chains (PA6) to obtain PA6-PI-PA6 type copolymers. The elemental analysis and infrared spectroscopic determination gave the proportion of PA6 (or PI) in the copolymers. The studies of thermal properties -DSC and TGA- allowed us to characterize the copolymers.

Introduction

Polyimides (PI) have good thermal properties and high temperature glass transition (1-4). Since polyamide 6 (PA6) has lower thermal properties, we studied the synthesis of block copolymers PA6-PI-PA6 with the purpose to improve the thermal stability of PA6 moieties. Thus, a polyimide having two amino chain ends was prepared, onto which PA6 moieties were grafted to give the block copolymers. Their thermal properties were studied by DSC and by TGA. The PI (or PA6) content was determined both by elemental analysis and infrared spectroscopy.

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Experimental part

All the percentages are mol-%, except PI/CL percentages which are wt-%.

1- Preparation of polyimide (PI) (5)

Oxydiphthalic anhydride (OPTA) was dissolved in nitrobenzene with a slight excess of 9,9-bis-(4-aminophenyl)fluorene (AΦ). The solution was heated for a few hours up to 180°C then, after cooling, the polymer was precipitated by pouring the solution into acetone. The crude polymer was extracted with ethanol to eliminate nitrobenzene, then dried in vacuo.

2- Copolymers with caprolactam (CL)

A mixture of 10 (or 20) weight-% of PI having different molecular weights, 60% of the total amount of CL and 0.3 to 0.8 mol-% of N,N'-isophthaloyl-di-ε-caprolactam (IPC) was heated 1h under vacuum at 25°C. Then the mixture was heated under argon at 150°C until all was dissolved. 0.3 to 0.8 mol-% of magnesium-caprolactam bromide (MgCLB) dissolved in CL was added so that the total amount of CL was 90 (or 80) wt-% of the mixture. During the reaction, small portions were extracted and treated with water or chloroform to determine the progress of the reaction. The results of the water extraction showed that the reaction is fast (about 10 min) and that more than 90% of CL was polymerized.

3- ε-caprolactam : It was purified by two crystallizations in benzene and dried in vacuo.

Magnesiumcaprolactam bromide (MgCLB) was prepared by reacting MgBrEt and caprolactam in a saturated hydrocarbon solution by the method described by Zacharkin et al.(6).

IPC was prepared by reacting caprolactam and isophthaloyl chloride in the presence of Et₃N in benzene (5).

4-DSC : The curves were registered with a Perkin-Elmer DSC 7 apparatus with an heating rate of 20 °C/min. The apparatus was calibrated using standards, 5 mg of polymers were used in sealed pans. The temperatures for the glass transitions were taken as the point of inflection, the determination being graphic.

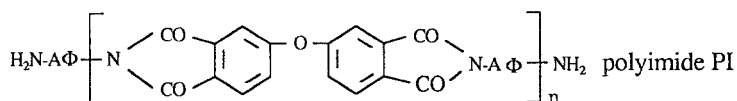
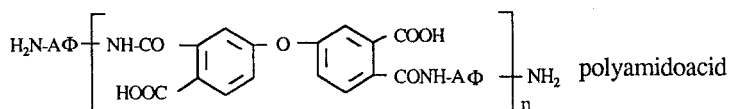
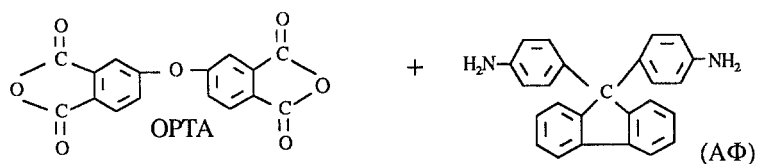
5- Thermal degradation (TGA) : The curves were obtained with a Perkin-Elmer TGA 7 apparatus between 30 and 600°C with an heating rate of 20 °C/min and with a nitrogen flow of 50 cm³/min.

6- Infrared : The spectra were recorded on a Bruker FTIR IFS 45, the polymers are included in KBr disks.

Results and discussion

Copolymer synthesis

Polyimide (PI)



The polyimides were prepared in order to obtain polymers having two amino chain ends by using a slight excess of 9,9-bis(4-aminophenyl)-fluorene with respect to anhydride. This excess allowed also the regulation of the molecular weight M of the final product (see Tab.1). The molecular weight of PI in Tab.1 was calculated from the initial composition of monomers.

Table 1 : PI and CL copolymerization conditions at 150°C

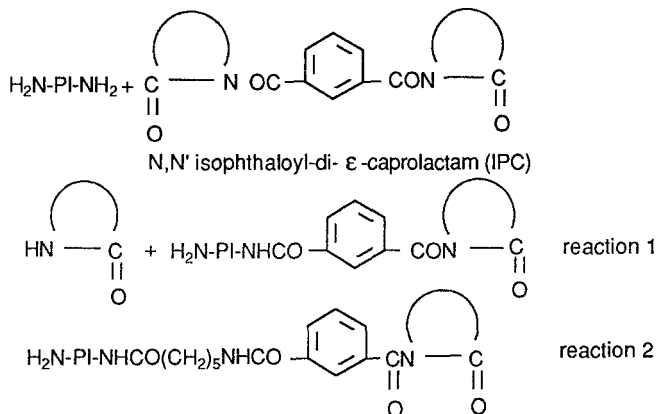
Polymer	PA 6	1	2	3	4
PI M_{calc}	—	8750	3460	6750	6750
PI wt-% ⁽¹⁾	0	10	10	10	20
CL (wt-%)	100	90	90	90	80
MgCLB (mol-%) ⁽¹⁾		0.8	0.725	0.3	0.8
IPC (mol-%) ⁽¹⁾		0.8	0.725	0.3	0.8
NH ₂ (PI)/imide (IPC) ratio R		3.2/12.8	5.6/11.5	3.2/4.8	6.4/11.4
Conversion	—	96.3	95.8	89.0	95.7
Elemental analysis ⁽²⁾	0	11.0	13.0	11.0	19.0
Infrared ⁽²⁾	0	11.8	13.8	11.0	21.8

(1) : with respect to CL

(2) : PI content of the resulting polymer

Copolymerization

When *N,N'*-isophthaloyl-di- ϵ -caprolactam (IPC) is heated to 150°C in the presence of polyimide in caprolactam solution, PI may react onto exocarbonyl (Reaction 1) or endocarbonyl (Reaction 2) groups (see formula below). In the first case, isophthaloyl group is fixed directly onto amino group of PI with elimination of a CL molecule (Reaction 1) and in the second case, IPC is fixed onto amino group of PI by the intermediate of a linear CL unit (Reaction 2).



The major reaction would be reaction (1), according to the conclusions of several authors who studied the aminolysis of *N*-acylcaprolactam using model compounds (7). Therefore the disubstitution onto PI is shown formula 1 with $q=1$, which represents the major part of the copolymers PA6-PI-PA6.(5). However, if we consider the ratio $R = \text{NH}_2(\text{PI})/\text{imide}(\text{IPC})$, the following values are obtained (calculated from experimental conditions : Table 1) : $R = 0.25 ; 0.49 ; 0.67 ; 0.56$ for copolymers 1 to 4 respectively. These values correspond to ratios : $1 \text{ NH}_2/4\text{IPC}$, $1\text{NH}_2/2\text{IPC}$, $2\text{NH}_2/3\text{IPC}$ and $1.1\text{NH}_2/2\text{IPC}$ for copolymers 1 to 4 respectively. Copolymer 2 and 4 having the same ratio would have nearly the same composition and a relatively low percentage of pure PA6. The probability to obtain a higher percentage of pure PA6 is shown in copolymerization 1. These three copolymers having various percentage of pure PA6 would have mainly the formula 1 as copolymer. In the case of copolymer 3, the ratio, $2\text{NH}_2/3\text{IPC}$, diamino PI may react onto both caprolactam ends of IPC instead of one, which has given a copolymer partially insoluble in usual solvents of pure PA6. The PI content of the insoluble fraction is about 85% (from elemental analysis). Anyway this fraction is not very important since the elemental analysis (11.0-13.0-11.0-19.0) as well as the infrared determination (11.8-13.8-11.0-21.0) of the crude product have given the same PI content which is not very different from that of Table 1. The difference observed may be due

either to the yields (89.0 to 96.3) and/or to the technique of polymerization. Copolymers 1 to 4 would be constituted mainly by the formula 1 with variable proportions of pure PA6 and of IPC multiple substitution by PI.

The copolymers being only partially soluble, it was not possible to prepare films for infrared study. All the infrared spectra were recorded with KBr disks between 1900 and 1500 cm^{-1} . In this area, there appear the amide I and II of pure PA6 (8) at 1642 and 1545 cm^{-1} and, in the copolymers, amide I and II and the carbonyl band of polyimide at 1780 and 1736 cm^{-1} . These carbonyl bands allow to determine the PI content of the copolymers.

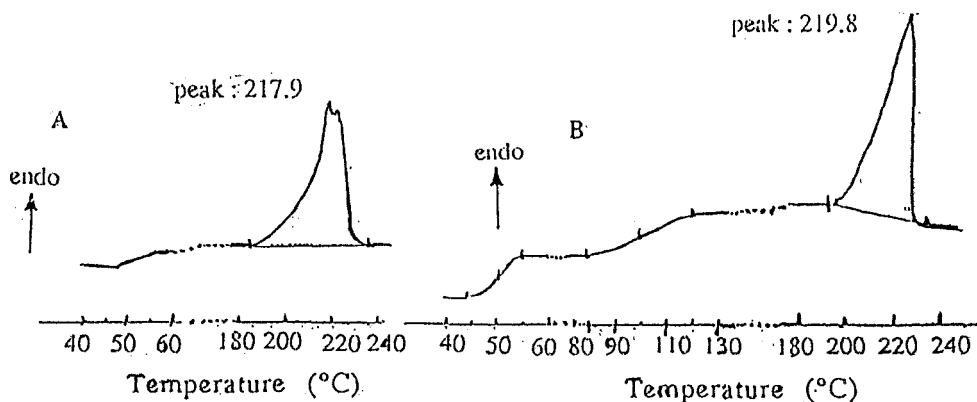
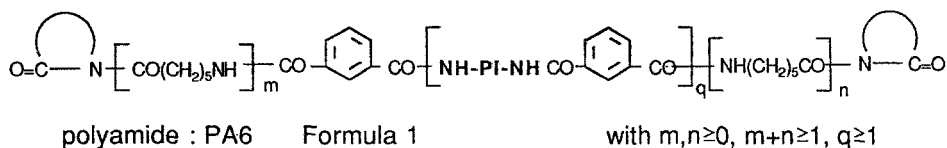


Figure 1 : DSC curves ; A : pure PA6, B : copolymer 4

Melting behavior : The experimental values of the enthalpies of melting of pure PA6 (Fig.1, curve A) and of PA6 moieties of the copolymers (Fig.1, curve B), ΔH_{exp} , were corrected taking into account the PI content of the copolymer to give ΔH_{corr} values (see Tab.2). From the value of pure PA6 and the PA6 content in the copolymer from elemental analysis, the enthalpies of fusion of PA6 moieties may be calculated, ΔH_{calc} . The presence of PI moiety in the copolymers did not have a strong influence on the structure of PA6 moieties since the enthalpies (ratio $\Delta H_{\text{corr}}/\Delta H_{\text{calc}}$ varies between 0.92 and 1.05) as well as the temperatures of fusion (about 220°C) of the copolymers are not different from that of pure PA6.

T_gamide : The glass transition of pure PA6 is situated at 48°C with a $\Delta C_p = 0.37$ J/g.deg. This transition can be seen in the DSC curves of copolymers (Fig 1, curve B). The organization of the amorphous phase of PA6 moiety may be changed from that of pure PA6. This perturbation, due to the presence of PI in the copolymers, is not strong enough to have an influence on T_g°C for copolymers 1 to 4. Anyway the ΔC_p values of the copolymers are about half of pure PA6 value : 0.16 instead of 0.37. The higher ΔC_p value of copolymer 4 (0.23 instead of 0.16) could be explained by a higher PI content in this copolymer. These observations show that ΔC_p is more sensitive to the environment than the ΔH of melting. The ratio $\Delta C_p(\text{copolymer})/\Delta C_p(\text{pure PA6})$ is about 0.5 whereas the values of $\Delta H_{\text{melting}}$ ratio (corr/calc) lie between 0.92 and 1.0.

Table 2 : Melting enthalpies of pure PA6 and of PA6 moieties of copolymers and glass transition of pure PA6 and of PA6 and PI moieties in the copolymers

polymer	PA6	1	2	3	4
$\Delta H_{\text{exp}}(\text{J/g})^{(1)}$	75.5	57.4	56.0	55.2	51.8
$\Delta H_{\text{corr}}(\text{J/g})^{(2)}$	--	64.5	64.4	62.0	64.0
$\Delta H_{\text{calc}}(\text{J/g})^{(3)}$	--	67.2	65.7	67.2	61.2
PA6 % (4)	100	89	87	89	81
ratio ΔH corr/calc	--	0.96	0.98	0.92	1.05
T _g (PA6) ⁽²⁾ °C [ΔC_p : J/gdeg]	48 [0.37]	45 [0.16]	49 [0.16]	45 [0.16]	49 [0.23]
T _g (PI) ⁽¹⁻²⁾ °C [ΔC_p : J/gdeg]	--	100[0.45]	100[0.28]	100[0.49]	110[0.45]

(1) : DSC, 20 K/min ; (2) : Corrected taking into account PI content in the copolymer ; (3) : Calculated from ΔH_{exp} of pure PA6 and the PA6 % in the copolymer ; (4) : PA6 % from elemental analysis.

T_gimide : All copolymers have an imide glass transition at about 100°C having a ΔC_p value of about 0.45 J/g.deg. Copolymer 2 has a value of 0.28 J/g.deg. This lower value would be due to a lower molecular weight of the PI moiety, 3500 instead of 6500 to 8700 for the others. The glass transition of pure PI should be much higher, but we must keep in mind that the molecular weights of our PI moieties have a maximum value of 8700, which limit the value of T_g.

Thermogravimetry (TGA)

We studied the thermal degradation of pure PA6 and of the copolymers. The curves are shown in Fig.2 :

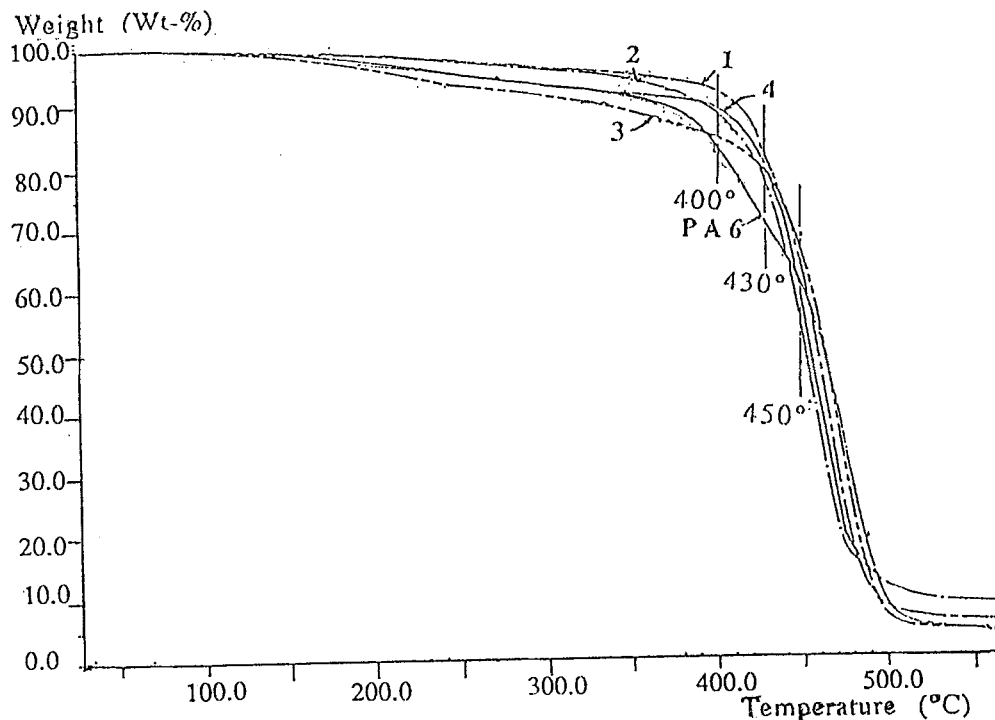


Figure 2 : Thermal degradation of PA6 and copolymers 1 to 4

a- No degradation occurs before 150°C ; b- At 250°C, copolymers 1 and 2 present practically no degradation whereas pure PA6 and copolymer 4 have about 5% and copolymer 3 about 10% of degradation ; c- At 400°C, copolymer 1 has only about 7.5% of degradation which reaches 12% for copolymers 2 and 4 and 15% for pure PA6 and copolymer 3. d- At 430°C, the copolymers have almost the same degradation, about 20%, whereas 30% of pure PA6 is degraded. e- Beyond 450°C (weight loss of about 40%), all polymers have nearly the same curves up to 480°C (weight loss about 80%).

Discussion :

Beyond 430°C, all curves of the copolymers 1 to 4 are super-imposable. At this temperature, the weight loss is about 20% for the copolymers instead of about 30% for pure PA6. It is well known that the

melted PA6 is in equilibrium with the CL monomer and that the fraction of cyclic monomer increases as the temperature is raised. This is essentially a splitting off of monomer. Above 450°C the degradation is not only due to a simple depolymerization but includes also to the chain splitting. Pure PA6 presents the same degradation as the copolymers from 450°C, i.e., above about 40% of weight loss. The difference of thermogravimetric behavior between pure PA6 and copolymers below 450°C is due to the presence of PI in the chain. It seems therefore that the block polyimide stabilizes the PA6 moiety since the apparent weakness of the PA6 between 380 and 450° has disappeared in the degradation curves of copolymers.

Conclusion :

The synthesis of block copolymers of ABA type, PA6-PI-PA6, has given polymers mainly having the expected structure, but also containing a certain proportion of copolymers of pure PA6 and of higher PI content. The proportion of these secondary structure depends mainly on the ratio $\text{NH}_2\text{PI/imide IPC}$ used in the synthesis. However the presence of the PI moieties have rather low influence on the melting. The influence is higher on the ΔC_p values of the glass transitions. This difference has been explained by some disturbance of the amorphous phase due to the presence of polyimide. TGA shows that the thermal behavior of pure PA6 has been improved in the copolymers.

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