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Thermal stability studies of polyamides and their block copolymers

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Abstract

Thermogravimetry-Fourier transform infra-red spectroscopy (TG-IR) was used to study the thermal stabilities and thermal degradation mechanism of α-carboxy-polycaprolactam prepolymers (PA6), amine-terminated rigid aromatic polyamide prepolymers (PPIA) and their block copolymers (PA6–PPIA–PA6). The results showed that the thermal stability of the block copolymers was improved by the block polycondensation, which eliminates the unstable terminal groups, and the strong hydrogen bond interaction between the amide linkages.

Keywords: Aromatic polyamide; Aliphatic polyamide; TG-IR thermal stability

1. Introduction

Although the effects of reinforcing fibers and fillers on the mechanical properties of polymeric composites are well documented [1], it still has adverse effects on the processable ability of the resultant materials. A concept called “molecular composites” has been developed by Takayanagi [2], in which the reinforcing molecules retain their rigidities and are dispersed uniformly in the ductile matrix polymer. Considerable efforts have been taken by many researchers [3–4] to explore this principle in order to prepare a new category of high-performance polymeric materials. One of the most important approaches is to design and synthesize the suitable reinforcing component, which is generally a block, graft or multipodes copolymer [5–6]. Thus, the synthesis of the prepolymers with designed molecular weight and reactive functional end-groups becomes more important.

A novel approach to prepare the so-called “melt-processable molecular composites” has been developed recently by Xu et al. [7], in which a series of model block copolymers with different rigid and flexible blocks were designed and synthesized. One of the most important tasks in such a work is to analyze the detailed structures and increase the thermal stability of the reinforcing phase, which directly affect processing and practical application.

TGA has previously been used to study the thermal stability of the block copolymers and the prepolymers [8]. The thermal degradation mechanism was based on the decomposition temperature, the fraction of weight loss and other estimated results. Thermogravimetry-Fourier transform infrared spectroscopy (TG-IR) is a novel analytic technique to study the chemical structures and thermal decomposition mechanism of a polymer [9–12]. TG-IR gives simultaneously a TGA curve and the IR spectrum of the gas from the TG system. The IR spectrum combined with the derivative thermograms (DTG) makes it possible to estimate the scission points on the polymer chain and deduce the thermal decomposition mechanism. In this work, this method was used to determine the thermal stability and decomposition mechanism of carboxy-polycaprolactam (PA6), amine-terminated rigid aromatic polyamide prepolymers (PPIA) and their block copolymers (PA6–PPIA–PA6).

In inert gases, there are two basic courses of thermal degradation, which depend on the chemical structure and the reaction conditions. One is the elimination of low molecular

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weight compounds at the chain-end or side-chain, and the other is main-chain random scission or stepwise depolymerization. The scission of main-chain will begin from the weakest chemical bonds. Depolymerization of main-chain will produce monomer, but random scission will result in molecular fragments, which might have different structures than the monomer. Therefore, in anaerobic thermal degradation, we can study in detail the decomposition mechanism through the information from the IR spectra.

2. Experimental

2.1. *Synthesis of pre-polymers and their block copolymers*

2.1.1. *Synthesis of the α-carboxy-polycaprolactam (PA6)*

ε-Caprolactam (0.531 mol), benzoic acid (40.5 mmol) and water (15.0 mmol) were mixed, placed in a reactor designed by our lab, degassed with vacuum for half an hour and then sealed. The reaction was carried out in a salt-bath at 250 °C for 5 h. Product was dissolved in formic acid, precipitated in water and filter. Molecular weight was determined by viscometry, related intrinsic viscosity is 0.11. Detailed descriptions and characteristics will be published in JAPS in 2004 [13]. The formulation is as follow:

$C_6H_5CO\!-\!\!\left[NH(CH_2)_5CO\right]_m\!\!-\!OH \qquad (m=12)$

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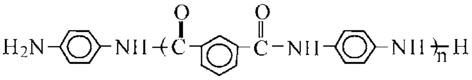
2.1.2. *Synthesis of the amine-terminated rigid aromatic polyamide prepolymers (PPIA)*

Direct high-temperature polycondensation of terephthalic acid (IPA), *p*-phenylene diamine (PPD; mole ratio of the two monomers IPA:PPD = 0.923) was carried out in the mixed solvent [pyridine (Py), *N*-methyl-2-pyrrolidone (NMP) and LiCl (LiCl: 3.5%, Py:NMP = 2:3)] in the present of triphenyl phosphate (56.11 mmol) in N_2 at 105 °C for 6 h. Products were extracted by ethanol for 48 h to remove residual monomer, and yield was 94.9%. Molecular weight was strictly controlled by the ratio of the two monomers. Fourier transform infra-red spectroscopy (FT-IR) and GC/MS were used to characterize the chemical structure, especially the nature of the end-group [14]. Formulation of the result is as follow:

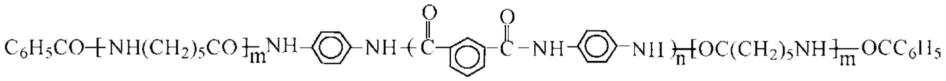


$H_2N\!-\!C_6H_4\!-\!NH\!-\!\left[\overset{O}{\overset{\|}{C}}\!-\!C_6H_4\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH\!-\!C_6H_4\!-\!NH\right]_n\!\!-\!H \qquad (n=25)$

.

2.1.3. *Synthesis of the block copolymers (PA6–PPIA–PA6)*

The block copolymers were synthesized by “two step high-temperature polycondensation” in our lab based on the phosphated reaction [15]. First the rigid block was synthesized as mentioned above, after the reaction, the solution of PA6 prepolymer ([*η*] = 0.11) in the mixed solvent of triphenyl phosphate, pyridine, *N*-methyl-2-pyrrolidone, and LiCl was added into the system and then the block polycondensation continued at 110 °C for 12 h. Product was precipitated in alcohol and then extracted by absolute alcohol for 48 h, dried, then extracted by formic acid for 48 h. Flaxen powder was gained and yield was found to be higher than 90%. FT-IR, HPyGC/MS and WAXD were used to characterized the chemical structure, especially the junction of the two prepolymers. Formulation of the copolymer is as follow:



$C_6H_5CO\!-\!\!\left[NH(CH_2)_5CO\right]_m\!\!NH\!-\!C_6H_4\!-\!NH\!\left[\overset{O}{\overset{\|}{C}}\!-\!C_6H_4\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH\!-\!C_6H_4\!-\!NH\right]_n\!\!\left[OC(CH_2)_5NH\right]_m\!\!OCC_6H_5$

(m = 12 and n = 25) .

2.2. *Instruments and experimental condition*

The thermal decomposition studies were performed over a temperature range of 20–800 °C with a NETZSCH TG-209 under nitrogen at the heating rate of 10 °C/min. The outlet of the TGA was coupled on-line with a BRUKER VECTOR-22 Fourier transform infra-red spectrophotometer through an interface that consisted of a gas cell heated to 230 °C to prevent condensation on the windows. A heatable line connects the interface with TGA. In the FT-IR, high sensitivity MCT detector is used and real-time dynamic response, three-dimensional spectra are recorded with a resolution of 2 cm^{-1}. All the samples were dried in vacuum for 24 h at 100 °C before analysis.

3. Results and discussion

3.1. *Thermal stability of the α-carboxy-polycaprolactam prepolymers (PA6)*

Fig. 1 shows the TGA weight loss and DTG of PA6 obtained in a nitrogen atmosphere. Fig. 2 is the stacked IR spectra of gas escaping from TGA at different temperature. In Fig. 1, the α-carboxy-polycaprolactam prepolymers decomposed above 300 °C by a two step decomposition, the first one at 300–400 °C, and the second one at 400–500 °C. The residue left is about 1.28%, which comes from high temperature carbonization of benzene rings. The FT-IR spectrum

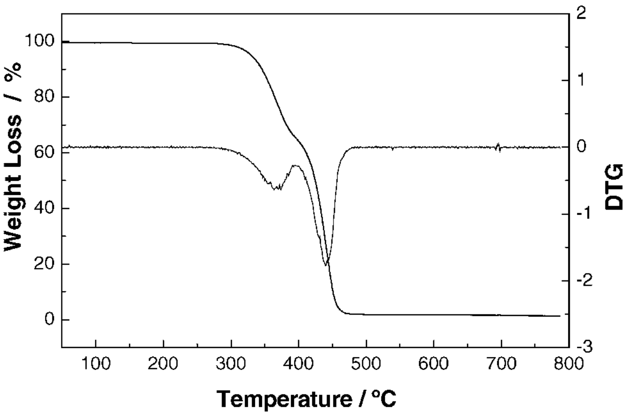


Fig. 1. TGA and DTG curves of PA6 prepolymer under N_2.

shows that random scission of the molecular chain occurred in the PA6 pre-polymer, and mainly on the C–N bonds of amido groups (–CONH–) and the C–C bonds of carbon –carbon skeletal chain, as related spectra (Fig. 2) did not show the three characteristic absorption bands of the amido groups (3256, 1646 and 1548 cm^{-1}). The primary bands were the absorption peaks of aliphatic aldehyde group (–COH, 1759 cm^{-1}), diketo group (–CO–CO–, 1711 cm^{-1}), methyl and methylene (2938 cm^{-1} and 2870 cm^{-1}) and amino group (3441 cm^{-1}), etc. At 370 °C, as shown in Figs. 1 and 2, a complete thermal breakdown of the chain started and yielded a mixture of simple hydrocarbons, absorption bands of carbon dioxide and carbon monoxide began to appear. The absorption band area reaches its maximum at about 440 °C, and derivative curve in Fig. 1 gives the same information with the maximum decomposition temperature ($T_{\max}$) at 441 °C. The pre-polymer was decomposed completely at 500 °C and micro-absorption of mono-substitution terminal benzene groups was detected in the IR spectra. Thermal decomposition products of PA6 prepolymer at different times are shown in Scheme 1.

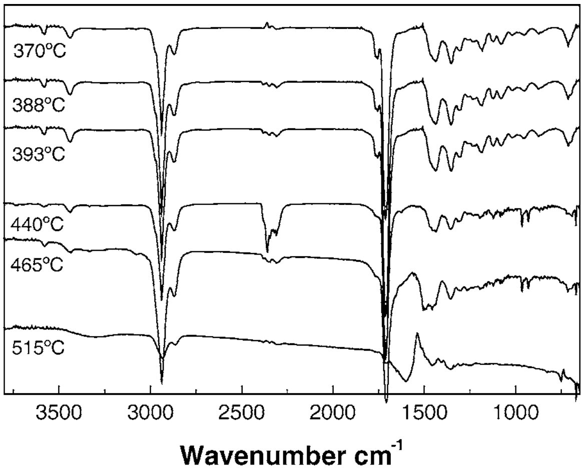
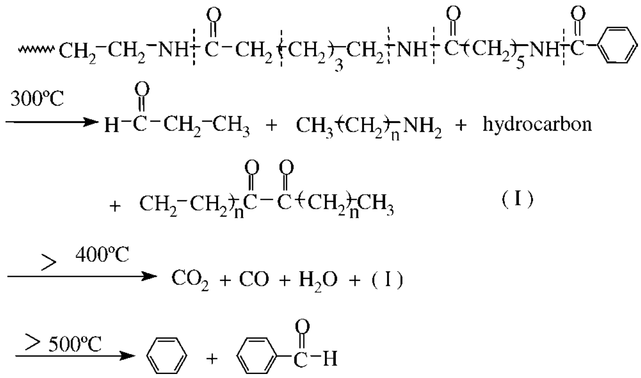


Fig. 2. IR spectra of gas escaping from PA 6 prepolymer at different temperature (in N_2).



Scheme 1. Thermal decomposition products of polycaprolactam prepolymers; (I) indicates the main decomposition products at the first step.

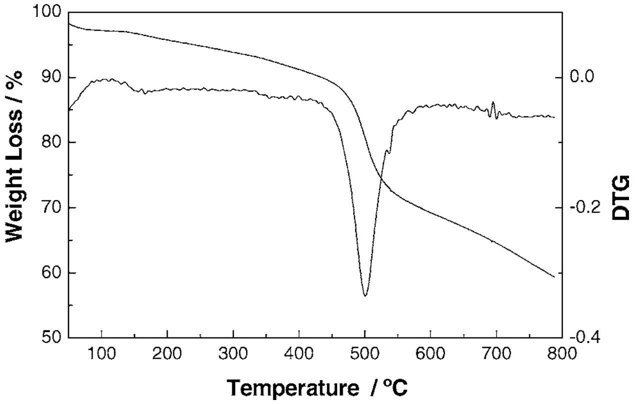


Fig. 3. TGA and DTG curves of PPIA prepolymer under N_2.

3.2. Thermal stability of the amine-terminated rigid aromatic polyamide prepolymers (PPIA)

Fig. 3 shows the TGA weight loss and DTG of the aromatic polyamide PPIA obtained in a nitrogen atmosphere. Fig. 4 is the stacked IR spectra of gas escaping from TGA at different temperature. Fig. 3 shows that the amine-terminated rigid

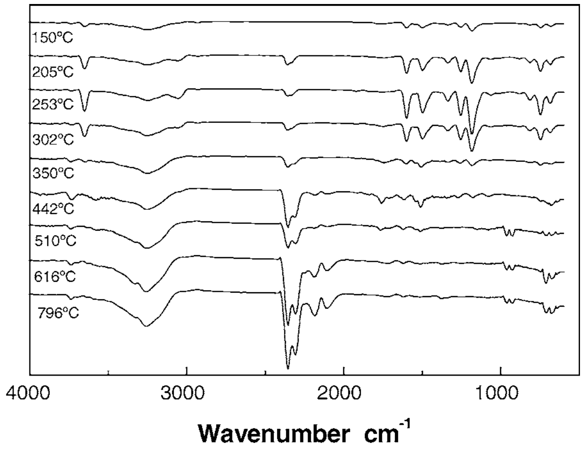
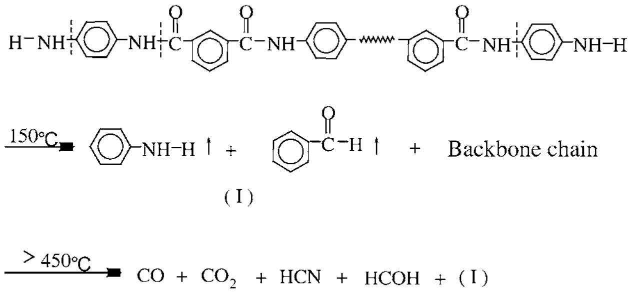


Fig. 4. IR spectra of gas escaping from PPIA at different temperature (in N_2).



Scheme 2. Thermal decomposition products of PPIA prepolymers; (I) indicates the two fragments at the first step.

aromatic polyamide did not show good thermal stability and began to scission at 150 °C. Decomposition of main-chain occurred over 450 °C, and finished at about 550 °C, but weight loss still occurred slowly at higher temperature. The T_{max} is about 500 °C and the residue left is about 61%. The aromatic polyamide should exhibit good thermal stability due to the planar benzene structure, linear molecular chain and excellent rigidity. But, because PPIA has reactive amine terminal groups, elimination will occur, as shown by Fig. 4. The fragments from low-temperature decomposition are $-NH_2$ (3367 and 3256 cm^{-1}) and some benzene derivatives from the chain-ends (3057, 1600, 880, 813 and 747 cm^{-1}, etc. At higher temperature (about 442 °C), the decomposition is mainly on the C–N bonds of amido groups (–CONH–), and the products are carbon dioxide (2356 cm^{-1}), carbon monoxide (2183 cm^{-1}), HCN (2309 cm^{-1}), and a small quantity of phenylamine (3325 and 3258 cm^{-1}), formaldehyde (1765 cm^{-1}) and benzaldehyde (1705 cm^{-1}). The fraction of weight lost is low mainly due to the benzene structure. Thermal decomposition products of PPIA prepolymer at different times are proposed in Scheme 2.

3.3. *Thermal stability of the block copolymer (PA6–PPIA–PA6)*

The nature of the chemical components present in a formulation is clearly the most important factor affecting the thermal stability. Many studies on the thermal stability of main-chain liquid crystalline polymers have shown that the instability is due to unstable, reactive terminal groups. So, to improve thermal stability, and to avoid self-aggregation and maintain the well-dispersed status of PPIA in the blends, a series of model block copolymers with a sequence PA6–PPIT–PA6 were designed and synthesized. The most important issue is that the reactive terminal groups of the rigid segments were substituted by the flexible PA6 blocks to eliminate the unstable factor and improve the thermal stability of the copolymers.

Fig. 5 shows the TGA and DTG curves of PA6–PPIT–PA6 block copolymer under N_2. Fig. 6 is the stacked IR spectra of gas escaping from TGA at different temperature. The block copolymer shows good thermal stability, thermal scission occurs above 335 °C. Comparing the three TGA curves (Figs. 1, 3 and 5), substitution of the reactive terminal groups in the rigid segments by the flexible PA6 blocks does lead to excellent structural stability at high temperature, better thermal stability than either the rigid block of PPIA or the flexible segments of PA6. The fraction of weight lost for the copolymer is intermediate of those for the two prepolymers. From the FT-IR spectra of gas escaping from PA6–PPIT–PA6 block copolymer at different temperature (Fig. 6), carbon dioxide was detected in the IR system at the very beginning of scission, and three characteristic absorption bands of amido bond (3256, 1646 and 1548 cm^{-1}) can be seen for the block copolymer, the major mechanism of thermal degradation is random scission, which is the same with PA6 prepolymer, but the breakpoint is not located at amido bond (–CO–NH–), but from the aliphatic carbon chain, and yields volatile products such as CO_2 (2356 cm^{-1}) and CO (2183 cm^{-1}). Change in the way of scission may be due to the strong hydrogen bond interaction between the rigid and flexible blocks, which enhances the stability of the amido bond. So bond scission of –C–N– in –CONH– does not happen at 300 °C (Fig. 6), leading to the improved thermal stability of the block copolymer. Complete scission of the aliphatic chain is at 410 °C, as the

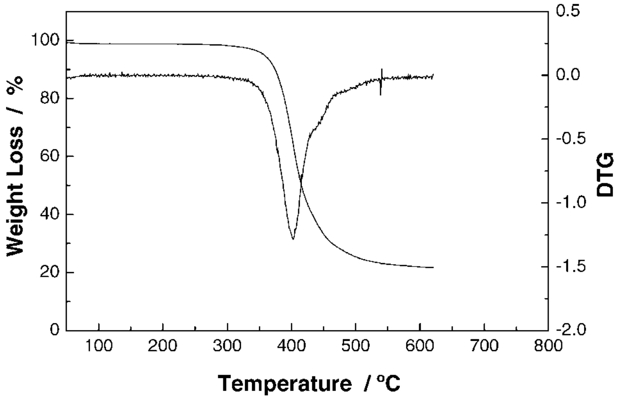


Fig. 5. TGA and DTG curves of PA6–PPIA–PA6 block copolymer under N_2.

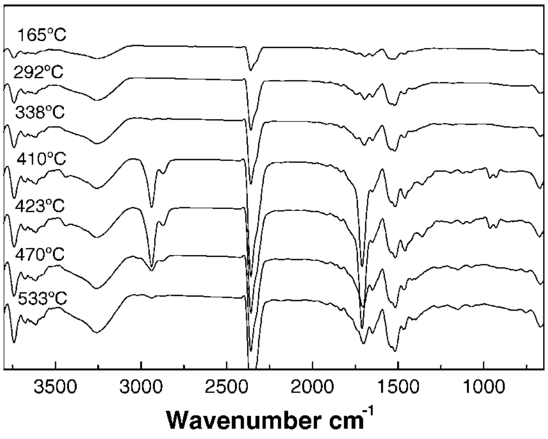


Fig. 6. IR spectra of gas escaping from PA6–PPIT–PA6, block copolymer at different temperature (in N_2).

IR spectrum shows the absorption bands of methyl methylene groups (2938 and 2871 cm^{-1}), unsaturated aldehyde group (1709 cm^{-1}) and amido bond.

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