Anionic Polymerization and Properties of Graft Copolymers Consisting of Alternating Styrene/Maleimide Copolymer Main Chains and Polyamide 6 Grafts

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ABSTRACT: This article is focused on the synthesis of a new type of graft PA6, which contained alternating styrene/maleimide copolymer main chains and PA6 grafts, by anionic polymerization. The preprepared styrene/maleimide copolymers with acylated caprolactam (ACL) pendants were used as macroactivators for the polymerization of molten ε-caprolactam (CL). Because of the low activating energy for the initial nucleophilic attack of CL anion on the *N*-ACL, the polymerization took place in a few minutes. The macroactivators were characterized by ^{1}H-NMR. And the thermal properties, dimensional stability, crystallinity, and solvent resistance ability of the graft PA6 were studied, using DSC, TGA, XRD, water absorption measurement, and solubility experiment. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1880–1886, 2008

Key words: polyamide 6; styrene/maleimide copolymer; graft copolymer; anionic polymerization; macroactivator

INTRODUCTION

Nowadays, because of the simplicity, polymer blends have been extensively studied and many new products have been manufactured to achieve improved properties generally not available in any single polymeric material, e.g., toughness, chemical resistance, ease of fabrication, etc.[1–3] This route has the concept of molecular composite. It is defined as being dispersion of a small amount of a reinforcing rigid-rod rod-like polymer in a random-coil polymer matrix. Such molecularly reinforced new polymers can show excellent mechanical properties and heat resistance.[4–7] Whereas phase separation at the interfaces between the dispersed phase and matrix has seldom been avoided. Generally speaking, most combinations are immiscible. So, a compatibilizer, which is able to improve the interfacial interaction between the polymers, is desirable. The compatibilizer is generally considered to have the ability of reducing the size of dispersed phases, and stabilize the dispersed phase. Thus, this article focused on the synthesis of a new serial of graft PA6 copolymers by chemical route.

It is well known that the polymers containing *N*-substituted maleimides and their derivatives can be classified as polyimides, important high-performance engineering plastics, being a class of rigid polymers. Because of the imide rings and flexible chain segments in the backbones,[8] such polymers are known to be resistant to high temperature ($T_g \geq 500$ K) and solvents, with high dimensional stability. Nevertheless, they have some disadvantages, such as very low impact strength at break, leading to crack under stress.[8,9] Polyamide 6, usually known as nylon 6, is a versatile material that combines excellent mechanical properties and good resistance to chemicals. But PA6 has a low T_g (about 320 K), a low heat distortion temperature and high moisture absorption. Thus, the drawbacks of the two types of mentioned polymers can be remedied by blending. Since the poor miscibility, a compatibilizer, with block or graft structure, containing imide rings and PA6 chains, will be necessary.[8–10]

This article focused on the synthesis of a kind of pure graft copolymers with PA6 grafts and alternating styrene/maleimide copolymer main chains. First, styrene/maleimide alternating copolymers were presynthesized. Second, acylated caprolactam (ACL) moieties were incorporated into the backbones, from which PA6 chains could grow. Unlike reactive compatibilization or *in situ* polymerization, both the interfacial area limitation and steric hindrance effects are supposed to be much reduced or totally absent by this route.[11]

EXPERIMENTAL

Materials

Styrene was distilled under reduced pressure and stored in a refrigerator. 2,2′-Azobis(isobutyronitrile)

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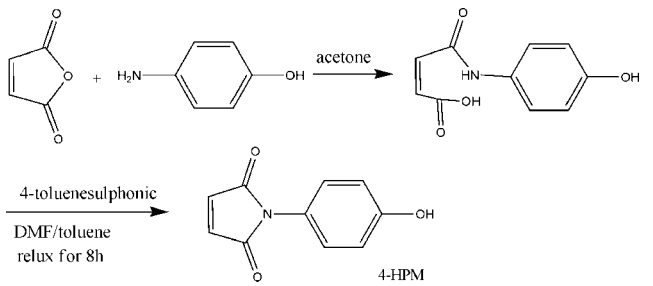

Figure 1 Synthesis of 4-HPM.

(AIBN) was recrystallized from methanol and dried at 60°C in a vacuum oven overnight. Aniline was distilled under reduced pressure. 4-Aminophenol was recrystallized from ethanol. Toluene was purified by distillation in the presence of anhydrous calcium oxide. ε-Caprolactam (CL) (China Petroleum and Chemical Corp.) was recrystallized from acetone twice (m.p.: 79–70°C and b.p.: 268.5°C). 2,4-Toluene diisocyanate (TDI) was purified by distillation under reduced pressure. Ethanol, methanol, petroleum ether (b.p.: 60–90°C), phosphorus pentoxide (P_2O_5) were used as received. *N*,*N*-dimethylformamide (DMF) was dried by 4A molecular sieve over night and distilled under reduced pressure. Chloroform ($CHCl_3$), dibutylin diaurate (DBTDA) (BZL Reagent), *m*-cresol, formic acid (HCOOH), NaOH, and LiBr were used without further purification.

Preparation of *N*-(4-hydroxyphenyl) maleimide

N-(4-hydroxyphenyl) maleimide (4-HPM) was synthesized from maleic anhydride and 4-aminophenol by two-step method described in Figure 1 according to the literature procedure.[12] This orange-yellow crystalline needles were obtained in a yield of 60%, m.p. 183°C. ^{1}H-NMR spectrum (DMSO-d_6, δ): 6.8 (2H, —CH=CH—), 7.0–7.1 (4H, aromatic protons), 9.7 (1H, —OH).

Preparation of *N*-phenyl maleimide

Phenyl maleimide (PM) was prepared (Fig. 2) according to Ref. 13 ^{1}H-NMR spectrum (DMSO-d_6, δ): 7.1 (2H, —CH=CH—), 7.3–7.5 (5H, aromatic protons).

General procedure for the synthesis of macroactivators containing alternating styrene/maleimide copolymer main chains and ACL pendants (α and β)

α: A three-necked flask fixed with a thermometer, a refluxcondenser, N_2 inlet tube, and a mechanical stirrer was charged with TDI (0.02 mol, 3.48 g), CL (0.02 mol, 2.26 g), three to four drops of DBTDA as catalyst, and toluene (80 mL). Reacted for 4 h at 105°C.

To another three-necked flask equipped with a thermometer, a refluxcondenser, N_2 inlet tube, and a mechanical stirrer was charged with styrene (0.02 mol, 2.3 mL), 4-HPM (0.01 mol, 1.89 g), PM (0.01 mol, 1.73 g), AIBN (0.13 g, 2 mol %), and 100 mL toluene. The polymerization was carried out at 75°C for 6 h. Then dropped the solution of the first step slowly in 30 min. The mixed solution gradually turned into yellow. At last, precipitated in petroleum ether with vigorous stirring for two times, a yellow powder was obtained. Dried in a vacuum oven overnight at 80°C. The synthesis procedure was showed in Figure 3 ($m = n$). The pendant density of ACL was 25%. Molecular weight by gel permeation chromatography (GPC): $M_w = 1.29 \times 10^4$, $M_n = 4.81 \times 10^3$. Elemental analysis: C, 71.41%; H, 5.48%; N, 8.47%. Found: C, 71.58%; H, 5.60%; N, 8.36%. And it was characterized by ^{1}H-NMR (DMSO, δ) (Fig. 4). 1.6–1.8 ppm (4H, lactam); 2.2 ppm (3H, aromatics-CH_3); 9.7 (1H, CL—CO—NH-aromatics); 11.4 (1H, —NH—COO-aromatics); 6.6–7.6 ppm (aromatics protons).

β was treated with styrene, 4-HPM, and PM (molar ratio 5 : 1 : 4) in the same manner described for α. In Figure 3, it can be seen that $m = 4n$. Pendant density of ACLs was 10%. $M_w = 1.25 \times 10^4$, $M_n = 4.28 \times 10^3$. Elemental analysis: C, 74.64%; H, 5.45%; N, 6.63%. Found: C, 74.81%; H, 5.62%; N, 6.55%. The ^{1}H-NMR spectrum (DMSO, δ) was showed in Figure 4.

Synthesis of graft PA6 copolymers from alternating styrene/maleimide copolymers containing acylated caprolactam moieties

Graft PA6 copolymers in this study were obtained by using functionalized alternating styrene/maleimide copolymers (α or β) as macroactivators (molar content of ACL moieties was varying from 0.4 to 1.5%). Sodium caprolactam (NaCL) was chosen as initiator and its molar content to ε-CL was kept constant at 3%. The graft copolymers prepared were summarized in Table I. In a typical synthesis (α-0.4), NaCL was prepared by reaction of stoichiometric amount of NaOH and ε-CL in a three-necked flask at about 100°C for 2 h, distilled under reduced pressure to

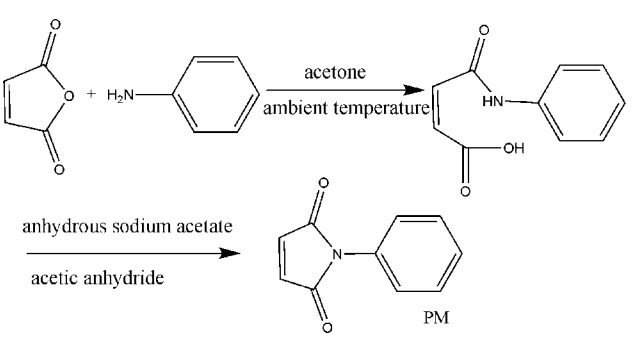

Figure 2 Synthesis of PM.

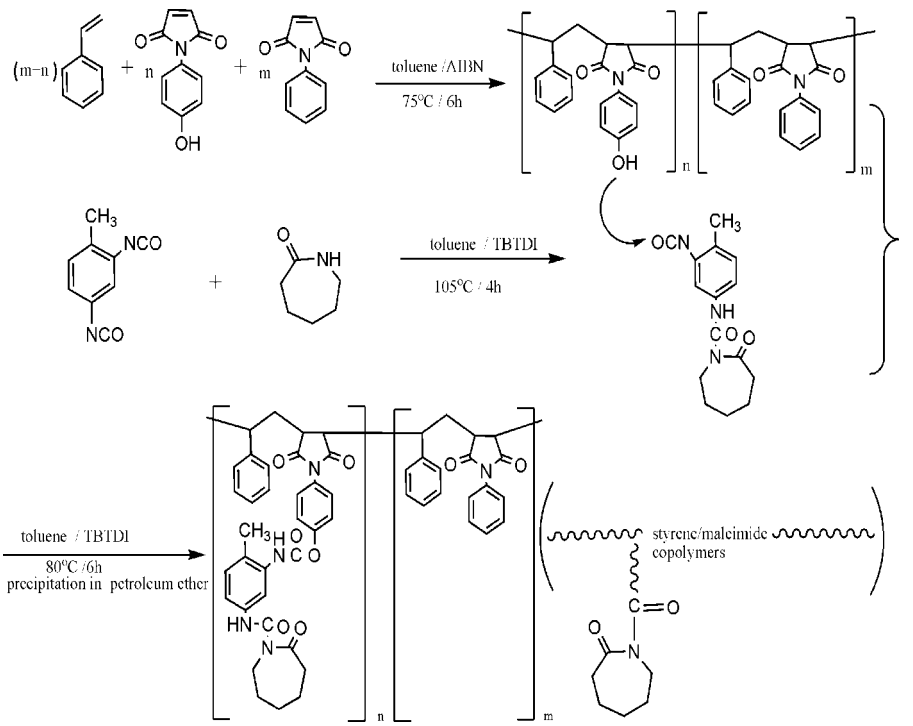

Figure 3 Synthesis of macroactivators: α ($m = n$) and β ($m = 4n$).

remove liberated H_2O. Then α (0.34 g, containing 0.61 mmol ACL moieties, 0.4 mol %) and CL (8.5 g, 75 mmol) were introduced into an ampoule, which were heated, evacuated, and filled with nitrogen several times. The mixture was dissolved and mixed at 140°C. After that, the NaCL component prepared earlier was poured into the ampoule and mixed well in an ultrasonicator at 75°C for 15 min. Finally, the mixed reactants were allowed to polymerize at 170°C for 30 min. All graft copolymerization was conducted in a heated-oil bath whose temperature was monitored by a thermocouple. For analysis, graft polymers obtained first were cut into pieces, then grinded in a Thomas Mill at room temperature. All samples were extracted with methanol in a Soxhlet extractor for 12 h, and dried at 80°C in a vacuum oven overnight.

Measurements

FTIR analysis was performed on a Nicolet Nexus 670 FTIR spectroscopy between 4000 and 400 cm^{-1} in the form of KBr pellets. ^{1}H-NMR spectra of macroactivators and monomers were recorded in DMSO-d_6 using TMS as internal standard on a 600 MHz Hitachi av600 NMR Spectrophotometer. GPC measurement of macroactivators was carried out with the DMF and LiBr (0.5 mol L^{-1}) mixture as the mobile phase at 55°C on a Waters instrument (Waters 1515 isocratic HPLC pump, Waters 2414 refractive index detector, PLgel MIXED-C column). The system was calibrated with PS standards whose molecular weights were 197,000, 55,100, 30,200, 13,900, and 2970, respectively. The flow rate chosen was 1.0 mL min^{-1}. DSC was performed on Perkin-Elmer DSC-7, with a temperature ranging from 20 to 300°C and sample weight of about 10 mg under nitrogen atmosphere. Samples, encapsulated in aluminum pans, were heated to 300°C at a rate of 10°C min^{-1} and held for 5 min at this temperature to cancel their thermal history, then cooled to 20°C at a rate of 40°C min^{-1}. Finally, the sample was reheated to 300°C at a rate of 10°C min^{-1}. The recorded temperatures were calibrated using Indium as standards. Crystalline melting temperature (T_m) was obtained as the maximum of the melting endotherm. Percentage

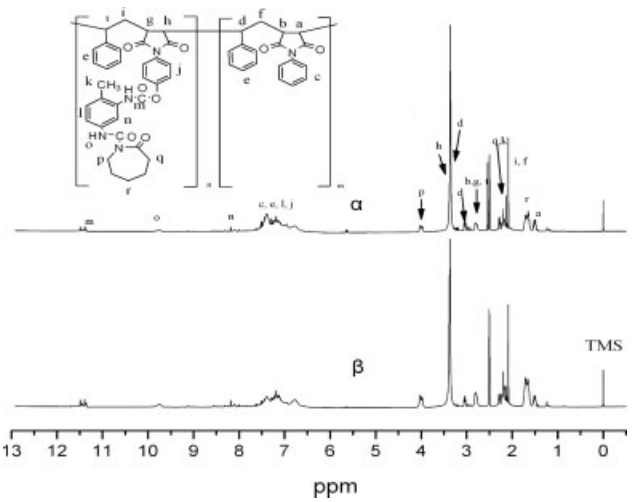

Figure 4 ^{1}H-NMR spectra of macroactivators: α and β.

TABLE I
Comparison of Pure PA6 and Graft PA6 Obtained from Two Kinds of Macroactivators

Sample	Graft density (%)	C_m (%)[a]	Macroactivator content (wt %)	Water absorption (%)[b]	η_{inh}[c]
Pure PA6		96.8		4.8	2.26
α-0.4	25	96.0	2.0	4.5	1.12
α-0.8	25	96.2	3.8	4.4	1.02
α-1.5	25	96.5	7.0	3.8	1.00
β-0.5	10	94.4	5.8	4.1	0.85
β-1.0	10	97.1	11.0	3.7	0.58

[a] Monomer conversion calculated by eq. (1).
[b] Water absorption calculated by eq. (2).
[c] Intrinsic viscosity measured at 25.0°C in H_2SO_4 (98%).

crystallinity (χ_{DSC}) of the copolymers was calculated via the ratio between the measured and equilibrium heats of fusion ($\Delta H_f/H_f^\circ$). The equilibrium heat of fusion ΔH_f° is 230 J g^{-1} for 100% crystalline MCPA6.[14] TGA was performed on a Perkin-Elmer DSC-7. Predried powders (about 2 mg) were heated from 25 to 500°C at 10°C/min under nitrogen. The degradation temperature was taken as the temperature at which the sample lost 5% of its original weight. XRD were performed on a Rigaku D/Max2500 diffractometer (Ni-filtered, Cu/Kα radiation of wavelength 0.154 nm) in the reflection mode over the range of diffraction angles (2θ) from 5° to 45° at ambient temperature. The voltage and tube current were 40 kV and 200 mA, respectively. Percentage crystallinity (χ_{XRD}) was calculated by a standard procedure.[15,16] The intrinsic viscosities of graft polyamide 6 and pure PA6 were measured on 98% sulfuric acid at a concentration of 1g dL^{-1} with a suspended level Ubbelohde viscometer at 25.0°C ± 0.1°C.

RESULTS AND DISCUSSION

In this research, alternating styrene/maleimide copolymers with ACLs were chosen as macroactivators. And pure PA6 was prepared by using TDI as microactivator. Because of the much lower activating energy for the initial nucleophilic attack of CL anion on the *N*-ACL, the polymerization took place in a few minutes. Both the microactivator and macroactivator own high activating capacities. In practice, *N*-ACL is the most commonly used activator for the conventional monomer cast process. Moreover, *N*-carbamoyl-caprolactam,[16,17] isophthaloyl-biscaprolactam,[18] and other performed ACLs[19] were also used as activators. In this study, NaCL was chosen as initiator and its molar content to ε-CL was kept constant at 3%. The use of TDI and macroactivators in this study resulted in the polymerization of CL in less than 20 min at 170°C.

Characterization of prepared macroactivators

Figure 4 is ^{1}H-NMR (DMSO, δ) spectra of macroactivators: α and β, with proton assignments of α. They display the same chemical shift, just with different proton numbers (look into detailed data of α). The peaks at 6.6–7.6 ppm are assigned to aromatics protons of styrene, TDI, and benzene rings of *N*-substituted maleimide, respectively. 1.6–1.8 ppm (4H, lactam), 2.2 ppm (3H, aromatics-CH_3); 9.7 (1H, CL—CO—NH-aromatics), 11.4 (1H, —NH—COO-aromatics). These characteristic peaks imply that ACL moieties have incorporated into the styrene/maleimide copolymer main chains. 1.5 ppm was the absorption band of maleimide (—C—CH—C=O—). Thus the results fully confirm the formation of macroactivators.

Preparation and characterization of graft PA6

The general procedure for the preparation of graft PA6 is showed in Figure 5, choosing two kinds of alternating styrene/maleimide copolymers containing ACL pendants (α and β, with different graft density) as macroactivators. They are expected to act as the main chains and react with the catalyst of NaCL to generate the graft PA6. FTIR spectra of pure PA6 and selected graft PA6 samples are shown in Figure 6. Pure PA6 displays characteristic absorptions at 3305

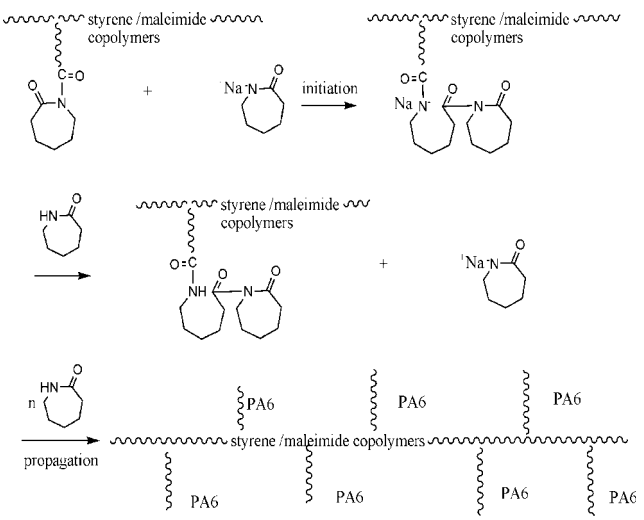

Figure 5 Mechanism for the synthesis of graft PA 6 using α or β as macroactivator.

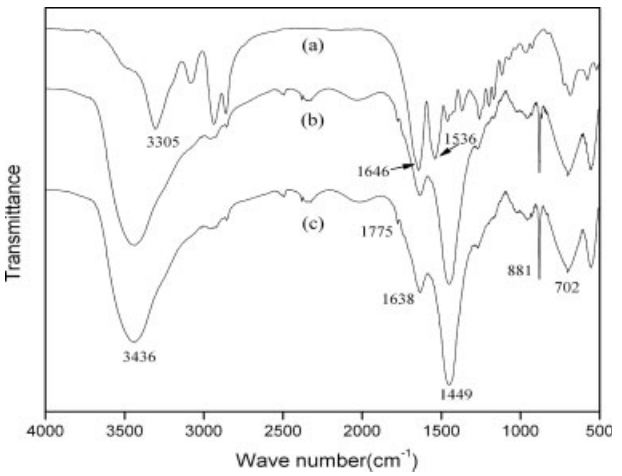

Figure 6 FTIR spectra of (a) pure PA6, graft PA6 of (b) α-1.5, and (c) β-1.0.

cm^{-1} (N—H stretch vibration), 1646 cm^{-1} (C=O), 1536 cm^{-1} (N—H deformation). It can be seen from Figure 6 that graft PA6 samples of α-1.5 and β-1.0 display somewhat the same FTIR absorptions, and show both the characteristic absorptions of pure PA6 and styrene/maleimide copolymers. This is evidence that styrene/maleimide main chains are linked to the PA6 chains. 3436 cm^{-1}(N—H stretch vibration), 1638 cm^{-1} (stretching, C=O), 1775 cm^{-1} (stretching of C=O, imide), 702 cm^{-1} (bending of C=O), 1449 cm^{-1} (= C—H, aromatics), and 881 cm^{-1} (=C—H).

Graft PA6 copolymers prepared in this work are listed in Table I. Take a typical graft PA6, α-1.5, for example. In this case, α refers to the macroactivator type (In Fig. 3, $m = n$). The number 1.5 designates the molar content of ACL moieties in total ε-CLs. The key question for this research is whether the PA6 chains are successfully grafted onto styrene/maleimide copolymer main chains. To answer this question, selective solvent extraction was chosen to evaluate the purities of the graft copolymers. This method was carried out by weighing powder samples before and after Soxhlet extraction by methanol for 12 h to remove unreacted CL and oligomers [eq. (1)]

$$\text{Monomer conversion } (\%) = \frac{(M_2 - M_1)}{(M_0 - M_1)} \times 100 \quad (1)$$

where M_0 is the weight of dried sample, M_1 is the pro rata weight of macroactivator contained in the sample, M_2 is the dried weight of sample left after extraction with hot methanol for 12 h.

After the successful extraction, dried powder samples were emerged in DMF at an elevated temperature (50°C), weighing before and after this procedure, and no weight lose could be observed. This phenomenon implies that the macroactivators, which could dissolve in DMF, have completely grafted by PA6 chains.

As can be seen in Table I, with the amount of the macroactivators (α or β) increases, the intrinsic viscosities of the graft PA6 decrease. This is because the length of PA6 segments decreases on amount of the more activator sites. Also, since the graft structure itself always relates to low intrinsic viscosity, the graft PA6 prepared in this study displays lower intrinsic viscosities compared to pure PA6.

Monomer conversion results are listed in Table I. With the added macroactivator content increasing, the monomer conversion increases. All graft PA6 samples own high monomer conversion as pure PA6 (from 94.4% to 97.1%). Thus, the activation capacity of macroactivators with ACL prepared in this research seems to be similar to that of a microactivator like TDI.

In summary, on the basis of the results reported earlier, there is no doubt that the polymerization of CL in the presence of NaCL as initiator and alternating styrene/maleimide copolymers with ACL pendants (α and β) as macroactivators leads to the formation of pure graft copolymers.

Thermal behaviors

To compare the thermal behaviors of graft PA6 with pure PA6, an accurate investigation into both the thermal transitions and the degree of crystallinity has been made by DSC and TGA analysis. Typical DSC thermalgrams of pure PA6 and graft copolymers are shown in Figure 7. Table II summarizes the thermal properties of pure PA6 and graft PA6. From it, T_m's of graft copolymers do not show obvious difference with that of pure PA6; several samples are a little higher and several lower. Theoretically, added alternating styrene/maleimide copolymers should result in increased $T_{m.}$ But they can also destroy the hydrogen bonding of polyamide and hinder crystallization of the PA6 segments, and relate to more PA6 imperfect

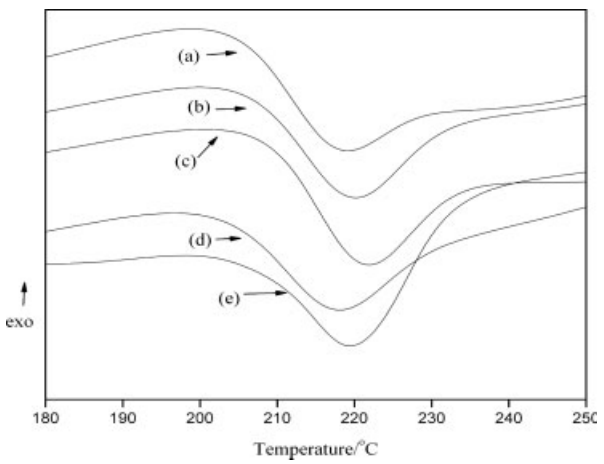

Figure 7 DSC traces of four different graft PA6 samples of (a) α-1.5, (b) β-0.5, (c) α-0.4, (d) β-1.0, and (e) pure PA6.

TABLE II
Thermal Properties and Crystallinity of the Graft Copolymers

Trial	T_g (°C)[a]	T_m (°C)[b]	T_{dec} (°C)[c]	ΔH_f (J g^{-1})[d]	χ_{DSC} (%)[e]	χ_{XRD} (%)[f]
Pure PA6	47	219	338	57.9	25.2	23.7
α-0.4	52	221	349	48.3	21.0	20.8
α-0.8	53	219	355	43.2	18.8	18.2
α-1.5	57	218	369	37.3	16.2	15.6
β-0.5	53	220	348	46.7	20.2	18.5
β-1.0	55	217	352	44.4	19.3	17.8

[a] Glass transition temperature.
[b] Melting temperature.
[c] Temperature at which a 5% weight loss occurred in N_2 with a heating rate of 10°C min^{-1}.
[d] Heat of fusion.
[e] Percentage crystallinity calculated by DSC.
[f] Percentage crystallinity calculated by XRD.

crystallites. Thus the contrary effects seem make the content and graft density of macroactivators do not exert any obvious relationship with T_m.

As far as T_g values are concerned, T_g's of graft PA6 are about 5–10°C higher than that of pure PA6. It is speculated that the increase in T_g is due to the constrained chain mobility in the PA6 segments.

The thermal decomposition properties of the graft PA6 have been evaluated by TGA analysis in a nitrogen atmosphere at a heating rate of 10°C/min (Table II). The decomposition temperature is about 10–31°C higher than that of pure PA6 upon the incorporation of 2–11 wt % alternating styrene/maleimide copolymers into the graft PA6. With their content increasing, the decomposition temperature rises.

Crystallinity

X-ray diffraction is a powerful method to evaluate the crystallinity in semicrystalline materials. DSC is also used to calculate the percentage crystallinity of PA6 samples. The results show that the degree of crystallinity decreases with increase in alternating styrene/maleimide copolymer content. There is an excellent agreement between the XRD and DSC estimates of crystallinity for all samples, although the DSC data are shifted to higher values. That is mostly because the crystallization of the graft PA6 will be hindered greatly by the added alternating styrene/maleimide copolymers, and the degree of imperfection of its crystals will increase. The crystalline content of PA6, by and large, defines the mechanical property. XRD patterns of pure PA6 and selected graft PA6 are shown in Figure 8. The crystalline regions of graft PA6 and pure PA6 give the same two characteristic peaks of α form at $2\theta = 20.0^\circ$ and $2\theta = 23.8^\circ$, corresponding to the reflections of the crystalline planes (200) and (002) + (202), respectively.[15,20] Russo and coworker[20] have reported that at relative low polymerization (<185°C) temperature, all PA6 almost exclusively present the α form, with very little or no content, if any, of γ form. It was conformed in this work.

Dimensional stability of graft copolymers

The dimensional stability of graft copolymers could be evaluated by water absorption. PA6 is semicrystalline material and extremely sensitive to water absorption because of the existence of interchain hydrogen bonding sites between amide groups. To compare the water absorption of graft PA6 with pure PA6, a relative way was chosen. First, emerged some dried powder samples (about 10 g, weighing M_0), which were extracted by hot methanol, at ambient temperature in water for 24 h. Second, they were removed, patted dry with a lint free cloth, and weighed (M_3). Water absorption of samples was calculated by the equation as follow.

$$\text{Water absorption } (\%) = \frac{(M_3 - M_0)}{M_0} \times 100 \quad (2)$$

The water absorptions of polymers are listed in Table I. It can be seen that all the graft copolymers obtained in this research have lower moisture absorption than that of pure PA6. With the increase in alternating styrene/maleimide copolymer amount, the water absorptions of graft copolymers decrease. The

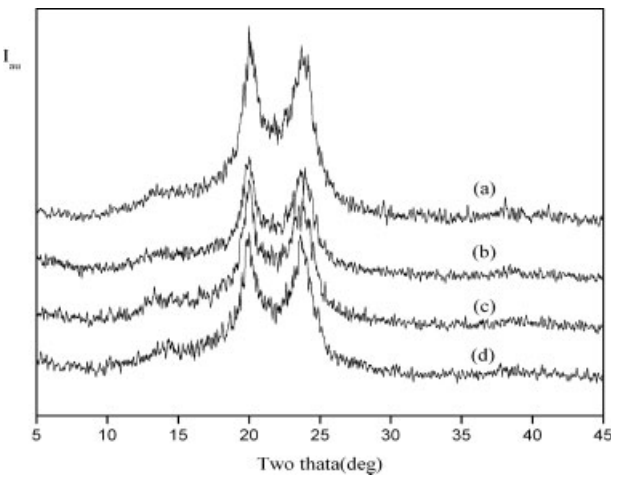

Figure 8 XRD patterns of (a) pure PA6 and graft PA6: (b) β-1.0, (c) α-1.5, (d) β-0.5.

TABLE III
Solubility of the Graft Copolymer Compared with Pure Polyamide 6

Solvent	ε-caprolactam	Macroactivator (α)	Pure polyamide 6	Graft copolymer
H_2O	+	−	−	−
HCOOH	+	+	+	+
Methanol	+	−	−	−
DMF/LiBr	+	+	+	−
DMSO	+	+	−	−
H_2SO_4 (98%)	+	+	+	+
m-cresol	+	+	+	+
$CHCL_3$	+	−	−	−

All solubility test were performed at ambient temperature. +, soluble; −, insoluble.

most possible reason for this phenomenon is that the alternating styrene/maleimide copolymers are of hydrophobic nature. With their weight percentage increasing, the hydrophilic PA6 chain content relatively decreases. And also, crystallinity should be taken into account. The degree of crystallinity decreases with increase in alternating styrene/maleimide copolymer content (Table II). It is worth mentioning that water molecules can only diffuse into the amorphous phase and displace ''disordered'' amide–amide hydrogen bonds, but they cannot penetrate into the crystal domain.[21] That is to say low degree of crystallinity always relates to high water absorption. Thus, from the results in Table I, this hypothesis was not conformed. So, it is postulated that the hydrophobic nature of styrene/maleimide copolymer displays the main reason for the decreased moisture absorption of graft polymers.

Solubility of copolymers

It is well known that polyamide 6 is resistant to most common chemical solvents, and is only soluble in HCOOH, phenol, DMF/LiBr, and *m*-cresol at ambient temperature or in aliphatic at an elevated temperature.[4–7] In this research, synthesized macroactivators (α and β) containing alternating styrene/maleimide copolymer main chains and ACL pendants can dissolve in aprotic polar solvents such as DMF, DMSO, but they are not soluble in $CHCl_3$, ethanol, and water. Comparing the solubility of obtained graft PA6 with pure PA6, it is found that they can almost dissolve in the same several solvents (Table III). But the pure PA6 can dissolve in DMF/LiBr solution while the graft PA6 cannot. From the above findings, it seems that graft PA6 shows better solvent resistance.[7]

CONCLUSIONS

In this research, a new kind of graft PA6 containing styrene/maleimide copolymer main chains and PA6 grafts has been successfully prepared by anionic polymerization with high monomer conversion. By this way, two types of macroactivators (α and β), with different graft densities, have incorporated into the PA6 matrix. On the basis of the earlier results, the following conclusions can be drawn: with the added macroactivator content increasing, graft PA6 copolymers show better thermal behaviors. More specifically, T_g's of graft PA6 are about 5–10°C higher than that of pure PA6, while the decomposition temperature is about 7–21°C higher. But the content and graft density of macroactivators seem do not exert any obvious relationship with T_m. The degree of crystallinity decreases with increase in alternating styrene/maleimide copolymer content, but the crystal structure of polyamide is not affected in this research. Moreover, the graft PA6 shows better solvent resistance ability and better dimensional stability than those of pure PA6. So, it is speculated that this graft PA6 may provide interesting practical application in various fields.

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