

Synthesis of Nylon 6,6 Copolymers with Aromatic Polyamide Structure

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Received 29 November 1999; accepted 7 July 2000

ABSTRACT: In this article, flexible nylon 6,6 was reinforced with rigid-chain aromatic polyamides based on poly(4,4'-diphenylsulfone terephthalamide) (PSA), poly(*p*-diphenyl oxide terephthalamide) (POA), poly(*p*-diphenylmethane terephthalamide) (PMA), and isophthaloyl chloride (IPC). Various high molecular weight block copolyamides were synthesized by solution polymerization using *p*-aminophenylacetic acid (*p*-APA) as a coupling agent. Their thermal properties show that the block copolyamides exhibit higher values of T_g and T_m and better thermal stability than those of nylon 6,6, especially the IPC-modified nylon 6,6. The order of increased thermal properties of copolyamides is IPC > POA > PMA > PSA. From wide-angle X-ray diffraction patterns, it was found that nylon 6,6 has two diffraction peaks, that is, $2\theta = 20.5^\circ$ and 23° , while the multiblock copolymers showed only one at $2\theta = 20^\circ$, indicating a different crystal structure. It was found that the mechanical properties of the IPC-modified nylon 6,6 were improved more than those of the semirigid copolyamides. The order of tensile strength was IPC > PSA > PMA > POA, but for elongation, it was POA > PMA > PSA > IPC. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2167–2175, 2001

Key words: modified nylon 6,6; poly(4,4'-diphenylmethane terephthalamide); poly(*p*-diphenyl oxide terephthalamide); poly(4,4'-diphenylsulfone terephthalamide)

INTRODUCTION

In the last few years, a number of attempts have been made to increase the mechanical properties of aliphatic nylons by incorporating aromatic polyamides such as Kevlar or polybenzamide (PBA).^{1–3,4–7} Recently, we took a different approach using the concept of a coupling agent, aminoacetic acid (*p*-APA), to link an aromatic polyamide to nylon 6 in the main chain. Several aromatic–aliphatic copolyamides were obtained using this approach.^{5–7}

In this article, aromatic polyamides such as poly(4,4'-diphenylsulfone terephthalamide) (PSA),

poly(*p*-diphenylmethane terephthalamide) (PMA), poly(*p*-diphenyl oxide terephthalamide) (POA), and isophthaloyl chloride (IPC) were used as reinforcing components in block copolymers to improve the mechanical and thermal properties of nylon 6,6 connected by the coupling agent. The effect of these aromatic polyamide structures on the thermal and mechanical properties of the block copolymers is discussed.

EXPERIMENTAL

Materials

Nylon 6,6 was obtained from the Monsanto Co. (USA). The sample was first dissolved in formic acid and poured into a large amount of water. The filtered precipitate was refluxed with methanol and hot water for 16 h each, then dried at 100°C under a vacuum for 8 h. 4-4'-Diaminodiphenyl

Contract grant sponsor: National Science Council, Republic of China.

Journal of Applied Polymer Science, Vol. 80, 2167–2175 (2001)
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Table I Elemental Analysis of Nylon 6,6 Prepolymer

| | Elemental Analysis (%) | | |
|-------|------------------------|------|------|
| | C % | H % | N % |
| Calcd | 66.4 | 8.86 | 12.9 |
| Found | 65.1 | 9.91 | 13.5 |

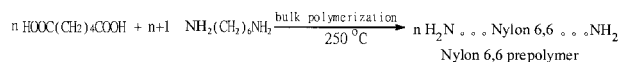
sulfone (DDS), *p*-diaminodiphenylmethane (DDM), and *p*-diaminodiphenyl oxide (DDO) were obtained from the Dah-Yi Chemical Industries Co. (Taipei, Taiwan). Both IPC and *p*-aminophenylacetic acid (*p*-APA) were purchased from the Merck Co. (Darmstadt, Germany) and used as received. The homopolymers of PMA, POA, and PSA were synthesized in our laboratory as described previously.^{7,8}

N-Methyl-2-pyrrolidone (NMP) was first distilled over CaH₂ at 92–94°C/14 mmHg and then stored over molecular sieves. Lithium chloride (LiCl) was dried under a vacuum at 160°C for 5 h and used with NMP as a solvent. The moisture content of a 5% LiCl solution in NMP was found to be 0.018 wt % by the Karl–Fischer Moisture Meter, MKA-3, Kyoto Electronic.

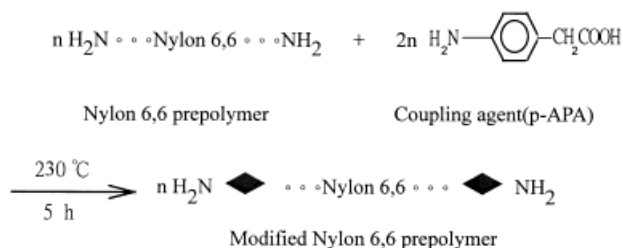
Synthesis of Block Copolyamides

Wholly Rigid Modified Nylon 6,6 Copolyamide

Before synthesizing nylon 6,6 with IPC, a low molecular weight diamine-terminated nylon 6,6 prepolymer was prepared using an excess of hexamethylenediamine (HMDA).^{4,7} Then, this prepolymer was reacted with a *p*-APA coupling agent at 230°C for 5 h to form the modified nylon 6,6 prepolymer:

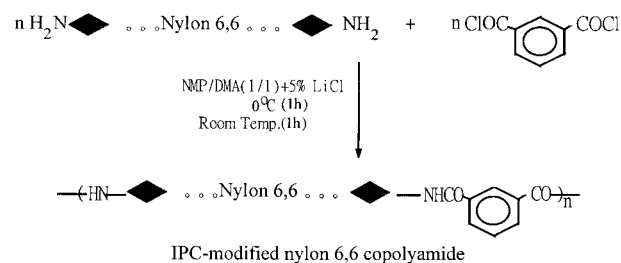


and then



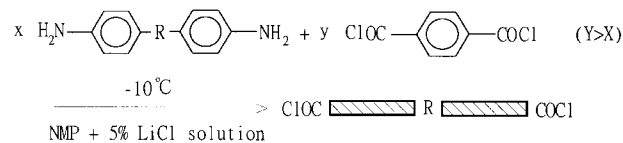
Finally, the diamine-terminated nylon 6,6 prepolymer was reacted with IPC in an NMP + 5%

LiCl solution to form an IPC-modified nylon 6,6 copolyamide, as shown below:



Semirigid Nylon 6,6 Copolyamides

Low molecular weight diacid chloride-terminated semiaromatic polyamides were prepared by low-temperature polycondensation of semiaromatic diamines with excess terephthaloyl chloride (TPC):



R = -CH₂-, -O-, or -SO₂-

This prepolymer was then reacted with the modified nylon 6,6 prepolymer to form a semirigid nylon 6,6 copolyamide, as shown below:

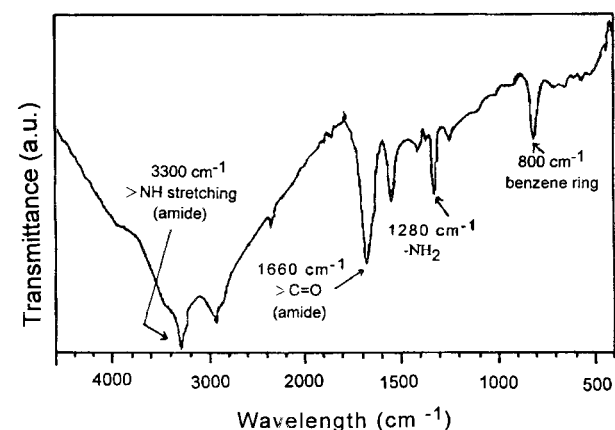
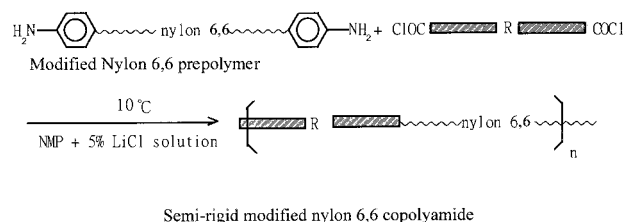


Figure 1 Infrared spectrum of modified nylon 6,6 prepolymer.

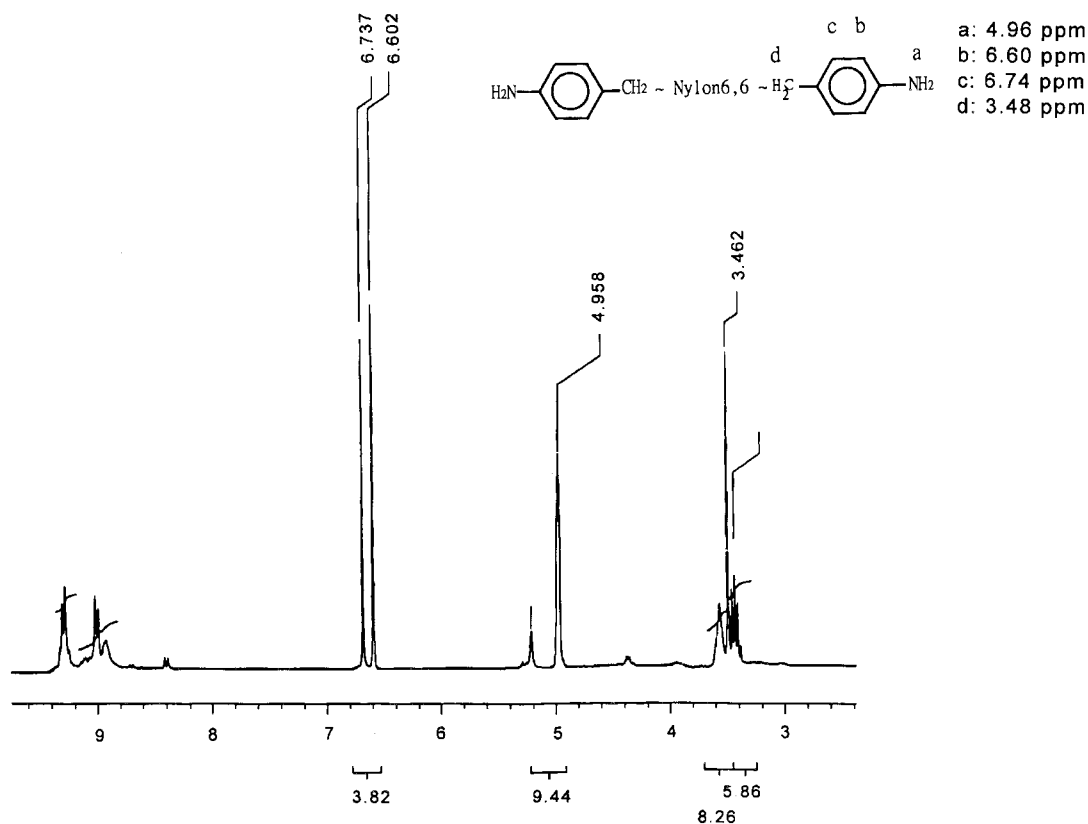


Figure 2 $^1\text{H-NMR}$ spectrum of modified nylon 6,6 prepolymer.

Measurements

Infrared (IR) spectra of the modified nylon 6,6 prepolymer and copolymers were obtained with a Hitachi Model 260-50, over a range $400\text{--}4000\text{ cm}^{-1}$. The samples were cast from the polymer solution without further purification in the form of films about 10 μm thick. Elemental analysis (C, H, N) was performed using a Perkin-Elmer 2400 analyzer. The $^1\text{H-NMR}$ spectra were obtained using a VXR-300/51 NMR spectrometer.

Differential scanning calorimetry (DSC) was performed with a DuPont Model 9900 DSC at a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere to obtain the glass temperatures (T_g 's) and the melting temperatures (T_m 's) from the second scan of the samples. Wide-angle X-ray photographs were taken with Ni-filter $\text{CuK}\alpha$ radiation using a Rigaku D/max-II type X-ray diffractometer. All stress-strain data were obtained on an Instron 1122 testing instrument at an extension rate of $5\text{ mm}/\text{min}$, with a 10-kg load cell. The size of each specimen was 50 mm in length, 10 mm in width, and 0.15 mm in thickness.

RESULTS AND DISCUSSION

Modified Nylon 6,6 Prepolymer Syntheses

A diamine-terminated nylon 6,6 prepolymer was prepared using an excess of HMDA. The molecular weight of this prepolymer was theoretically 794. The prepolymer was then reacted with the *p*-APA coupling agent (molar ratio 2/1) to form the modified nylon 6,6 prepolymer. From the results of elemental analysis, the found values were in reasonable agreement with the calculated ones. The results of the elemental analysis are shown in Table I.

The IR spectrum of the modified nylon 6,6 prepolymer (Fig. 1) exhibits the NH stretching vibrations of amide groups at 3300 cm^{-1} , C=O stretching at 1660 cm^{-1} , and the characteristic benzene ring absorption at 800 cm^{-1} . Figure 2 shows the $^1\text{H-NMR}$ spectrum of the modified nylon 6,6 prepolymer; all the expected absorptions are observed. The δ values are 6.74 ppm (d, 4H, Ar-NH₂), 6.60 ppm (d, 4H, Ar-NH₂), and 4.96 ppm (s, 4H, amine). These values supported the forma-

Table II Code of Nylon 6,6 and Copolymer Films

| Code | Polymer | Nylon | p-APA | IPC | DDO | DDS | DDM |
|-------|--------------------------|----------------|-------|-----|-----|-----|-----|
| Ny | Nylon | — | — | — | — | — | — |
| Ny-O1 | Nylon-aromatic copolymer | 1 ^a | 2 | 2 | 1 | — | — |
| Ny-O2 | | 1 | 2 | 3 | 2 | — | — |
| Ny-O3 | | 1 | 2 | 4 | 3 | — | — |
| Ny-S1 | | 1 | 2 | 2 | — | 1 | — |
| Ny-S2 | | 1 | 2 | 3 | — | 2 | — |
| Ny-S3 | | 1 | 2 | 4 | — | 3 | — |
| Ny-M1 | | 1 | 2 | 2 | — | — | 1 |
| Ny-M2 | | 1 | 2 | 3 | — | — | 2 |
| Ny-M3 | | 1 | 2 | 4 | — | — | 3 |
| Ny-Ar | | 1 | 2 | 1 | — | — | — |

^a The number indicates the molar ratio used in the synthesis.

tion of a diamine-terminated nylon 6,6 prepolymer.

Syntheses of Modified Nylon 6,6 Copolyamides

Ten modified nylon 6,6 copolyamides with aromatic comonomers were synthesized as listed in Table II. To obtain the multiblock copolymers with a high structural order, prepolymers with terminated functional groups were first synthesized prior to subsequent polymerization.⁹⁻¹¹ Co-

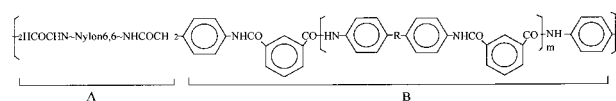
polymerization was carried out using an amino acid (*p*-APA) as a coupling agent. The various copolyamides were obtained by varying the amounts (mol ratios) of the aromatic polyamide prepolymers.

The inherent viscosities of the block copolyamides are shown in Table III and found to be between 0.52 and 0.68, suggesting that the block copolyamides are of medium molecular weight.

Table III Inherent Viscosity of Polymers

| Code | η_{inh}^a (dL/g) | Aliphatic Amide Content (%) | Aromatic Amide Content (%) |
|-------|-----------------------|-----------------------------|----------------------------|
| Ny | 0.82 | 100 | 0 |
| Ny-O1 | 0.62 | 57.6 | 42.4 |
| Ny-O2 | 0.54 | 47.4 | 52.6 |
| Ny-O3 | 0.64 | 40.2 | 59.8 |
| Ny-S1 | 0.52 | 55.9 | 44.1 |
| Ny-S2 | 0.62 | 45.0 | 55.0 |
| Ny-S3 | 0.60 | 37.7 | 62.3 |
| Ny-M1 | 0.65 | 57.7 | 42.3 |
| Ny-M2 | 0.66 | 47.5 | 52.5 |
| Ny-M3 | 0.59 | 40.3 | 59.7 |
| Ny-Ar | 0.68 | 73.6 | 26.4 |

^a Measured at a concentration of 0.5 g/dL in NMP + 5% LiCl.



R: —O—, —SO₂—, —CH₂—; *m* = 1–3. Aliphatic amide content = $[A/(A + B)] \times 100\%$; aromatic amide content = $[B/(A + B)] \times 100\%$.

Table IV Elemental Analysis of Copolyamides

| Code | Elemental Analysis | | | |
|-------|--------------------|-------|-------|-------|
| | | C (%) | H (%) | N (%) |
| Ny-O1 | Calcd | 68.39 | 7.25 | 10.88 |
| | Found | 68.06 | 7.37 | 11.02 |
| Ny-O2 | Calcd | 69.16 | 6.72 | 10.46 |
| | Found | 69.54 | 7.02 | 10.22 |
| Ny-O3 | Calcd | 69.69 | 6.35 | 10.16 |
| | Found | 68.54 | 5.89 | 9.20 |
| Ny-S1 | Calcd | 66.33 | 7.04 | 10.55 |
| | Found | 65.29 | 8.58 | 11.26 |
| Ny-S2 | Calcd | 65.79 | 6.40 | 9.95 |
| | Found | 64.69 | 5.97 | 11.05 |
| Ny-S3 | Calcd | 63.79 | 5.81 | 9.30 |
| | Found | 65.42 | 6.79 | 8.23 |
| Ny-M1 | Calcd | 69.26 | 7.39 | 10.89 |
| | Found | 71.19 | 8.56 | 8.96 |
| Ny-M2 | Calcd | 70.59 | 6.95 | 10.48 |
| | Found | 71.28 | 6.75 | 11.37 |
| Ny-M3 | Calcd | 71.52 | 6.64 | 10.19 |
| | Found | 72.38 | 7.79 | 9.36 |
| Ny-Ar | Calcd | 67.22 | 8.07 | 11.53 |
| | Found | 65.49 | 9.33 | 12.29 |

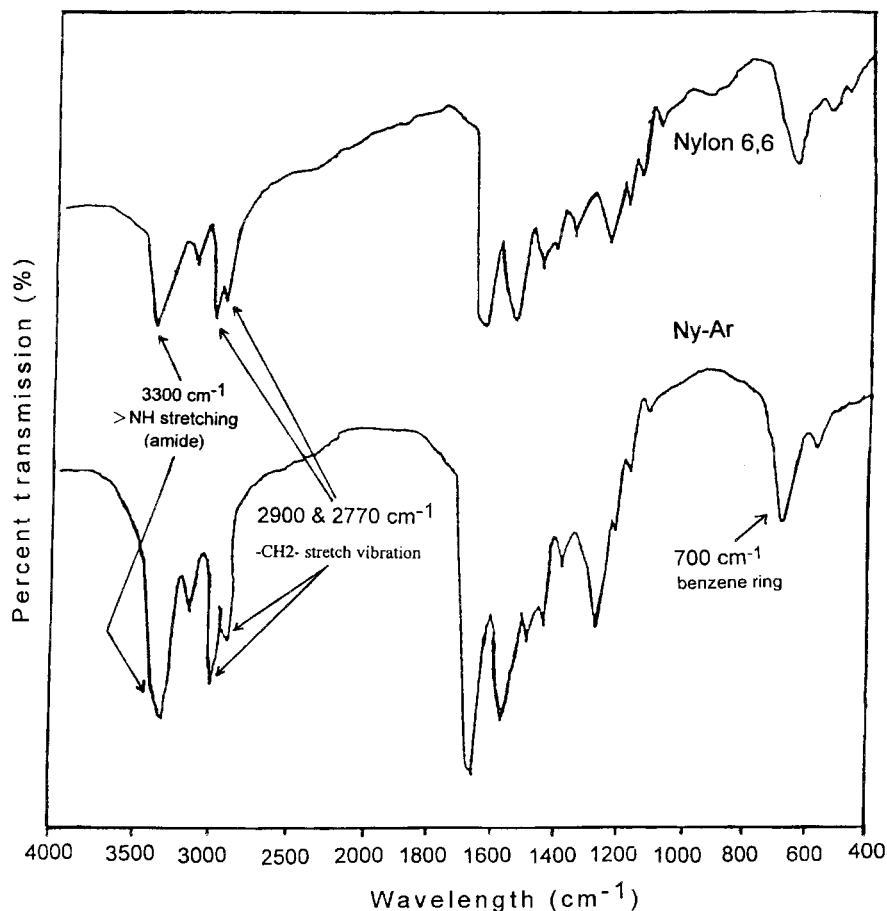


Figure 3 Infrared spectra of nylon 6,6, Ny-Ar films.

The reaction of the amine-terminated nylon 6,6 with the acid chloride-terminated aromatic polyamide prepolymer is rapid enough in NMP with 5% LiCl solutions. Generally, chain-extending reactions utilizing *p*-APA as a coupling agent can be completed in about 10 min after the start of the reaction (η_{inh} no longer increases). However, if *N,N*-dimethylacetamide (DMAc) was used as a solvent, only low molecular weight copolyamides were obtained.⁷ This might be due to a side reaction or the lower solubility of nylon 6,6 in DMAc with 5% LiCl. Furthermore, the results of elemental analysis as seen in Table IV show that the found values are in reasonable agreement with the calculated ones. Thus, copolymers of nylon 6,6 with rigid aromatic polyamides were successfully synthesized, but not in high purity or high molecular weight.

Infrared spectra were obtained by using the thin-film technique. The transmission IR spectra of nylon 6,6 and nylon 6,6-IPC copolyamide (Ny-Ar) are shown in Figure 3. Characteristic peaks of

nylon 6,6 were seen at 3300 cm^{-1} (N—H stretch vibration), 1650 cm^{-1} ($\text{C}=\text{O}$) and 1560 cm^{-1} ($\text{N}-\text{H}$ deformation), and 2900 and 2770 cm^{-1} ($-\text{CH}_2-$ stretch vibration). The IR spectra of the nylon 6,6-IPC copolymer (Ny-Ar) showed peaks at 3300 cm^{-1} (N—H stretch vibration), 1660 cm^{-1} ($\text{C}=\text{O}$), 1610 and 1540 cm^{-1} (C—C), 1315 – 1550 cm^{-1} ($\text{N}-\text{H}$ on *meta*-substituted), and 3000 – 3150 cm^{-1} ($\text{N}-\text{H}$ on *para*-substituted). Noticeable is the absorption of the $-\text{CONH}-$ at 1315 – 1550 cm^{-1} for the nylon 6,6-IPC copolyamides. This came from the reaction of the $-\text{NH}_2$ of the nylon 6,6 prepolymer with the $-\text{COCl}$ group of IPC.

The transmission IR spectrum of other semirigid nylon 6,6 copolyamides (PMA, POA, and PSA) as exemplified for the nylon 6,6-PSA copolyamide (Ny-S1) is seen in Figure 4 and showed characteristic absorptions for both nylon 6,6 and the aromatic segments. Noticeable was a characteristic absorption of 1340 and 1120 cm^{-1} ($-\text{SO}_2-$) for the presence of a SO_2 group in the PSA copolymer.

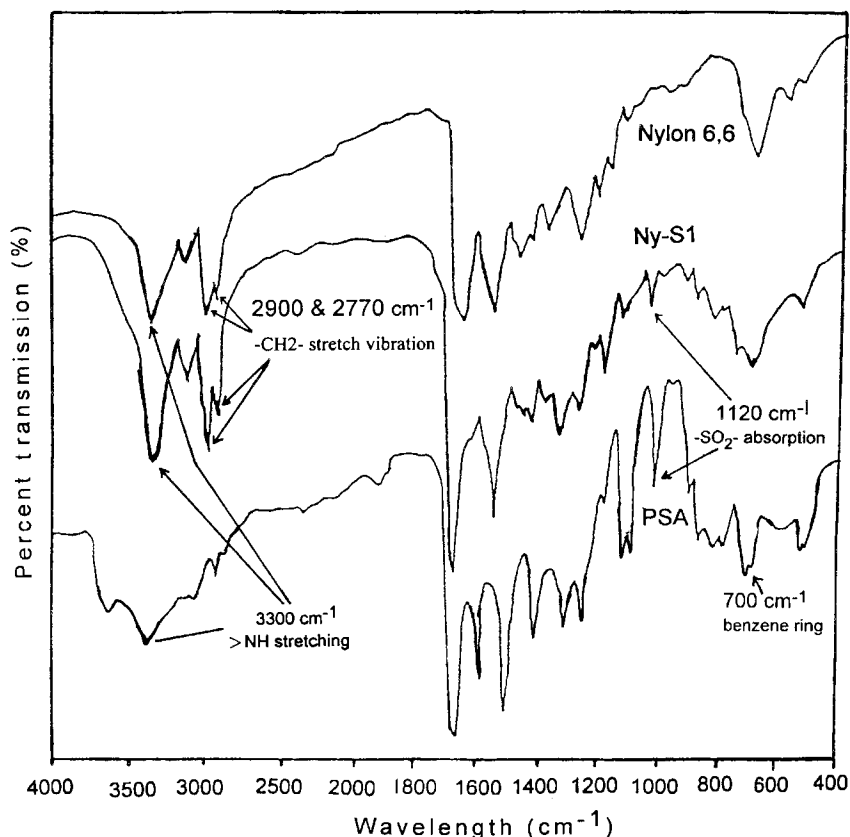


Figure 4 Infrared spectra of nylon 6,6, PSA, and copolyamide Ny-S1 films.

Thermal Properties of Nylon 6,6 and Block Copolyamides

The thermal properties of all polymers were evaluated by DSC and TGA and the data are listed in Table V with each example in Figures 5 and 6,

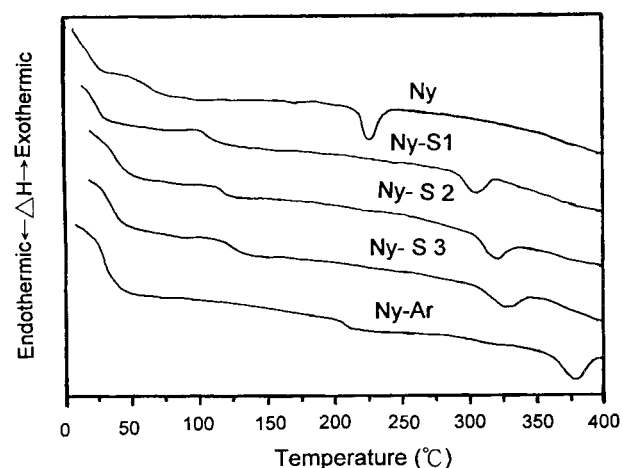


Figure 5 DSC plots of nylon 6,6 and copolyamide Ny-PSA films.

respectively. The results show that the transition temperature (T_g) of the copolyamides is increased with increasing aromatic content. This indicates that the micro-Brownian motion of amorphous nylon 6,6 chains is restrained by the rigid aromatic molecules, especially at high content. Similarly, the T_m 's of the copolyamides increased with increasing aromatic content. Since the melting behavior shows only one peak, a mixed crystal structure of aromatic polyamides with nylon 6,6 was proposed for the copolyamides.¹²⁻¹⁵

Comparisons of the thermal properties of rigid and the semirigid copolyamide-reinforced nylon 6,6 are seen in Table V. Both the T_g and T_m increase in the order IPC > POA > PMA > PSA. The rigid IPC has the best thermal property due to its wholly rigid aromatic structure. The PSA with the sulfonyl structure exhibits the lowest thermal properties, and PMA and POA display thermal properties in between.

Table V also summarizes the thermogravimetric data of all the polymers. Good thermal stability and thermooxidation stability, with no significant weight loss up to the temperature of approx-

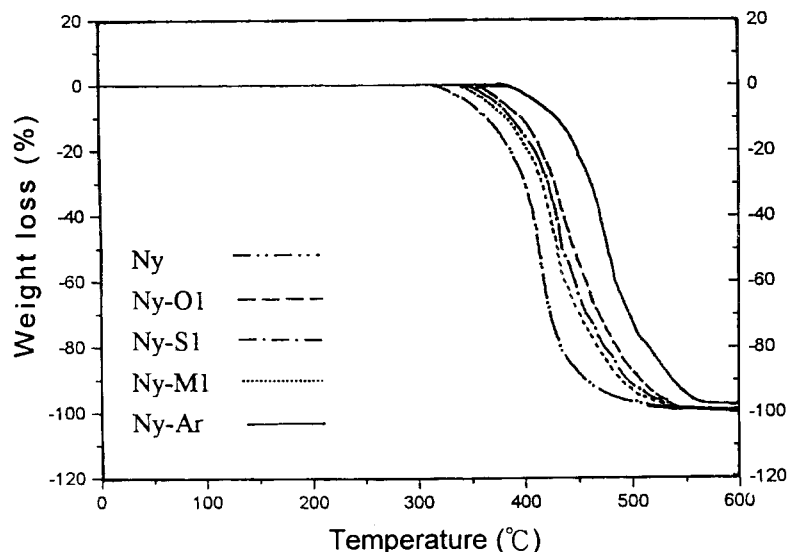


Figure 6 Weight loss of nylon 6,6 and copolyamide films in nitrogen.

imately 310°C in a nitrogen atmosphere and 300°C in an air atmosphere was seen. Moreover, the wholly aromatic copolyamide Ny-Ar has the best thermal stability and 10% weight-loss properties. The decomposition temperatures at 10% weight loss of these copolymers are 372–438°C in air and 385–460°C in a nitrogen atmosphere. With increasing aromatic content, the 10% weight-loss temperature was increased. This suggests that the aromatic amide linkage does contribute better thermooxidative stability than that of aliphatic amide.

Table V Melt, Glass Transition, and Degradation Temperature of Nylon 6,6 and Copolyamides

| Code | Thermal Degradation Temperature (°C) | | T_g (°C) | T_m (°C) |
|-------|--------------------------------------|-----------------------|------------|------------|
| | Air 10 (%) | N ₂ 10 (%) | | |
| Ny | 372 | 385 | 65 | 255 |
| Ny-O1 | 401 | 415 | 132 | 328 |
| Ny-O2 | 414 | 430 | 140 | 340 |
| Ny-O3 | 426 | 441 | 148 | 344 |
| Ny-S1 | 392 | 411 | 107 | 306 |
| Ny-S2 | 409 | 426 | 116 | 320 |
| Ny-S3 | 422 | 433 | 123 | 326 |
| Ny-M1 | 396 | 412 | 118 | 317 |
| Ny-M2 | 411 | 425 | 130 | 332 |
| Ny-M3 | 426 | 439 | 135 | 339 |
| Ny-Ar | 438 | 460 | 203 | 378 |

Wide-angle X-ray Diffraction

The wide-angle X-ray diffraction patterns of nylon 6,6, and the copolymers were measured by the Rigaku diffractometer; one example is shown in Figure 7. From the WAXS diffraction patterns, it was found that nylon 6,6 has two diffraction peaks, that is, $2\theta = 20.5^\circ$ and 23° . However, the copolyamide of wholly rigid IPC with nylon 6,6 has only one peak at $2\theta = 20^\circ$, indicating a dif-

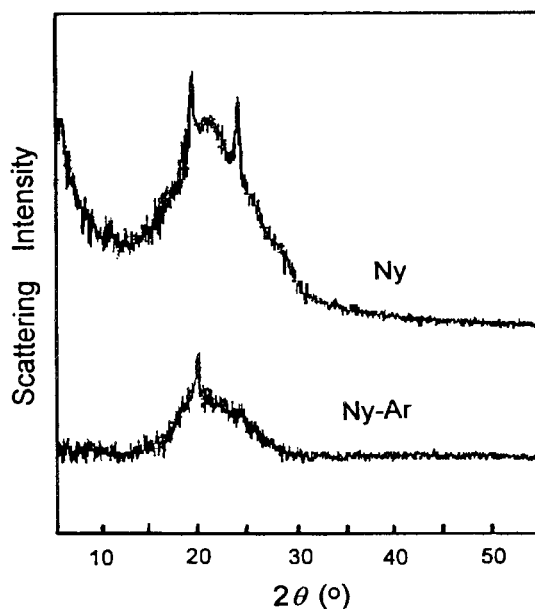


Figure 7 X-ray diagrams of nylon 6,6 and copolyamide Ny-Ar films.

Table VI Mechanical Properties of Nylon 6,6 and Copolyamides

| Code | Tensile Strength (MPa) | Elongation at Break (%) | Initial Modulus (GPa) | Aliphatic Amide Content (%) | Aromatic Amide Content (%) |
|-------|------------------------|-------------------------|-----------------------|-----------------------------|----------------------------|
| Ny | 55 | 40 | 0.92 | 100 | 0 |
| Ny-O1 | 64 | 23 | 1.62 | 57.6 | 42.4 |
| Ny-O2 | 73 | 18 | 1.87 | 47.4 | 52.6 |
| Ny-O3 | 73 | 17 | 1.89 | 40.2 | 59.8 |
| Ny-S1 | 69 | 19 | 1.86 | 55.9 | 44.3 |
| Ny-S2 | 77 | 14 | 1.98 | 45.0 | 55.0 |
| Ny-S3 | 78 | 14 | 2.00 | 37.7 | 63.3 |
| Ny-M1 | 68 | 21 | 1.69 | 57.7 | 42.3 |
| Ny-M2 | 74 | 16 | 1.92 | 47.5 | 52.5 |
| Ny-M3 | 75 | 15 | 1.94 | 40.3 | 59.7 |
| Ny-Ar | 88 | 9 | 2.84 | 73.6 | 26.4 |

ferent crystal structure for copolyamide. The wide-angle X-ray diffraction patterns of the semi-rigid copolyamides were also measured with the Rigaku diffractometer and again only one peak at $2\theta = 20^\circ$ was observed.

Mechanical Properties of Nylon 6,6 and Copolyamides

The mechanical properties of nylon 6,6 and the block copolymers are presented in Table VI and illustrated in Figures 8–10. The tensile strength (T_b) and the initial modulus (M_i) were found to progressively increase with the aromatic amide content, which causes a higher intramolecular stiffness, but also to increase the intermolecular forces between polymer chains, through aromatic H—H interactions.

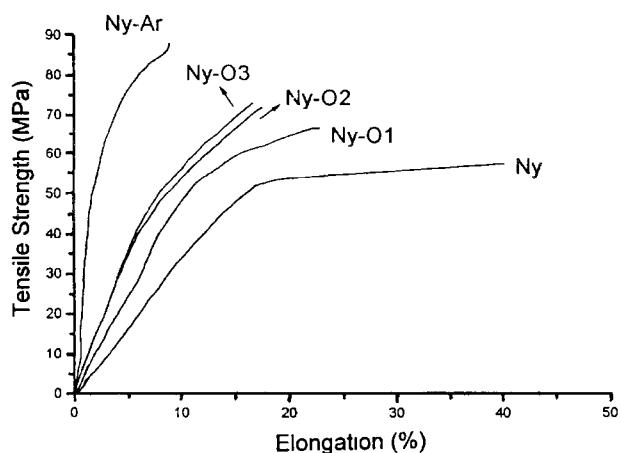


Figure 8 Stress–strain curves for nylon 6,6 and copolyamide films.

Comparisons of the copolyamides indicate that the order of physical properties (such as tensile strength) is $IPC > PSA > PMA > POA$, but for the elongation, it is $POA > PMA > PSA > IPC$. The rigid IPC has the highest strength but the lowest elongation due to its wholly rigid aromatic structure. The POA with the soft ether moieties exhibits the lowest strength and the highest elongation while PMA and PSA display properties in between. For the modulus, the order is $IPC > PSA > PMA > POA$, consistent with the tensile strength.

CONCLUSIONS

Ten copolyamides of nylon 6,6 and aromatic oligomers were synthesized by chemical extension

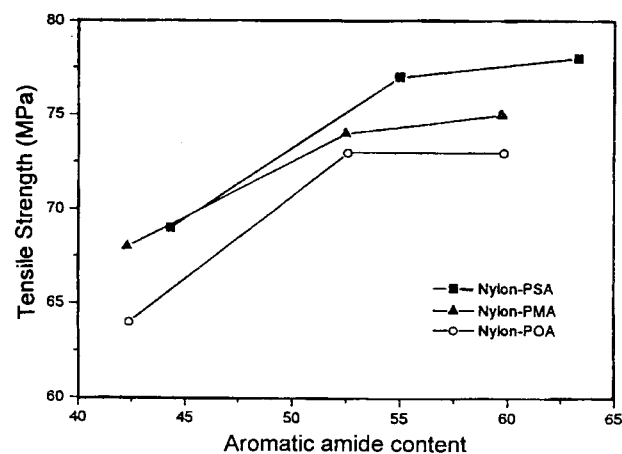


Figure 9 Relationship between tensile strength and aromatic amide content.

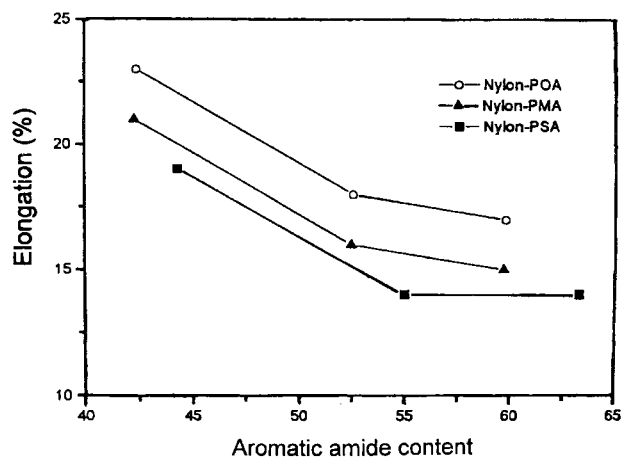


Figure 10 Relationship between tensile elongation and aromatic amide content.

using *p*-APA as a coupling agent. The reinforcement of nylon 6,6 with rigid aromatic segments proved to be successful, especially for the IPC copolyamide. All block copolymers possessed better mechanical properties than those of pure nylon 6,6. The copolyamides all exhibited higher glass transition temperatures than those of nylon 6,6, especially the IPC copolyamide. The order of increased thermal properties is IPC > PMA > POA > PSA. X-ray diffraction showed that nylon 6,6 has two diffraction peaks, that is, 2θ 20.5° and 23° , while the copolyamides showed only one at $= 20^\circ$, indicating a different crystalline structure for the copolyamides.

The authors gratefully acknowledge the financial support of this research project by the National Science

Council, Republic of China.

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