

Synthesis and Properties of Nylon 6 Modified with Various Aromatic Polyamides

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ABSTRACT: In this study, flexible nylon 6 was reinforced by the following rigid-chain aromatic polyamides: poly(*m*-phenylene isophthalamide) (PmIA), poly(4,4'-diphenylsulfone terephthalamide) (PSA), poly(*p*-diphenyloxide terephthalamide) (POA), and poly(*p*-diphenylmethane terephthalamide) (PMA). Various high-molecular-weight block copolyamides were synthesized by solution polymerization using *p*-aminophenylacetic acid (*p*-APA) as a coupling agent. Their thermal properties have shown that the block copolyamides exhibit higher T_g and T_m and better thermal stability than those of nylon 6, especially PmIA-modified nylon 6. The order of their thermal properties of aromatic modified nylon 6 copolyamides is PmIA > PMA > POA > PSA. Besides, the T_g and T_m of multiblock copolyamides are higher than those of triblock copolyamides. From the wide-angle X-ray diffraction pattern, it is found that the triblock copolyamides have two diffraction peaks (i.e., $2\theta = 20.5$ and 24°). However, the multiblock has only one at $2\theta = 20^\circ$, indicating a different crystal structure for multiblock copolyamides. This can be further confirmed from scanning electron microscopy. It shows that the triblock copolyamides are a dispersed phase structure, although the multiblock copolyamides exhibit a homogeneous texture rather than an aggregated one. For the mechanical properties, it is found that the multiblock copolyamides have a more significant reinforcing effect than the triblock copolyamides. Also, the order of their physical properties of aromatic modified nylon 6 copolyamides, such as tensile strength, is PmIA > PMA > POA > PSA; but for the elongation, the order is PSA > POA > PMA > PmIA.
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Key words: modified nylon 6; poly(*m*-phenylene isophthalamide); poly(4,4'-diphenylmethane terephthalamide); poly(4,4'-diphenylsulfone terephthalamide)

INTRODUCTION

In the last few years, a number of attempts were made to increase the mechanical properties of the aliphatic nylons by using the chemical modification of aromatic polyamides such as Kevlar or polybenzamide (PBA).^{1–3,16–19} Nevertheless, their modification was always in the side chains. Recently, we took a different approach to increase

the mechanical properties of the aliphatic nylons by using the concept of a so-called coupling agent, aminoacetic acid (*p*-APA), to link the aromatic polyamide to nylon 6 in the main chain. Thus, a number of aromatic aliphatic polyamides was obtained.

In this article, the aromatic polyamides such as poly(*m*-phenylene isophthalamide) (PmIA), poly(4,4'-diphenylsulfone terephthalamide) (PSA), poly(*p*-diphenylmethane terephthalamide) (PMA), and poly(*p*-diphenyloxide terephthalamide) (POA) were used as a reinforcement part for block copolymers to improve the mechanical and thermal

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Table I Characteristics of Nylon 6 Prepolymers and Aromatic Polyamides

	N ₆ ^a	N ₆ H ^b	PMA	POA	PSA	PmIA
<i>M_n</i> ^c	1300	10,700	132,000	135,000	134,000	146,000

^a Aromatic diamine-terminated nylon 6 prepolymer modified by *p*-APA.

^b Aromatic monoamine-terminated nylon 6 prepolymer.

^c For nylon 6 prepolymer $\bar{M}_n = (15,600) \times \eta_{inh}^{1.49}$; for aromatic polyamides, from gel permeation chromatography measurement.

properties of nylon 6 connected by the coupling agent. The effect of different aromatic polyamide structures to the solubility,⁶ thermal stability, and mechanical properties of the block copolymers will be discussed.

EXPERIMENTAL

Materials

The nylon 6 was obtained from the Formosa Chemical and Fiber Corporation (Taipei, Taiwan, R.O.C.). The sample was first dissolved in formic acid and then poured into a large amount of water. Then, samples were refluxed with methanol and

hot water for 16 h and, after that, dried at 100°C under vacuum for 8 h. Its inherent viscosity [$\eta_{(inh)} = 1.24$] and \bar{M}_n (21,500) were obtained according to the literature.

4,4'-Diaminodiphenyl sulfone (DDS), *m*-phenylene diamine (MPA), *p*-diaminodiphenyl methane (DDM), and *p*-diaminodiphenyl oxide (DDO) were obtained from the Dah-Yi Chemical Industries Co. Both terephthaloyl dichloride (TPC) and *p*-aminophenylacetic acid (*p*-APA) were purchased from Merck Co. and used as received.

N-Methyl-2-pyrrolidone (NMP) was first distilled over CaH₂ at 92–94°C/14 mm Hg and then stored in the presence of molecular sieves. The moisture content of a 5% LiCl solution in NMP

Table II Characteristics of Homopolymers, Copolyamides, and Prepolymers

Code	Polymer	Reaction time (h)	η^a
PmIA		—	—
PmIA-10M	Multiblock 10%	0.5	1.25
PmIA-20M	Multiblock 20%	0.5	1.36
PmIA-20T	Triblock 20%	0.5	1.36
PMA		—	—
PMA-10M	Multiblock 10%	0.5	1.26
PMA-20M	Multiblock 20%	0.5	1.44
PMA-20T	Triblock 20%	0.5	1.54
POA		—	—
POA-10M	Multiblock 10%	0.5	1.30
POA-20M	Multiblock 20%	0.5	1.44
POA-20T	Triblock 20%	0.5	1.56
PSA		—	—
PSA-10M	Multiblock 10%	0.5	1.22
PSA-20M	Multiblock 20%	0.5	1.54
PSA-20T	Triblock 20%	0.5	1.57
N ₆		—	0.11
N ₆ H	Nylon 6 prepolymer	—	0.78

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

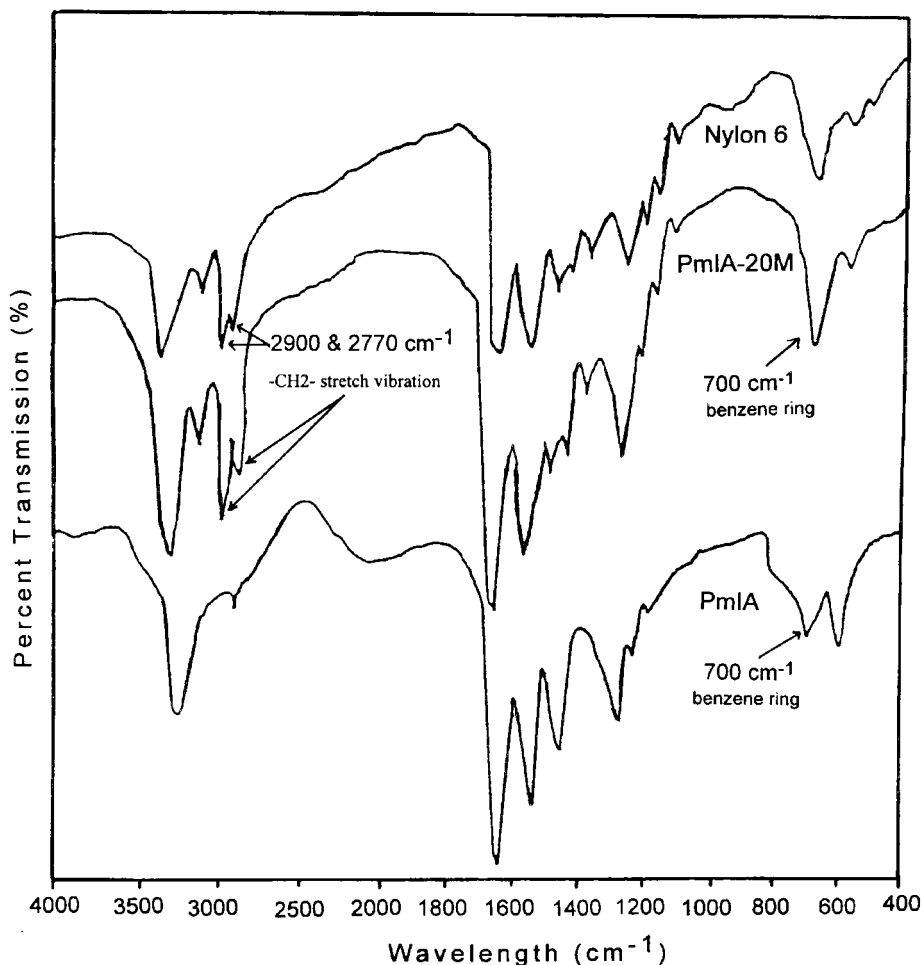


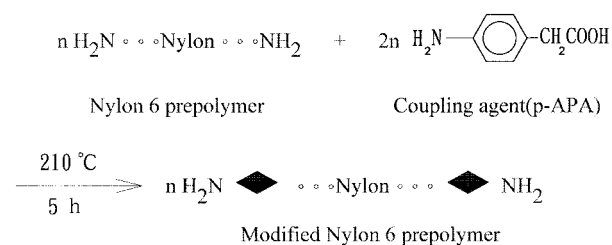
Figure 1 Infrared spectra of homo- and copolyamide films: nylon 6, PmIA, and multiblock copolyamide of PmIA-20M.

was 0.018 wt % by the Karl-Fischer Moisture Meter, MKA-3, Kyoto Electronic. Lithium chloride (LiCl) was dried under vacuum at 160°C for 5 h.

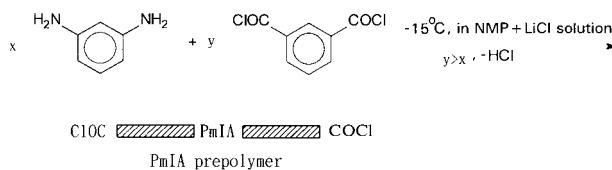
Synthesis of Block Copolymers

Wholly Rigid Modified Nylon 6 Multiblock Copolyamides

Before synthesizing nylon 6 with wholly aromatic polyamide (PmIA), a low-molecular-weight diamine-terminated nylon 6 prepolymer was prepared by an excess of hexamethylene diamine (HMDA).^{4,7} Then the prepolymer was reacted with *p*-APA coupling agent at 210°C for 5 h to form the modified nylon 6 prepolymer, as follows:



Also, a low-molecular-weight PmIA was prepared by excess isophthaloyl chloride (IPC) with MPA in NMP + 5% LiCl solution, as follows:



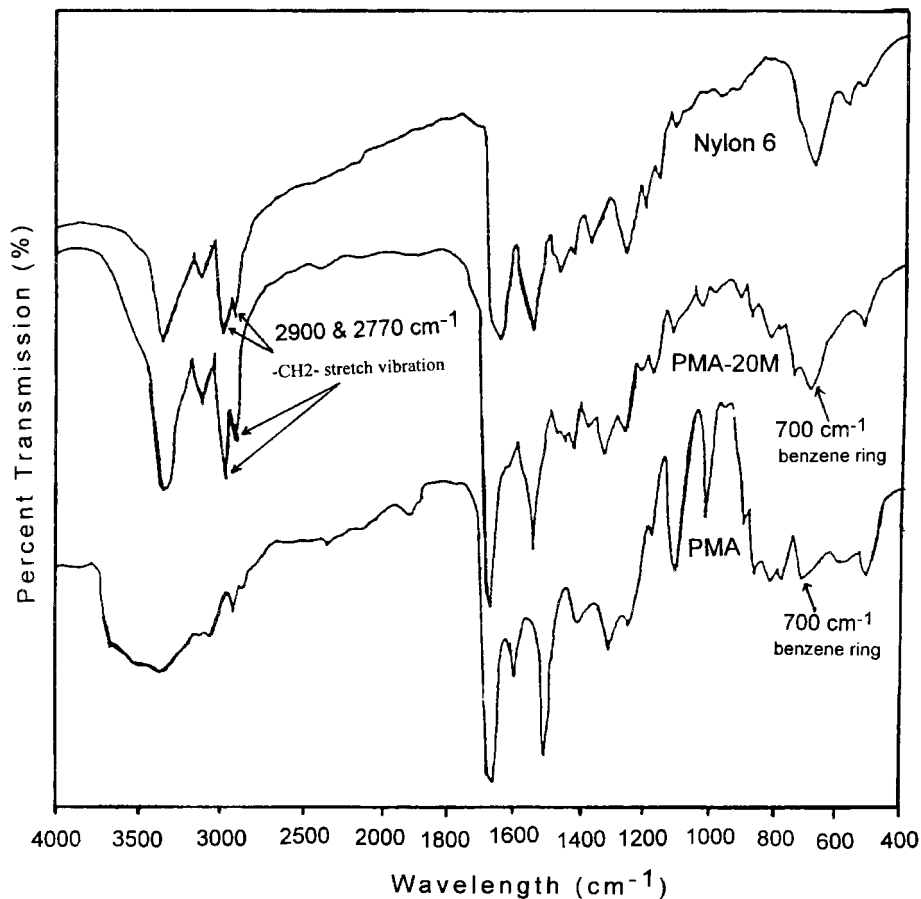
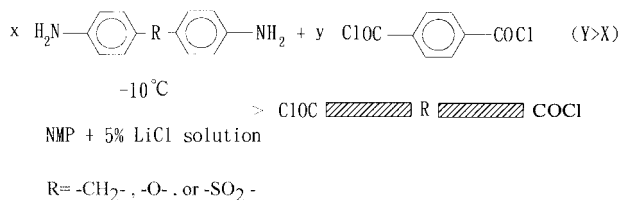
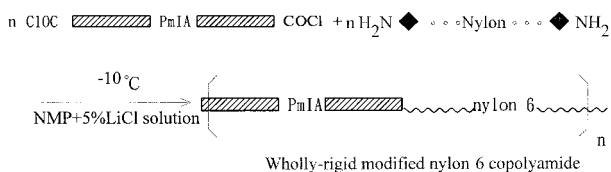
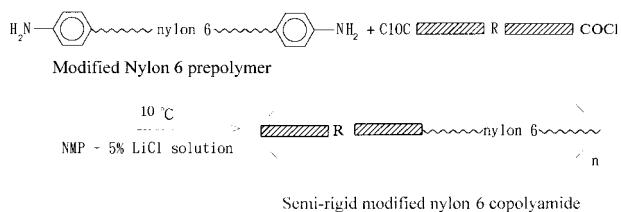


Figure 2 Infrared spectra of homo- and copolyamide films: nylon 6, PMA, and multiblock copolyamides of PmIA-20M.

Then the PmIA prepolymer was reacted with the modified nylon 6 to form a wholly rigid modified nylon 6 copolyamide, as follows:



Then the semiaromatic polyamide prepolymer was reacted with the modified nylon 6 to form a semirigid modified nylon 6 copolyamide, as follows:



Semirigid Modified Nylon 6 Multiblock Copolyamides

Low-molecular-weight diacid chloride-terminated semiaromatic polyamides were prepared by low-temperature polycondensation of semiaromatic diamines with an excess molar amount of TPC.

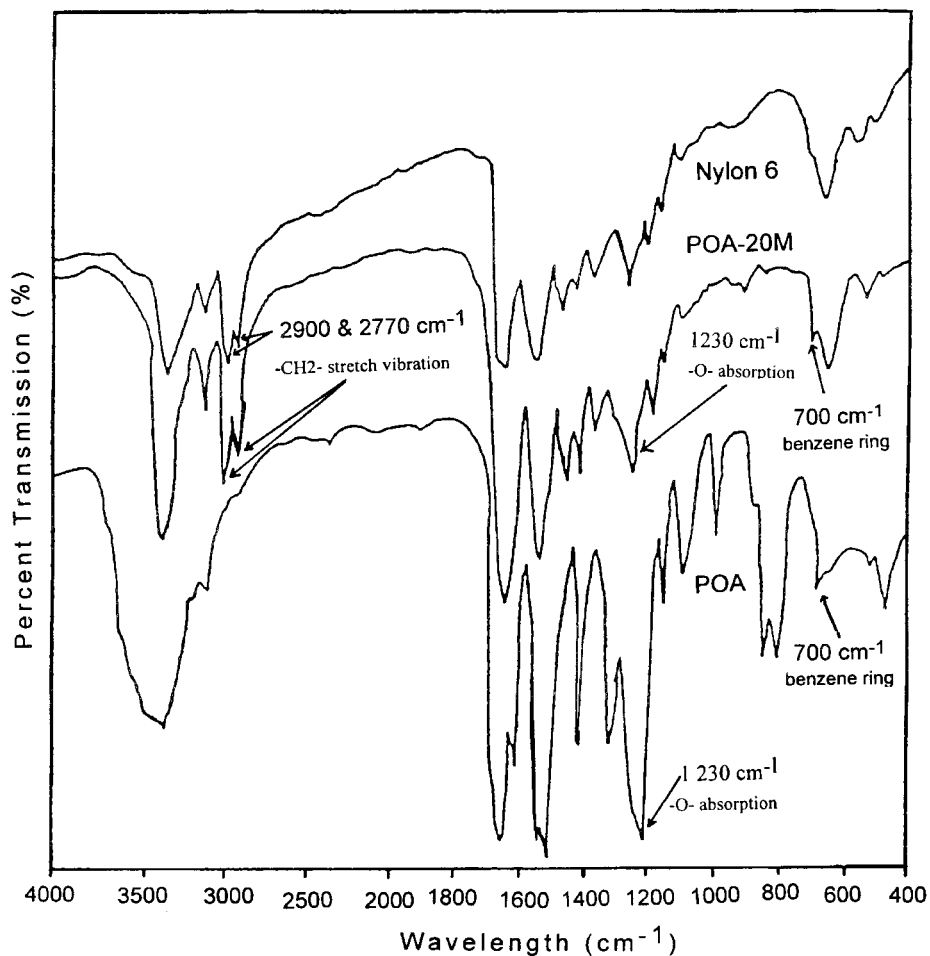
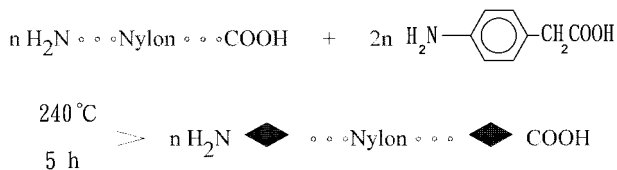


Figure 3 Infrared spectra of homo- and copolyamide films: nylon 6, POA, and multiblock copolyamide of POA-20M.

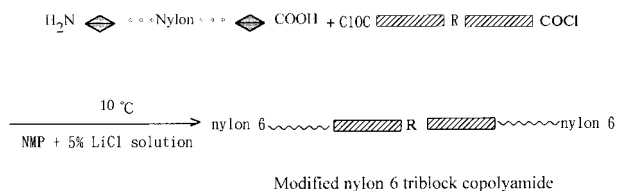
Modified Nylon 6 Triblock Copolyamides

The long-chain monoamine-terminated nylon 6 prepolymer was first prepared by bulk polymerization at 240°C for 5 h, as follows:



Then the monoamine-terminated nylon 6 prepolymer ($\bar{M}_n = 10,700$) in NMP + 5% LiCl and the semi-rigid or wholly rigid polyamide prepolymer were mixed and stirred vigorously in N₂ atmosphere at -5 to -10°C for 30 min, then

raised to room temperature and stirred continuously for 1 h. The reaction scheme is shown as follows:



Measurements

Infrared (IR) spectra of homopolymers and copolymers were obtained by Hitachi Model 260-50 type over a range 400–4000 cm⁻¹. The samples were cast from the polymer solution without fur-

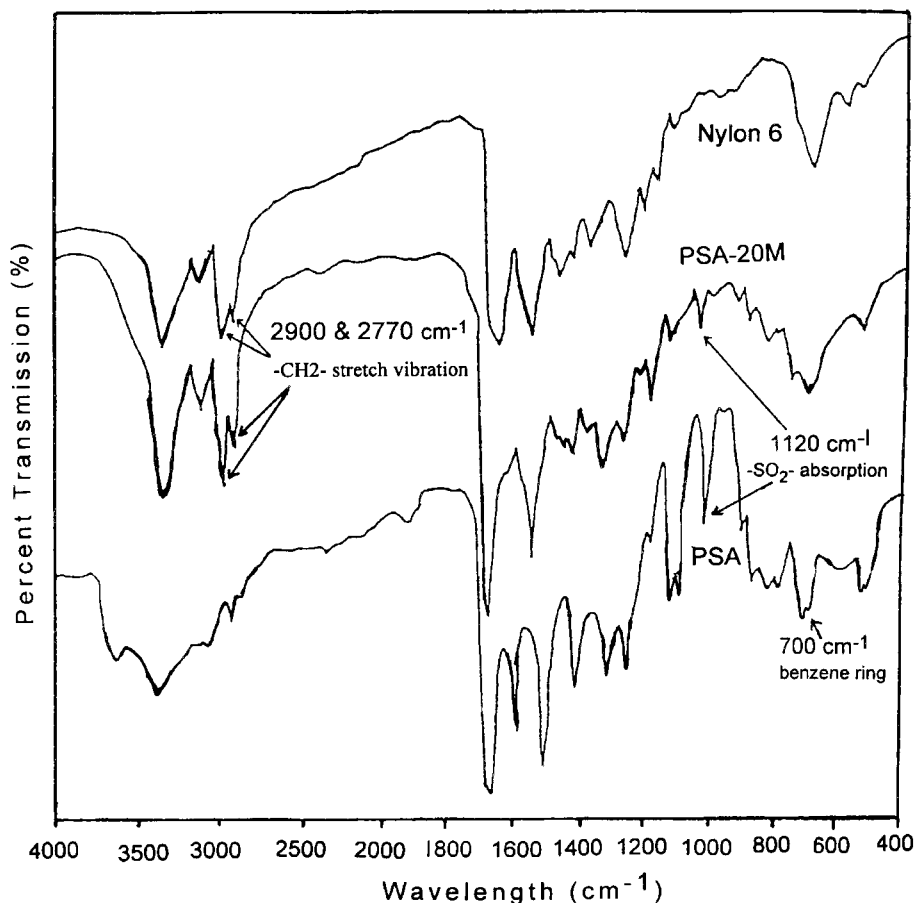


Figure 4 Infrared spectra of homo- and copolyamide films: nylon 6, PSA, and multiblock copolyamide of PSA-20M.

ther purification and in the form of film about 10 μm thickness.

Differential scanning calorimetry (DSC) was performed by Du Pont model 9900 DSC, at a heating rate of 20°C/min under nitrogen atmosphere to obtain the glass temperature (T_g) and the melting temperature (T_m) from the second scanning of samples, respectively.

Wide-angle X-ray photographs were taken with Ni-filter $\text{CuK}\alpha$ radiation using Rigaku D/max-II type X-ray diffractometer. A scanning electron microscope, Cambridge Stereoscan-600, was also used to observe the morphological structure on samples that were sputter-coated with Au to prevent their oxidation.

All stress-strain data were obtained on the Instron 1122 type testing instrument at an extension rate of 5 mm/min, and the full load 10 kg.

The size of specimen is 50 mm length, 10 mm width, and 0.15 mm thickness.

RESULTS AND DISCUSSION

Characteristics of Prepolymers, Aromatic Polyamides, and Modified Nylon 6 Copolyamides

The characteristics of nylon 6 prepolymers and aromatic polyamides are listed in Table I. Also, the viscosities of eight multiblock and three triblock copolyamide-modified nylon 6, which were prepared by low-temperature polymerization of the polyamides of low molecular weights, are summarized in Table II. To obtain the multiblock copolymers with a high structural order, prepolymers with ter-

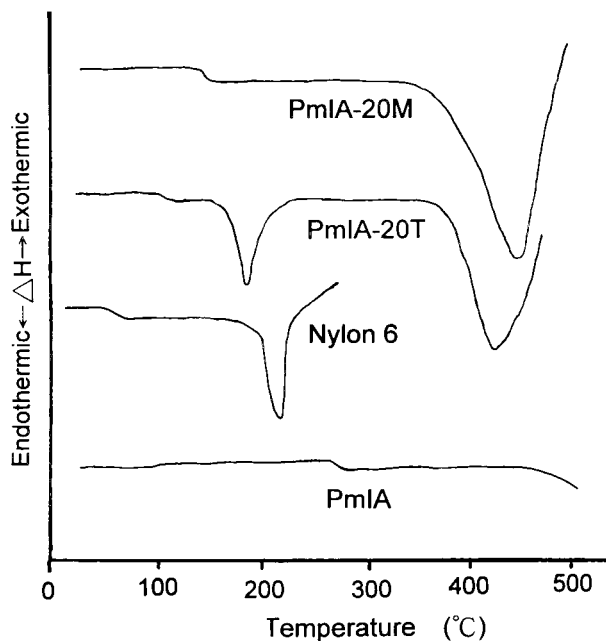


Figure 5 DSC plots of homo- and copolyamide films: nylon 6, PmIA, multiblock PmIA-20M, and triblock PmIA-20T.

minated functional groups were first synthesized prior to the subsequent polymerization.⁹⁻¹¹ In this study, copolymerization was carried out using an amino acid (*p*-APA) as a coupling agent. The various copolyamides were obtained by varying different amounts (wt %) of aromatic polyamide prepolymers.

The inherent viscosities of the block copolyamides, as shown in Table II, are found to be greater than those of the prepolymers, suggesting that the block copolyamides are of sufficient high molecular weight. The reaction of the amine-terminated nylon 6 with the acid chloride-terminated aromatic polyamide prepolymer is believed to be rapid enough to minimize the side reaction in the NMP with 5% LiCl solutions. Generally, the chain-extending reaction utilizing the *p*-APA as a coupling agent can be completed about 10 min after the start of reaction and yields a high molecular weight (the η_{inh} no longer increased after 10 min). However, if dimethylacetamide (DMAc) was used as a solvent, then only low-molecular-weight copolyamides were obtained.⁷ This might be due to (1) the acid chloride-terminated groups of polyamide prepolymers could partially react with the DMAc solvent (therefore, a side reaction occurred), and (2) the solubilization

of nylon 6 in DMAc with 5% LiCl was less than that of NMP with 5% LiCl.

Infrared spectra were obtained by using the thin film technique. The transmission IR spectra of homopolymers and nylon 6–PmIA block copolymer (PmIA-20M) (multiblock PmIA 20%) are shown in Figure 1. As seen in the figure, the IR spectra of nylon 6 are characterized at 3300 cm^{-1} ($=\text{N}-\text{H}$ stretch vibration), 1650 cm^{-1} ($=\text{C}-\text{O}$), 1560 cm^{-1} ($=\text{N}-\text{H}$ deformation), and 2900 and 2770 cm^{-1} ($-\text{CH}_2-$ stretch vibration) absorptions. The characteristic IR spectra of PmIA are shown at 3400 cm^{-1} ($\text{N}-\text{H}$ stretch vibration), 1680 cm^{-1} ($\text{C}=\text{O}$), 1610 and 1540 cm^{-1} ($\text{C}-\text{C}$), $1315-1550\text{ cm}^{-1}$ ($\text{N}-\text{H}$ on metasubstituted), and $3000-3150\text{ cm}^{-1}$ ($\text{N}-\text{H}$ on para-substituted) absorptions. The nylon 6–PmIA block copolymers (PmIA-20M) do show both the characteristic absorption of nylon 6 and PmIA. Noticeable is a characteristic absorption of the $-\text{CONH}-$ at $1315-1550\text{ cm}^{-1}$ on metasubsti-

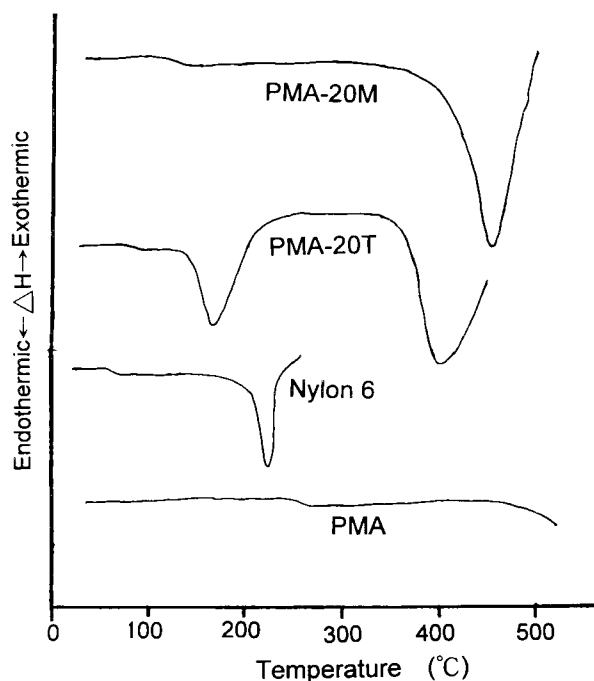


Figure 6 DSC plots of homo- and copolyamide films: nylon 6, PMA, multiblock PMA-20M, and triblock PMA-20T.

Table III Thermal Properties of Homopolymers and Block Copolyamides

Code	Polymer	T_g (°C)	T_m (°C)	T_g/T_m (K)
Ny	Nylon 6	67	219	0.69
PmIA		275	> 520	0.69
PmIA-10M	Multiblock 10%	134	438	0.57
PmIA-20M	Multiblock 20%	140	454	0.57
PmIA-20T	Triblock 20%	110	170, ^a 410	0.56
PMA		260	510	0.68
PMA-10M	Multiblock 10%	129	425	0.58
PMA-20M	Multiblock 20%	135	448	0.57
PMA-20T	Triblock 20%	105	161, ^a 398	0.56
POA		265	516	0.68
POA-10M	Multiblock 10%	115	435	0.58
POA-20M	Multiblock 20%	124	442	0.56
POA-20T	Triblock 20%	95	159, ^a 395	0.55
PSA		256	502	0.68
PSA-10M	Multiblock 10%	107	365	0.59
PSA-20M	Multiblock 20%	112	378	0.59
PSA-20T	Triblock 20%	75	138, ^a 325	0.58

^a The melting point of the soft segment in the triblock copolyamides.

tuted and at 3000–3150 cm^{-1} on parasubstituted for the nylon 6–PmIA block copolymers. This came from the reaction of the $-\text{NH}_2$ on paraposition of benzene with the metaposition $-\text{COCl}$ group of PmIA prepolymer.

Moreover, the transmission IR spectra of other three semirigid modified nylon 6 copolyamide films (PMA, POA, and PSA) are shown in Figures 2–4. The block copolymers showed both the characteristic adsorptions of nylon 6 and semirigid aromatic polyamides. These confirm that semirigid aromatic polyamide segments do link to the nylon 6. The IR spectra of PMA are characterized at 3400 cm^{-1} ($\text{N}-\text{H}$ stretch vibration), 1680 cm^{-1} ($\text{C}=\text{O}$), 1610 and 1540 cm^{-1} ($\text{C}=\text{C}$), and 1530 cm^{-1} ($-\text{CH}_2\text{CH}_2\text{CH}_2-$). Noticeable is a characteristic absorption of the 1530 cm^{-1} ($-\text{CH}_2\text{CH}_2\text{CH}_2-$) and 700 cm^{-1} (benzene ring) absorptions for the block copolymer of PMA. The IR spectra of POA are shown at 3400 cm^{-1} ($=\text{N}-\text{H}$ stretch vibration); 1650 cm^{-1} ($\text{C}=\text{O}$); 1520–1560 cm^{-1} ($\text{N}-\text{H}$ deformation); and 1510, 1620 ($\text{C}=\text{C}$), and 1230 cm^{-1} ($-\text{O}-$) absorp-

tions. The nylon 6–POA block copolymer (POA–20M) (multiblock POA 20%) show both the characteristic absorption of nylon 6 and POA. Noticeable is a characteristic absorption of the block copolymers at 1230 cm^{-1} ($-\text{O}-$). This comes from the presence of ether group in the copolymer of nylon 6–POA. And finally, the IR spectra of

PSA are characterized at 3400 cm^{-1} ($\text{N}-\text{H}$ stretch vibration), 1680 cm^{-1} ($\text{C}=\text{O}$), 1610 and 1540 cm^{-1} ($\text{C}=\text{C}$), and 1340 and 1120 cm^{-1} ($-\text{SO}_2-$). Noticeable was a characteristic absorption of the 1340 and 1120 cm^{-1} ($-\text{SO}_2-$) for block copolymers of PSA with nylon 6. This comes from the presence of SO_2 group in the nylon 6–PSA copolymers.

Thermal Properties of Homopolymer and Block Copolymers

Polymers with aromatic ring structure could contribute to their thermal stability. In this study, the presence of aromatic polyamides in nylon 6 could be expected to provide better thermal properties. The thermal behavior of homopolymers

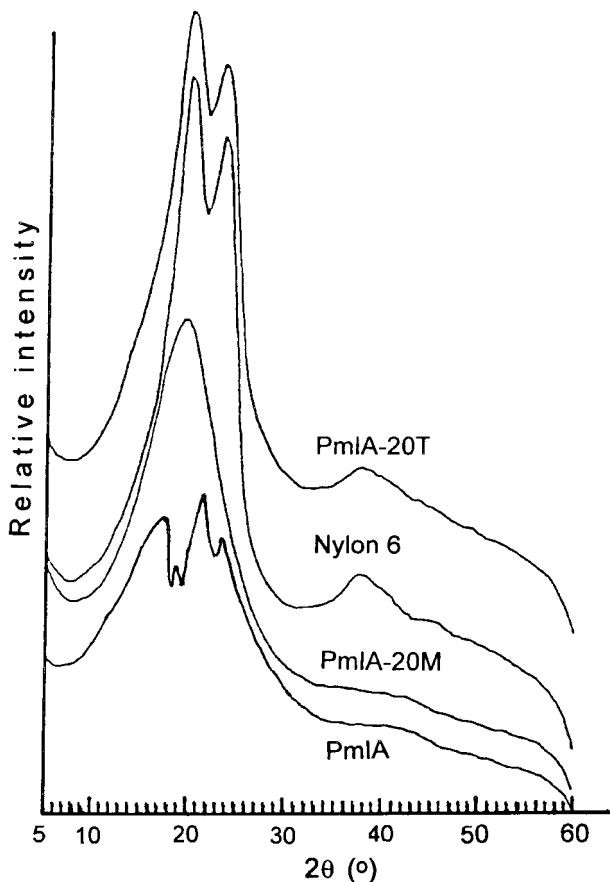


Figure 7 X-ray diagrams of homopolymers and block copolyamides: nylon 6, PmIA, multiblock PmIA-20M, and triblock PmIA-20T.

and block copolymers that were measured by DSC are typically shown in Figures 5 and 6 and Table III. The results show that the transition temperature (T_g) of the copolyamides is increased with the increase of aromatic polyamide wt % content. This indicates that the micro-Brownian motion of amorphous nylon 6 chains does suffer from the restraint of the rigid aromatic polyamide molecules, especially if the amounts of aromatic polyamide are increased. Similarly T_m of copolyamides is increased with increasing of aromatic content.

It is also shown in Table III that the glass transition temperature (T_g) and the melting point (T_m) of the block copolyamides increase significantly as compared with that of the original nylon 6. Since the melting temperature (T_m) of multiblock copolyamides shows only one peak (Figs. 5 and 6); therefore, a mixing crystal structure of aromatic polyamides with nylon 6 is formed in the multiblock copolymer. For example, it is seen that

the melting temperature of the multiblock PmIA copolyamides is 454°C; whereas the triblock PmIA has two melting points (i.e., 170 and 410°C). Since the homopolymer of PmIA having triclinic structure is not the same as that of monoclinic structure of nylon 6, this indicates that the multiblock PmIA behaves as a new microstructure; that is, the aromatic PmIA segment mixes with the nylon 6 segment to form a new copolyamide crystal structure.¹²⁻¹⁵ This can be further confirmed by the wide-angle X-ray diffraction (WAXD) pattern.

For the thermal behavior of the semirigid modified nylon 6 copolyamides (PMA, POA, and PSA), it is found that the glass transition temperature (T_g) and the melting point (T_m) of the block copolyamides are also increased significantly as compared with that of the original nylon 6. But the ratio of T_g to T_m remains almost constant (0.55–0.59), irrespective of increasing the wt % of aromatic polyamide prepolymer content. Also,

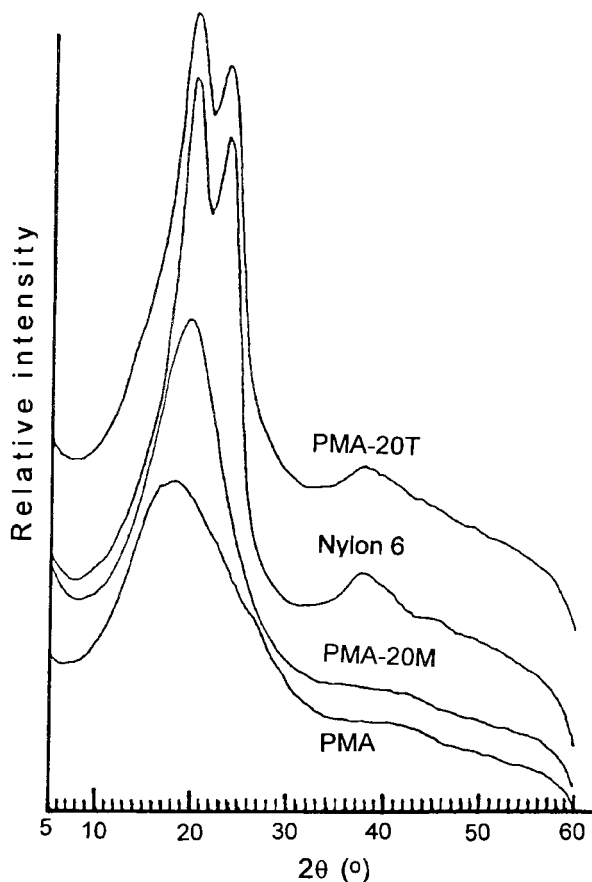


Figure 8 X-ray diagrams of homopolymers and block copolyamides: nylon 6, PMA, multiblock PMA-20M, and triblock PMA-20T.

Table IV *d*-Spacing and Crystallite Size of Nylon 6 Homopolymers and Copolyamides

Code	Polymer	<i>d</i> (200) A	<i>d</i> (002,202) A	L (200) A	L (002,202) A
Ny	Nylon 6	4.373	3.719	132	125
PmIA		—	—	—	—
PmIA-10M	Multiblock 10%	4.340	—	110	—
PmIA-20M	Multiblock 20%	4.346	—	—	—
PmIA-20T	Triblock 20%	4.378	3.731	127	107
PMA		—	—	—	—
PMA-10M	Multiblock 10%	4.366	—	121	—
PMA-20M	Multiblock 20%	4.368	—	—	—
PMA-20T	Triblock 20%	4.451	3.777	128	108
POA		—	—	—	—
POA-10M	Multiblock 10%	4.352	—	122	—
POA-20M	Multiblock 20%	4.358	—	—	—
POA-20T	Triblock 20%	4.386	3.733	129	106
PSA		—	—	—	—
PSA-10M	Multiblock 10%	4.361	—	120	—
PSA-20M	Multiblock 20%	4.367	—	—	—
PSA-20T	Triblock 20%	4.393	3.738	127	107

thermal analysis of the copolyamides reveals that the melting temperature of PSA copolyamide is up to 378°C. This might be due to the two prepolymers (nylon 6 and PSA) having the same monoclinic crystal structures and strong H bonds, thus enhancing the T_m . However, all modified nylon 6 triblock copolyamides show two peaks in the DSC diagram; therefore, dispersed aromatic polyamide segments among nylon 6 occurs in the triblock copolymer. The thermal properties of triblock copolyamides are found to be much lower than those of multiblock copolyamides.

Comparisons of the rigid and the semirigid copolyamide-reinforced nylon 6, the effect of their chemical structure to the thermal properties (T_g and T_m) of copolyamides is PmIA > PMA > POA > PSA. The rigid PmIA has the best thermal property due to its wholly rigid aromatic structure. The PSA with the soft suphonyl structure exhibits the lowest thermal properties, and the PMA and POA behave with thermal properties in between.

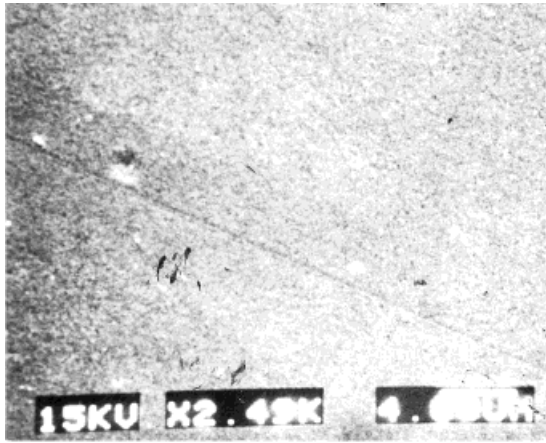
Wide-Angle X-ray Diffraction and Morphological Observation

The WAXD patterns of nylon 6 homopolymers and block copolymers were measured by the Rigaku

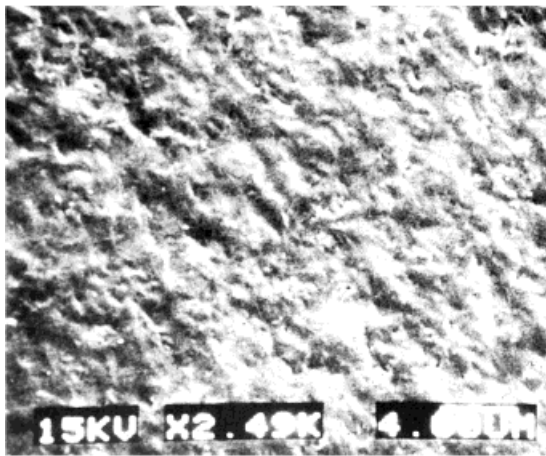
diffractometer and shown in Figures 7 and 8 and Table IV. From the wide-angle X-ray scattering (WAXS) diffraction patterns in Figure 7, it is found that the multiblock copolyamides of wholly rigid PmIA with nylon 6 have only one peak at $2\theta = 20^\circ$, evidently indicating that a new crystal structure of multiblock copolyamides formed; that is, the (200) plane of nylon 6–PmIA multiblock copolyamide in a structure of nylon 6 forms a new crystal structure.

Furthermore, the WAXD patterns of the semi-rigid modified nylon 6 block copolymers were also measured by the Rigaku diffractometer and are typically shown in Figure 8. From the result of X-ray diffractions (XRD) of these multiblock copolyamides, there is also only one peak at $2\theta = 20^\circ$, evidently indicating a new crystal structure formed; for example, the (200) plane of nylon 6–PMA multiblock copolyamide in a structure of nylon 6 forms a new crystal structure.

However, analysis by XRD in Figures 7 and 8 shows that nylon 6 homopolymer and triblock copolyamides have two diffraction peaks (i.e., $2\theta = 20.5$ and 24°), although the multiblock copolyamides have only one at $2\theta = 20^\circ$. This indicates that the triblock copolyamides behave as the microstructures of nylon 6 and aromatic polyamide



(a) Multiblock PMA-10M (2.49K)



(b) Triblock PMA-10T (2.49K)



(c) Triblock PMA-10T (4.49K)

separately; that is, noncompatible aromatic polyamide segments do not affect the formation of nylon 6 crystal in the copolyamide; therefore, a separated two-phase structure formed.

Data show a reduction in crystallite size of the nylon 6 matrix in Table IV. However, it should be noted that the crystallite size in the α (002,202) plane became smaller; but that in the α (200) plane did not, as aromatic block copolyamides are present. In addition, the d -spacing remains at almost a constant value. Thus, it could be concluded that if higher amount of the aromatic polyamide was copolymerized, the more the crystal growth of nylon 6 chain in the α (002,202) plane could be retarded. The effect of wholly-rigid PmIA is greater than those of semirigid chains (PMA, POA, and PSA).

Scanning electron microscopy (SEM) was used to visualize the microstructure of the copolymers. Photomicrographs in Figure 9 show a more homogeneous surface structure for the multiblock copolyamide (PMA-10M), but the triblock (PMA-10T) show a dispersed grain size. The grain particles are considered to be aggregates of the segments of the aromatic polyamides.

Mechanical Properties of Homopolymer and Copolyamides

Mechanical properties of homopolymers and block copolymers are presented in Table V and typically shown in Figures 10 and 11. The tensile strength (T_b) and the initial modulus (M_i) of various copolyamides of nylon 6 are found to progressively increase as the content of aromatic content is increased. This trend may result from the introduction of aromatic rigid units, which causes a higher intramolecular stiffness, but also the increase of the intermolecular forces between polymer chains, therefore forming a more uniform and compatible structure.

Comparisons of the rigid and the semirigid copolyamide-reinforced nylon 6, the order of their physical properties, such as tensile strength, is PmIA > PMA > POA > PSA; but for the elongation, the order is PSA > POA > PMA > PmIA. The rigid PmIA has the highest strength but poor elongation due to its wholly rigid aromatic struc-

Figure 9 SEM of block copolyamides: multiblock PMA-10M, triblock PMA-10T (2.49 K), and triblock PMA-10T (4.49 K).

Table V Mechanical Properties of Homopolymers and Copolyamides

Code	Polymer	T_b (MPa)	E_b (%)	M_i (GPa)
Ny	Nylon 6	45	44	0.88
PmIA		70	11	9.6
PmIA-10M	Multiblock 10%	79	16	8.3
PmIA-20M	Multiblock 20%	82	14	9.0
PmIA-20T	Triblock 20%	44	11	3.0
PMA		62	16	7.8
PMA-10M	Multiblock 10%	66	27	5.4
PMA-20M	Multiblock 20%	70	24	6.3
PMA-20T	Triblock 20%	38	18	3.43
POA		63	14	8.0
POA-10M	Multiblock 10%	67	26	5.8
POA-20M	Multiblock 20%	71	23	6.8
POA-20T	Triblock 20%	39	17	2.78
PSA		69	13	7.2
PSA-10M	Multiblock 10%	72	46	5.6
PSA-20M	Multiblock 20%	78	39	7.4
PSA-20T	PSA 20%	42	25	2.7

ture. The PSA with the soft suphonyl structure exhibits the lowest strength and the highest elongation; as far as the PMA and POA are concerned, they behave with properties in between. For the modulus property, the order of aromatic modified nylon 6 is PmIA > PSA > PMA > POA. The reason for the high initial modulus property of PSA modified nylon 6 is believed to be due to its sulfonyl structure.

However, from the mechanical properties of homopolymers and triblock copolymers in Figures 10 and 11, it is shown that the triblock copolyamides have much lower tensile strength, elongation, and modulus properties than those of multiblock copolyamides. This indicates that the triblock copolyamides, which are composed of two microstructures of nylon 6 crystalline and aromatic polyamide amorphous part, behave with lower mechanical properties.

CONCLUSIONS

Eight multiblock and three triblock copolyamides of nylon 6–aromatic polyamides were synthesized by chemical extension using *p*-APA as a coupling agent. The reinforcement of nylon 6 with rigid

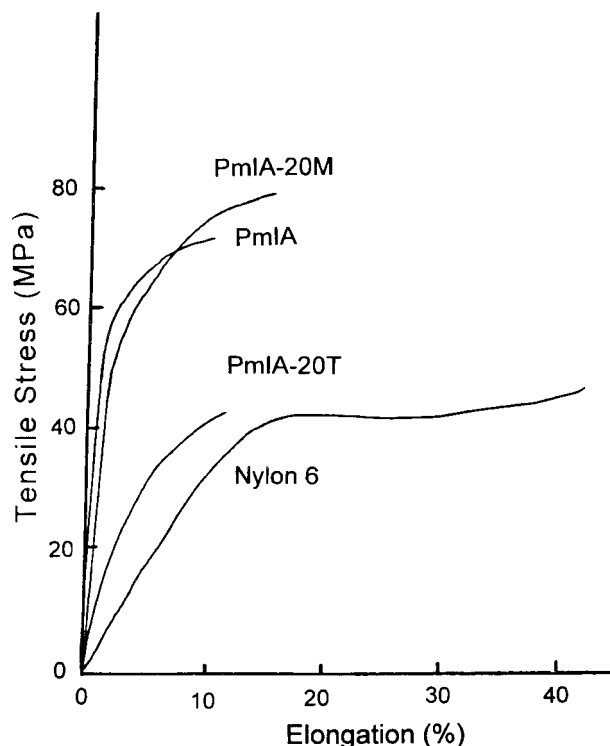


Figure 10 Stress–strain curves for homopolymers and block copolyamides: nylon 6, PmIA, multiblock PmIA-20M, and triblock PmIA-20T.

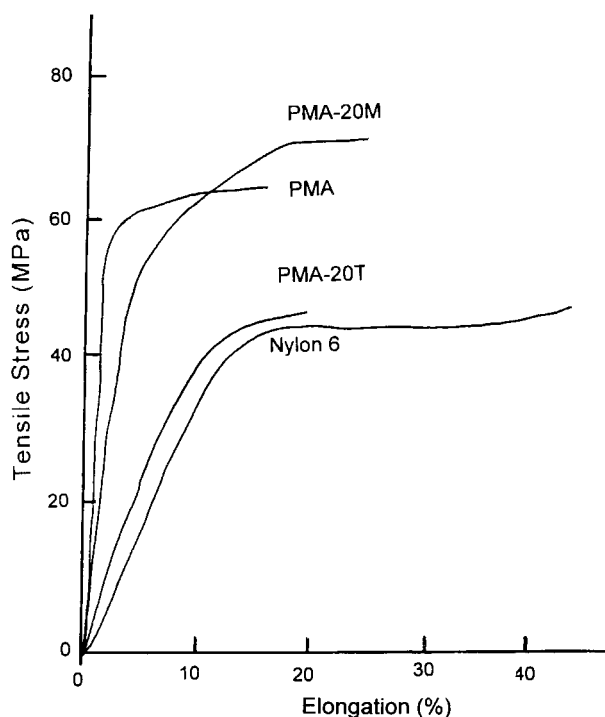


Figure 11 Stress-strain curves for homopolymers and block copolyamides: nylon 6, PMA, multiblock PMA-20M, and triblock PMA-20T.

aromatic polyamides proves to be successful, especially those of multiblock copolyamide. Block copolymers irrespective of PmIA, PMA, POA, and PSA show, for the same content of aromatic polyamide, better mechanical properties than those of nylon 6.

From DSC analysis, it is shown that copolyamides exhibit higher glass transition temperatures than that of nylon 6 homopolymer, which increases with the increase of rigid segment content, and also the multiblock copolyamides exhibit a more homogeneous structure than the triblock copolyamides. The order of thermal properties of aromatic modified nylon 6 copolyamides is PmIA > PMA > POA > PSA. Besides, the T_g and T_m of multiblock copolyamides are even higher than those of triblock copolyamides.

Analysis by XRD shows that the nylon 6 homopolymer and triblock copolyamides have two diffraction peaks, that is, $2\theta = 20.5$ and 24° . However, the multiblock copolyamides have only one at $2\theta = 20^\circ$, indicating a different crystal structure of multiblock copolyamides. This is further confirmed by the SEM.

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