Mechanical reinforcement and thermal transition behaviors in nylon 6-b-polyimide-b-nylon 6 triblock copolymers[1]

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Abstract

The mechanical properties and thermal transition behaviors of nylon 6-b-polyimide-b-nylon 6 triblock copolymers have been studied with varying block length and rigidity of the polyimide backbone and compared with those of pure nylon 6, in situ and physical solution blends. From differential scanning calorimetry experiments for liquid nitrogen quenched triblock copolymers, it is found that the crystallization temperature, which appears on successive heating, increases by 10–15°C, indicating relatively slow crystallization kinetics. Dynamic mechanical (DM) experiments show that the triblock copolymers exhibit a storage modulus which is 2 times higher than that of pure nylon 6 in the temperature range of –50°C to 150°C. As the rigidity of the polyimide backbone increases, the storage modulus of the copolymers decreases. In addition, the system with a polyimide block length of 12 000 g mol^{-1} shows the highest E' than any others with the block length shorter or longer than this value. Glass transition behaviors of these materials are also studied via α relaxations from DM observations. The relaxation peak temperature of tan δ increases from 60°C of pure nylon 6 to 82°C with 5% incorporation of the polyimide block component in the triblock copolymers. By incorporating a fully aromatic polyimide backbone into the triblock copolymer system, the tan δ peak of the α relaxation increases even further to 105°C with the same weight percentage of polyimide block incorporation.

Keywords: Nylon 6-b-polyimide-b-nylon 6 triblock copolymer; Mechanical reinforcement; Thermal transition

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1. Introduction

For many years attempts have been made to achieve maximum mechanical properties in polymers via reinforcement on the molecular scale using rigid rod polymers to form so-called "molecular composites". The concept of molecular composites was first proposed by Takayanagi in the early 1980s from a study of aliphatic polyamides and poly-(phenylene terephthalamide) (PPTA) polymer blends [1–4]. Later, this concept was extended and presently molecular composites are defined as being dispersions of a small amount of rigid molecules in a flexible chain (or coil) matrix to significantly improve the mechanical properties of the system [5,6].

Based on the theory put forward by Flory [7], it was predicted that it is thermodynamically impossible to obtain a complete molecular dispersion of rigid rods in a flexible coil matrix due to the highly unfavorable entropic consideration. This introduces the primary question in order to successfully develop a molecular composite: how to make these two different components in the composite compatible. Enormous efforts have been made to prevent the segregation of the rigid rod molecules from the coils and thus, provide a homogeneous mixture. However, a thermodynamically stable dispersion of rigid rods in a flexible coil matrix cannot be achieved except for the introduction of specific interactions between these two components and/or by increasing the chain flexibility of the rigid rod component. Sometimes, the kinetics of phase separation may be controlled to overcome the thermodynamic driving force for phase separation, resulting in a homogeneous frozen-in system with a thermodynamic metastability. Another approach consists of synthesizing copolymers which graft the flexible polymer chains onto the backbone of the rigid molecules or block-copolymerizes these two components. Recently, success has been achieved in our laboratories with the synthesis of stable graft and multi-block copolymers of flexible and semirigid rod polymers.

The goal of this research was to characterize a class of nylon-6-b-polyimide-b-nylon 6 triblock copolymers and search for the usefulness of these copolymers in applications of property reinforcement. The strategy followed in this research was first to synthesize a series of these triblock copolymers by varying the weight percentage of the semirigid rod polyimide block component, as well as the block length (molecular weight) of the polyimide. The triblock copolymers were then characterized through the study of their thermal and mechanical properties. From these results, a better understanding of the reinforcing capability of aromatic polyimides in copolymers was obtained. It is confirmed that multi-block copolymers are a viable and effective way to acquire maximum reinforcement of flexible coil polymers without macroscopic phase separation. In this paper, we repeat our first-hand results in these systems.

2. Experimental

### 2.1. Synthesis and preparation of samples

Nylon 6-b-polyimide-b-nylon 6 triblock copolymers were synthesized via both condensation and anionic polymerization. The synthetic route has been reported elsewhere

[8]. In brief, it included first making the poly(amic acid) precursor by reacting the dian-hydride and diamine in appropriate stiochiometric amounts in N-methyl-2-pyrrolidone (NMP) at room temperature to obtain the desired polyimide block length. The poly(amic acid) chains were then end-capped with caprolactam initiators and the polymers were chemically imidized to form the polyimide macroinitiator. They were then dissolved in caprolactam monomers and an anionic polymerization was carried out with a Grignard catalyst at 140°C under nitrogen. In this synthetic procedure the weight percentage of the polyimide component was chosen to be between 5 and 15 wt%. Three different poly-imide block lengths were controlled (6000, 12 000 and 18 000 g mol⁻¹). Different dian-hydrides and diamines were also used to compare rigidity effects of the polyimide back-bone on the thermal transition behavior and the mechanical properties of the resulting copolymers.

In situ blends of nylon 6 and the polyimides were also synthesized in which no chemi-cal bonds between nylon 6 and the polyimide molecules exists. In order to obtain the in situ blends, the same synthesis procedure was used as described above except for the fact that the poly(amic acid) chains were end-capped with phenyl rings rather than caprolac-tam initiators and then the polyimides were dissolved in the caprolactam monomers, fol-lowed by the polymerization of caprolactam to form nylon 6 in the presence of poly-imides. Finally, both of these samples were compared to solution blends of the two com-ponents and to pure nylon 6. The solution blend was prepared by first dissolving the ny-lon 6 and polyimide polymers in a common solvent such as m-cresol and then casting films from the solution.

All of the bulk samples obtained from the polymerization must first be extracted with hot water in order to remove unreacted monomers. For dynamic mechanical (DM) and differential scanning calorimetry (DSC) experiments, the samples were prepared by first dissolving the bulk material at 10% solids (w/v) in m-cresol at 60°C. Films, which varied in thickness from 0.1 to 0.3 mm, were then cast from the homogeneous solution. A dry-ing procedure was used to remove all traces of the solvent and complete removal was verified via thermogravimetric experiments. The films were first dried under vacuum at 160°C for 30 h and then slowly cooled to room temperature.

The monomer chemical structures in the polyimide or copolyimide block components are

Bis A-DA/Bis P (PI-39)

BTDA/6F-diamine (PI-64)

Bis A-DA/OTOL/BPDA (PI-48)
50/100/50
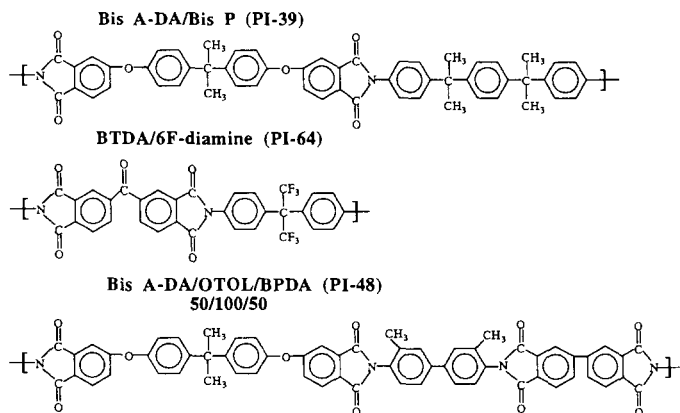
2.2. Characterization

Differential scanning calorimetry (DSC) experiments were conducted on a Seiko DSC 220C. The temperature and heat flow scales were precisely calibrated at different heating rates (2.5–40°C min^{-1}) using standard materials in the range of temperature studied. Sample weights were approximately 12 mg. A heating rate of 5°C min^{-1} was commonly employed. The as-polymerized samples were first run from −50 to 250°C to calculate the original percent crystallinity of the polymers. The equilibrium heat of fusion ($\Delta H_f°$) of pure nylon 6 is 26.0 kJ mol^{-1} [9]. The DSC crystallinity can be calculated via the ratio between the measured and the equilibrium heats of fusion ($\Delta H_f/\Delta H_f°$). The samples were then held at 250°C for 2 min to ensure the destruction of all crystal nuclei and rapidly quenched in a low temperature bath consisting of glass beads, diameter of the order of 1 mm, surrounded by liquid nitrogen [10]. The purpose of this quenching technique was to obtain completely non-crystalline samples. After the samples were quenched, they were immediately transferred to the DSC cell which was held at −50°C to eliminate the possibility of moisture condensation. The polymers were then heated to 250°C to observe the glass transition temperature as well as the melting and crystallization transitions. The samples for the experiments were enclosed in aluminum pans. The weights of the reference pans and the sample pans was kept constant within ±0.001 mg and the sample weights were measured to an accuracy of ±0.002 mg. Also, each sample was used only once to prevent sample degradation.

Isothermal crystallization experiments were conducted on a Perkin-Elmer DSC-7 equipped with an intercooler. As mentioned above, the samples were enclosed in aluminum pans but the weights of the samples were kept below 0.5 mg to minimize the lack of thermal homogeneity within the samples. Each sample was first heated to 275°C and held for 2 min to ensure the destruction of all crystal nuclei and destroy the previous thermal history of the samples. The polymers were then quenched to their respective crystallization temperatures and held there until all detectable crystallization was complete. After this time, the samples were then heated at 10°C min^{-1} to 275°C to observe the melting transition.

DM measurements were carried out on a Seiko DMS 200 equipped with a liquid nitrogen cooling tank to observe the relaxation behavior of the samples. Film samples were cut into rectangular strips with dimensions of 25 mm × 8 mm × 0.1 mm (length × width × thickness). The experiments were conducted over a temperature range of −130°C to 250°C at a heating rate of 2°C min^{-1}. The frequency used was 0.1 Hz.

3. Results and discussion

3.1. Crystallization and melting

The crystallization and melting behavior of the nylon 6-b-polyimide-b-nylon 6 triblock copolymers were compared with those of an anionically synthesized, pure nylon 6 sample via non-isothermal DSC experiments. The DSC curves for one of the liquid N$_2$ quenched triblock copolymers as well as the nylon 6 sample are shown in Fig. 1. The
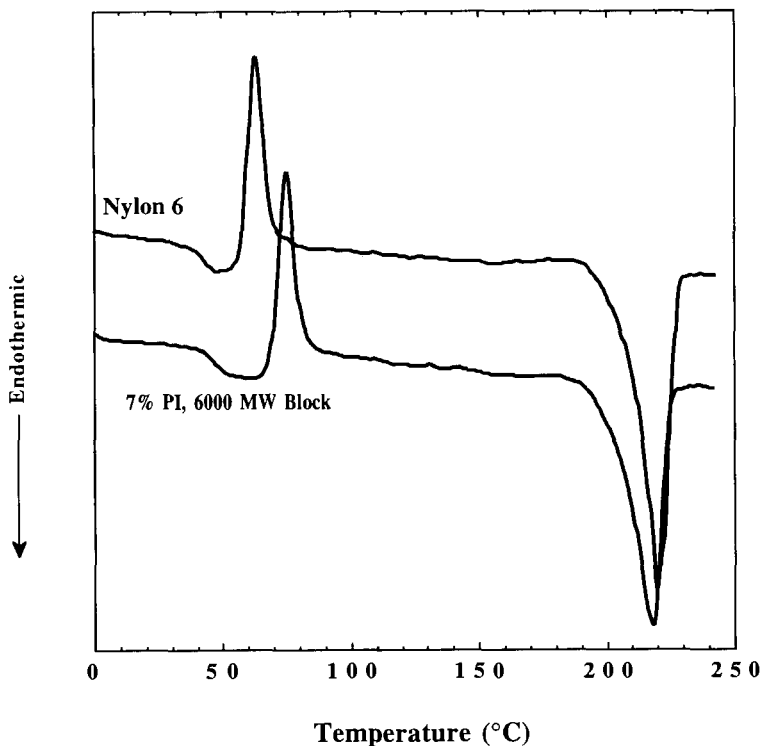
Fig. 1. Non-isothermal DSC curves for liquid nitrogen quenched nylon 6-b-polyimide-b-nylon 6 triblock copolymer (PI-47, 7% with a block length of 6000 g mol^{-1}) and a pure nylon 6 sample.

polyimide used in this triblock was actually a copolyimide of 6FDA/BPDA/OTOL (50:50:100) and abbreviated as PI-47 in this paper. The percentage of polyimide block component by weight was 7% and the polyimide block length was 6000 g mol^{-1} for this sample. As can be seen in this figure, the quenched copolymer has a slightly lower melting temperature and a slightly higher glass transition temperature compared with nylon 6. However, it can be noticed that the cold crystallization temperature peak is increased by a substantial amount with the rigid block component incorporation. We can therefore, conclude that the polyimide segments slow down the overall crystallization rate of the nylon 6 notably at even low weight percentage incorporation. This is due mostly to the decreased mobility of the nylon 6 chains caused by the rigid polyimide mid-block components.

Table 1 lists the thermal properties of some of the triblock copolymers studied in this research. All of the triblock copolymers studied have similar thermal properties to that of nylon 6. In addition to the PI-47 system examined, we have also investigated a relatively flexible polyimide based on Bis A-DA/Bis P, which is abbreviated as PI-39. It is interesting to note that the DSC crystallinity of the samples, as calculated from the equation shown in Section 2, does not substantially decrease with the incorporation of the poly-

Table 1

Non-isothermal DSC results for quenched nylon 6-b-PI-b-nylon 6 triblock copolymers and pure nylon 6 samples

Type	% PI	MW of PI block	T_g/°C half-height	T_c (peak)/ °C	T_m (peak)/ °C	w^c 1st run in %
Nylon 6	0	N/A	43	67	218	43
47-triblock	3	6000	45	68	218	42
	7	6000	47	75	217	40
	4	12000	45	66	218	43
	6	12000	45	68	217	43
BisP/BisA-DA	100	12000	220	–	–	–
39-triblock	5	6000	45	69	215	43
	5	12000	44	69	215	44
	5	18000	44	70	218	39
	15	12000	48	75	213	44
39: in situ blend	5	12000	44	68	216	45

imide blocks into the nylon 6 after the normalization of the nylon weight in the calculations.

The crystallization behavior of the nylon 6 component in these copolymers has been further studied via DSC isothermal crystallization experiments. Of particular interest is the time necessary to reach the peak of the crystallization exotherm, t_p, which is close to the time for the development of 50% of the overall crystallinity. This value is used for comparing the overall crystallization rate for each different triblock copolymer, as well as to compare those polymers with a pure nylon 6 sample. A lower value for t_p indicates that the crystallization rate is actually faster since it took less time to reach the peak of the exotherm. In Fig. 2, the logarithm of the t_p is plotted against the crystallization temperature for some triblock copolymers of this study. Three different polyimide segments were used with differing backbone rigidities: Bis A-DA/Bis P (PI-39) ($T_g = 220$°C) [11]; BTDA/6FDA (PI-64) ($T_g = 308$°C) [11]; and Bis A-DA/BPDA/OTOL (PI-48) (50:50:100) ($T_g = 320$°C) [12]. As expected, nylon 6 has the highest crystallization rate. This was followed by the in situ blend and the triblock copolymers. The PI-48 sample has the lowest crystallization rate of these three copolymers while the other two have almost identical rates in between these two limiting cases. Since PI-48 possesses the most rigid polyimide backbone studied, it seems that as the rigidity of the polyimide backbone increases, the overall crystallization rate of the nylon 6 component is decreased. This could be primarily due to the enhanced restriction on the mobility of the nylon 6 chain components to rearrange and crystallize brought by the more rigid polyimide block component, which is chemically bonded into the molecules. It also must be pointed out that the in situ blend crystallized faster than the triblocks because of the lack of covalent bonding between nylon 6 and polyimide components. Thus, the mobility of nylon 6 chains in this case is perhaps, less inhibited. Further investigation must be carried out in order to examine this explanation.
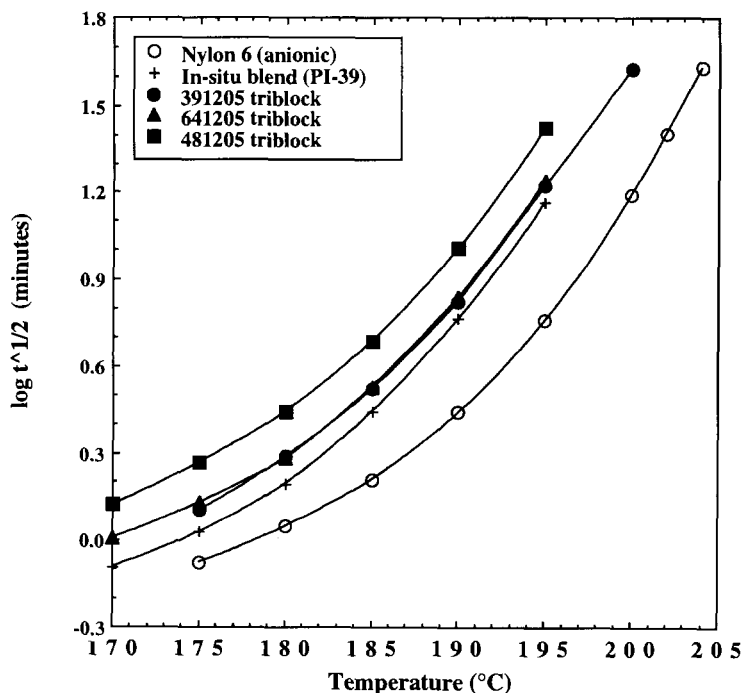
Fig. 2. Isothermal crystallization kinetics of triblock copolymers and pure nylon 6.

3.2. Glass transitions and relaxation behaviors

The reinforcing ability of the polyimide block components on the nylon 6 has also been examined via DM measurements. Specifically, the effect of the polyimide block components on the α relaxation process or the glass transition of the triblock copolymers is studied. In this research, four different systems have been investigated and compared so that we may obtain some understanding on miscibility–mechanical property relationships for these triblock copolymers. Two of these systems are the triblock copolymer (PI-39) and the pure nylon 6 sample. In addition, an in situ blend, in which the polyimide chain molecules were dissolved in caprolactam monomers and thus trapped inside the nylon matrix, and a solution blend of the two components are also studied. Each system, except for the pure nylon 6, has a 5% polyimide block component by weight and block length of 12 000 g mol⁻¹. The polyimide chemical structure is Bis A-DA/Bis P as described earlier. The tan δ curves examined for these four systems are shown in Fig. 3. Specifically, we are interested in the α relaxation peaks of these systems because this relaxation in aliphatic polyamides is known to be distinctly related to large-scale segmental, cooperative motion of the amorphous chains and thus, the glass transition of these polymers. As can be seen in this figure, the α relaxation peak for the triblock copolymer (PI-39) is 22°C higher than that of pure nylon 6. This is a large increase in the glass transition temperatures for the copolymer with only 5% of the polyimide molecules in-
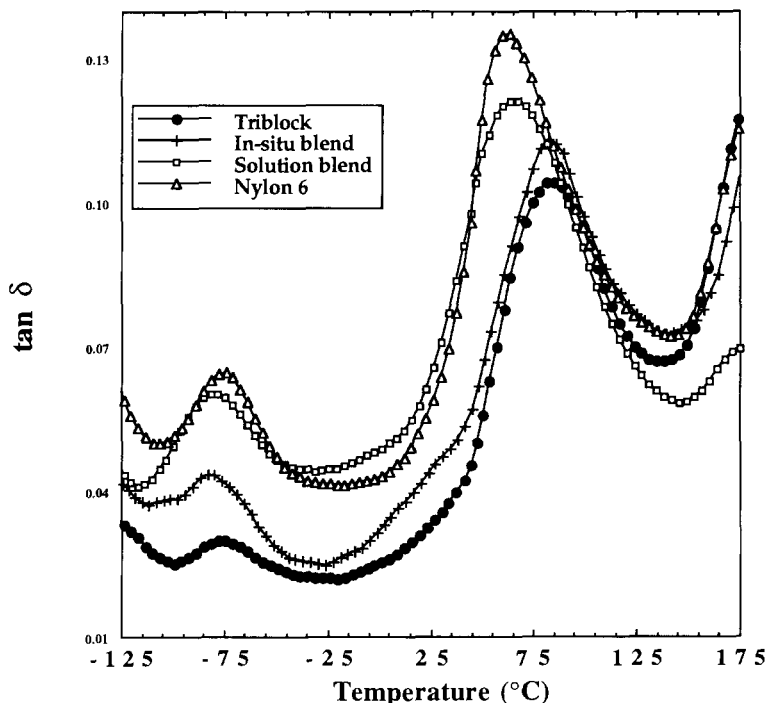
Fig. 3. DM tan δ curves for 5% polyimide incorporation with a block length of 12 000 g mol^{-1} (frequency = 0.1 Hz).

corporated into the flexible matrix, and this is much greater than a prediction based on the rule of ideal mixing. From the curves we also see that the in situ blend possesses an α relaxation peak temperature which is close to that of the copolymer whereas, the α relaxation peak temperature of the physical (solution) blend is only slightly higher than that of the pure nylon 6. We can, therefore, speculate that probably the in situ blend contains some minor degree of microscopic phase separation of the nylon 6 and polyimide molecules which does not have a detrimental effect on the lowering of the α relaxations of the polymer. The solution blend, on the other hand, must possess a large degree of phase separation which may not allow the polyimide molecules to affect the α relaxation of nylon 6 as much as in the other two systems.

The effect of three different polyimide backbones having varying rigidities on the relaxation behaviors of the triblock copolymers has also been explored via DM. These three copolymer systems are the same ones used in the isothermal DSC study (Fig. 2). Fig. 4 shows the comparison of the tan δ curves as a function of temperature for these three different systems. The PI-39 copolymer with the most flexible polyimide backbone shows the lowest α relaxation peak temperature of 82°C, while the one with the most rigid polyimide backbone, PI-48, has an α relaxation peak temperature of 105°C. Furthermore, the PI-64 copolymer possesses an α relaxation peak temperature of 94°C,
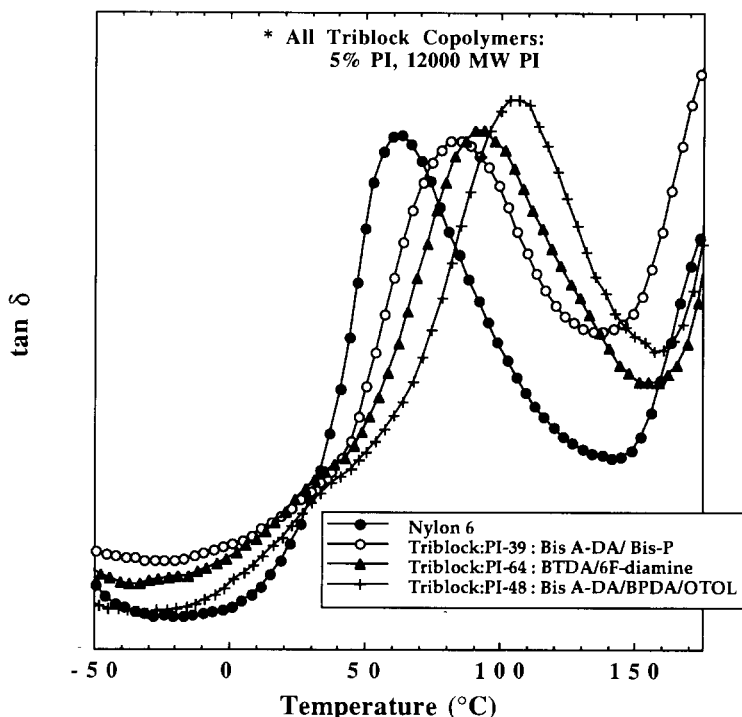
Fig. 4. DM tan δ curves for the study of rigidity effect on the α relaxation processes of the different triblock copolymers (frequency = 0.1 Hz).

which is in between the two glass transition temperatures of the previous systems. In any case, these values are extraordinary in that only 5% of the polyimide chains are copolymerized, with a block length of 12 000 g mol^{-1} and still, the increase in the α relaxation peak temperature over pure nylon 6 is substantial. It is certain that the polyimide block components do not join the crystalline part of the nylon 6 since the crystal structure in the solid state of these copolymers is found to be the same as that in pure nylon 6 [11]. As a result, the weight percentage of the polyimide component in the remaining amorphous state is almost doubled if a typical crystallinity of 45% in pure nylon 6 is assumed (see also Table 1). Based on the calculation of the glass transition temperature in a completely miscible copolymer system [13], the glass transition of these three copolymers should be 74°C, 82°C and 83°C, respectively under the assumption that only two phases exist in the systems, namely, no effect of the crystallinity on the glass transition or the α relaxation process is considered. From these results it can be speculated that microscopic phase separation which is obviously present in the more rigid triblock systems does not have an adverse effect on the synergistic increase in the glass transition observed over pure nylon 6. However, more research must be done to clarify the effect of microscopic phase separation on the α relaxation peak temperatures of these polymers.
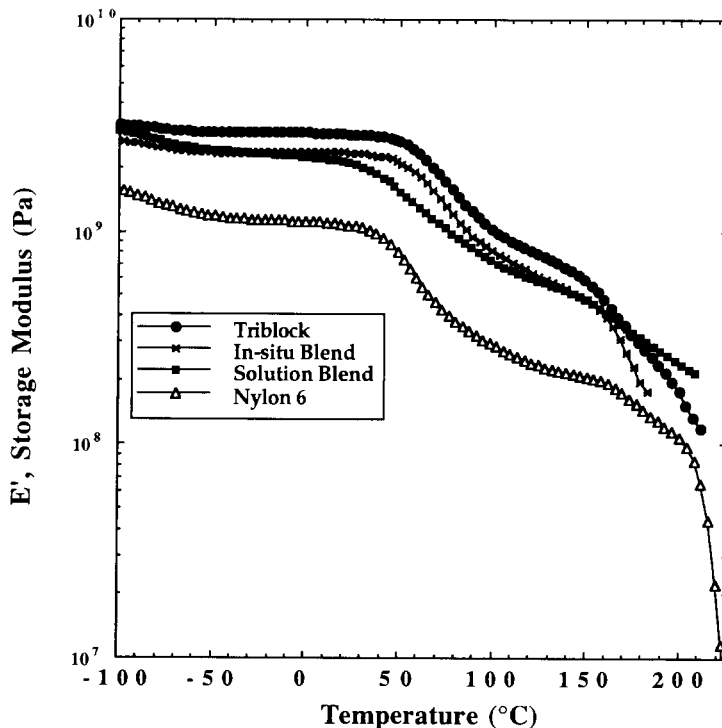
Fig. 5. DM storage modulus E' curves for 5% polyimide incorporation with a block length of 12 000 g mol^{-1} (frequency = 0.1 Hz).

3.3. Dynamic mechanical properties

The reinforcing ability of the polyimide block components on the nylon 6 matrix has also been examined via the storage modulus, E'. In Fig. 5, the storage modulus curves as a function of temperature can be seen for the four systems described in Fig. 3 (the tri-block copolymer PI-39, the in situ blend, the physical blend, and the pure nylon 6). As expected, the triblock copolymer has the highest storage modulus compared with the other three. It is particularly surprising that the value of E' for the triblock copolymer with only 5% polyimide components is approximately twice that of the pure nylon 6 sample. Therefore, for this system we must be getting excellent dispersity of the poly-imide segments throughout the nylon 6 on the molecular scale and it behaves similarly to a microfibilliar reinforced composite. It is also interesting to look at the E' values for two other blends, which exhibit lower values than the copolymer. This is perhaps due to the lack of chemical bonding between these two components which permits some degree of phase separation to take place in these samples. Consequently, the polyimide compo-nent's aspect ratio decreases due to the aggregation of the polyimide molecules, causing a loss in the polyimide's reinforcing ability.
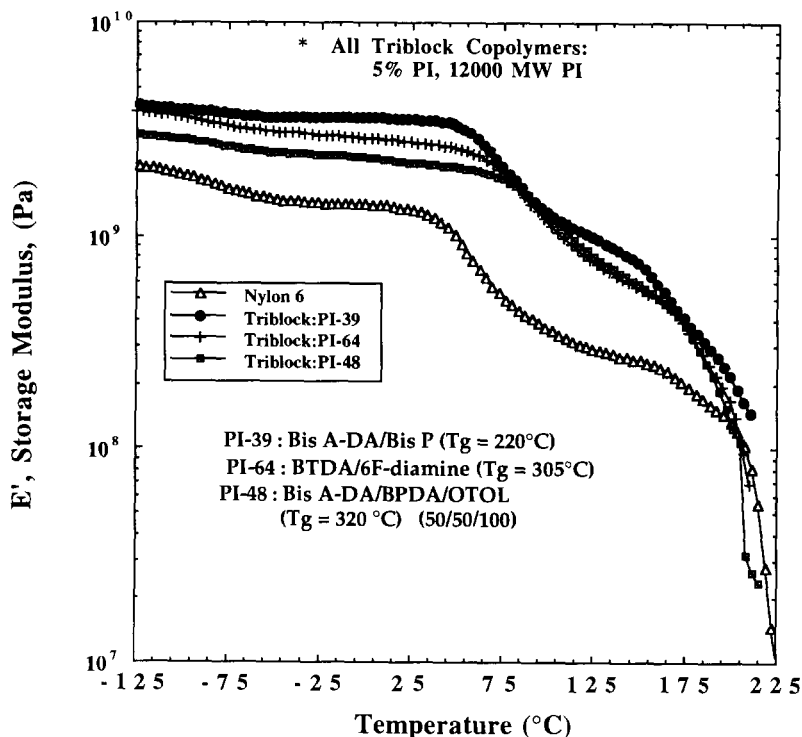
Fig. 6. DM storage modulus E' curves for the study of rigidity effect on the mechanical reinforcement of the different triblock copolymers (frequency = 0.1 Hz) .

Finally, the storage moduli changes in the triblock copolymers with different rigidities of the polyimide backbones are shown in Fig. 6. These systems studied are the same as those shown in Fig. 4. It is interesting that as the rigidity of the polyimide backbone is increased in these triblock copolymers, the E' values actually decrease in the whole temperature range up to the glass transition temperature. All the DM results in Figs. 5 and 6 are listed in Table 2. In order to quantitatively compare the storage modulus results for each system, the data shown in this table are at three specific temperatures, 0°C, 75°C and 150°C. It is evident that the storage modulus of the triblock copolymer with a polyimide having a relatively rigid backbone or a block length of 18 000 g mol^{-1} does not exhibit the highest value. A possible explanation for the decrease in E' with increasing polyimide rigidity or block length is that the partially phase separated morphology in these systems may drastically affect the mechanical properties. This can be explained using the Gibbs free energy equation in polymer mixing [14]. As the rigidity of the polyimide block components increases, the combinatorial entropy of the mixing term, ΔS_{mix}, becomes more unfavorable, hence, there is a better chance for phase separation. Furthermore, the interaction parameters between nylon and polyimide components also play an important role. It has been found that the χ parameter of the polyimide compo-

Table 2

Dynamic mechanical analysis results for nylon 6-b-PI-b-nylon 6 triblock copolymers and other potential molecular composite systems

Type	% PI	M_n PI	Storage moduli (0.1 Hz) $\times 10^8$ Pa			Tan δ/ °C α-peak (0.1 Hz)	Peak temp. β-peak (0.1 Hz)
			E' 0°C	E' 75°C	E' 150°C		
Nylon 6	0	N/A	13.1	7.64	5.19	60	−78
Bis P/Bis A-DA	100	12000	49.8	36.0	26.0	220	−
39: triblock	5	6000	36.0	15.9	6.69	76	−80
	5	12000	36.4	21.5	7.49	82	−78
	5	18000	27.7	16.9	7.09	78	−77
39: in situ blend	5	12000	23.6	13.2	4.77	82	−78
39: solution blend	5	12000	27.5	13.0	6.02	64	−78
64: triblock	5	12000	29.0	19.3	5.56	94	−80
48: triblock	5	12000	23.4	18.6	5.90	105	−79

nent increasingly deviates from that of pure nylon 6 with increasing rigidity in the polyimide backbone [12].

4. Conclusions

From our experimental observations, it is surprising that nylon 6-b-polyimide-b-nylon 6 triblock copolymers show remarkable improvement of the dynamic mechanical storage modulus compared with the pure nylon 6. From the study of their thermal properties including crystallization, melting, glass transition and relaxation behaviors, it is speculated that microscopic phase separation is the key factor to decrease the E' value. This has also been supported by the comparison of thermal properties in the in situ and physical blend systems as well as in the triblock copolymers having varying rigidity of the polyimide backbones or the block length.

Finally, for at least several systems studied, such as PI-39 having 5% polyimide and block length of 12 000 g mol^{-1}, all of the thermal property criteria examined have indicated that these copolymers possess a rather homogeneous dispersion of the polyimide block components. However, more structural and molecular motion studies must be conducted such as wide angle and small angle X-ray scattering, transmission electron microscopy, and ^{13}C solid state nuclear magnetic resonance methods, to prove whether the dispersion of the polyimide components is truly on the molecular or a larger nanometer scale.

Acknowledgements

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