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Polymer Communication

# A novel approach to melt-processable molecular composites

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Received 24 May 2000; received in revised form 28 August 2000; accepted 28 August 2000

## Abstract

A series of model tri-block copolymers having a chain sequence of polycaprolactam-*b*-poly(*p*-phenylene terephthalamide)-*b*-polycapro-lactam with varied block length were designed, synthesized and characterized. The optimization and harmonization of the rigid and flexible block length lead to copolymers showing meltability. Blends of nylon-6 with the tri-block copolymer showed much better phase stability than that of normal blends. The preliminary results suggest that the proposed approach may be practicable to prepare melt-processable molecular composite. © 2000 Published by Elsevier Science Ltd.

*Keywords*: Molecular composites; Melt-processable molecular composites; Nylon-6 blends

## 1. Introduction

The concept of molecular composites was introduced by Takayanagi and Helminiak two decades ago [1–3] to describe the polymeric composite systems in which the reinforcing micro-fibrils are rigid polymers. These systems consist of two polymeric components with dissimilar characteristics: a stiff and strong rigid-rod polymer dispersed at the molecular scale in a matrix of flexible polymer. The rigid-rod component is assumed to act as reinforcing fibers similar to those in conventional fiber-filled composites. Considerable efforts have been taken by many researchers [4–20] to explore this principle in order to prepare a new category of high-performance polymeric materials, and were summarized in a number of contributions [21–24]. A systematic review also has been published recently by Schartel and Wendorff [25] to scrutinize the success and failure of the concept of molecular reinforcement.

The essential prerequisite for molecular composites is to get molecularly dispersed polymeric rods in a flexible matrix. The major obstacle to attaining a molecular composite, however, is the homogenous miscibility [25]. Almost all the works showed that direct blending of rigid and flexible polymers has resulted in heterogeneous composites, even for those with a fine dispersion of the rigid component, owing to the poor miscibility and phase segregation even in the case of chemically similar constituents. Possible routes have thus been developed in an attempt to solve these problems, including rapid preparation technologies [7,26–27], advanced synthesis approaches such as in situ and precursor techniques [23,28–31], introduction of favorable interactions such as ionic, dipole–dipole, or hydrogen bonding between components [24,32–34], and molecular structure design such as block, graft or multipode copolymers [11,14,21,35–37].

Another problem involved in the molecular composite study is the poor processability of the materials, as most of the materials are prepared in solution using toxic and/or strong solvents such as sulfuric acid, and can hardly be melt-processed. The rigid-rod polymers generally have a much higher melting point than the processing temperature allowed for matrix polymers, and some of them do not melt inherently. Moreover, phase segregation seems to be unavoidable during heating because the dispersion of the rigid-rod component in the matrix is far from thermodynamically stable. Some attempts to prepare thermally processable systems have been reported for blends of aramid/poly(ethersulfone) [38] and aramid/amorphous nylon [39], whereas these blends can only be processed by hot-compression since the melting point of the aramid is either much higher than the processing temperature or not observed. This should be considered as an encouraging but not a satisfactory start, although it was still believed that melt-processing of molecular composites could hardly be performed without phase segregation [27]. In this communication, a novel approach to melt-processable molecular composites is proposed and the preliminary results are given to support this scheme.

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Table 1
Nomenclature of the tri-block copolymers and their composition

| Tri-block copolymer | Average monomer units of polycaprolactam block[a] | Average PPTA units in rigid block | Length of PPTA block (nm) | Mass ratio of rigid/flexible blocks |
|---|---|---|---|---|
| N1P2 | 12 | 2 | 2.56 | 0.20 |
| N1P3 | 12 | 3 | 3.84 | 0.28 |
| N1P4 | 12 | 4 | 5.12 | 0.36 |
| N1P5 | 12 | 5 | 6.40 | 0.44 |
| N3P2 | 18 | 2 | 2.56 | 0.13 |
| N4P3 | 25 | 3 | 3.84 | 0.14 |
| N5P4 | 38 | 4 | 5.12 | 0.12 |

[a] Each model tri-block copolymer has two polycaprolactam blocks.

### 1.1. The proposition and the theoretical considerations

It is well known that the dispersion of the discontinuous phase in the matrix is associated directly with the miscibility and interaction between the polymeric components. To improve the dispersion thermodynamically, enthalpy and entropy contributions to the mixing behavior should be taken into consideration, with the former related to the chemical structure and molecular/segment interactions and the latter to the configuration of the macromolecules [25]. We therefore designed model block copolymers having the following chain sequences:



(A)        or        (B)
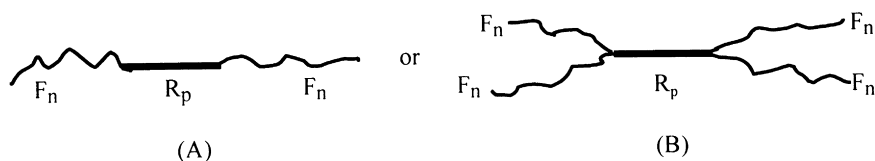
where R denotes the rigid-rod block with length $p$, and F the flexible block with length $n$.

According to the solvation theory of polymer solution, when the interaction between the segments of polymer and the molecules of solvent (or the segments of another polymer) is stronger than the cohesion, the polymer will be dissolved (or the system is miscible). Likewise, if the segmental interaction of the flexible blocks (F blocks) with the matrix polymer is greater than that of the rigid-rod blocks (R blocks), the tendency of self-aggregation of the R blocks should be reduced to promote the dispersion. The solubility or meltability of the block copolymer should consequently be improved.

One of the most important considerations for this proposition is the optimization and harmonization of the length of the rigid and flexible blocks. It would not be necessary to couple an excessively long rigid-rod block into the copolymer while ensuring that the reinforcing block has sufficient strength, which would be helpful in decreasing the self-aggregation tendency of the R blocks. On the other hand, the junction of the F blocks to the R block would contribute to: (a) enhancing the miscibility between the reinforcing phase and the matrix with the proper selection of chemical structure similarity for the F blocks; (b) hindering the strong intermolecular interaction of the rigid blocks to promote the dispersion of the rigid phase; (c) eliminating the stress concentration at the ends of the R block; and (d) improving the solubility of the copolymer with the optimization of the length and structure of the rigid and flexible blocks, and hopefully assigning meltability to the copolymer.

## 2. Experimental

Model tri-block copolymers having a chain sequence of polycaprolactam-*b*-poly(*p*-phenylene terephthalamide)-*b*-polycaprolactam with varied block length were chosen to verify the above notion, of which rigid-rod block PPTA has been commonly used in molecular composites. To synthesize the copolymer, monocarboxyl-end-grouped polycaprolactam oligomers with different degrees of polymerization were first prepared prior to copolymerization [40]. The reaction called the direct high-temperature poly-condensation of terephthalic acid, *p*-phenylene diamine and the polycaprolactam oligomer was carried out in the presence of triphenyl phosphate, pyridine, *N*-methyl-2-pyrrolidone, and LiCl, and the chemical composition and properties of the resultant products were characterized by FT-IR, FT-NMR, High Resolution Pyrolyzer GC/MS, DSC, TGA, and WAXD. The copolymerization procedure and identification of the reactants are to be reported in detail separately.

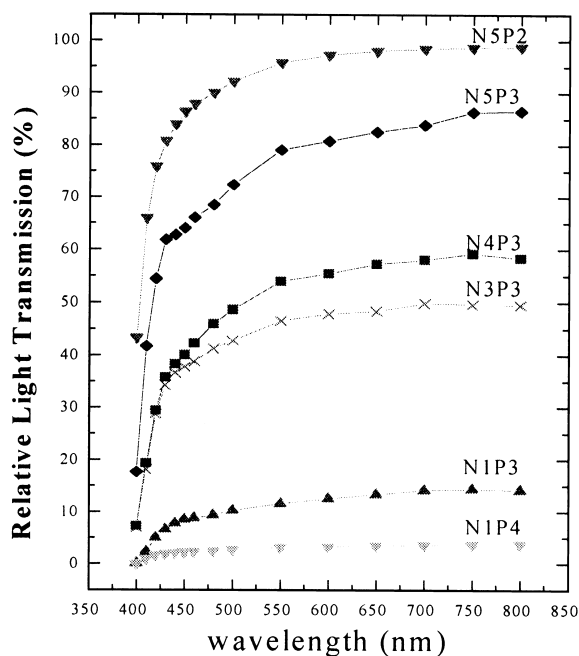Table 1 lists the nomenclature of the tri-block copolymers

Fig. 1. The relative light transmission of the tri-block copolymer solutions as a function of wavelength (1 wt% in formic acid).

used in the study and their composition. The block length is expressed in terms of average number of monomer unit.

The matrix polymer used was nylon-6 (UBE-1013B, a commercial product by Yubu, Japan). To ensure complete mixing, blends were prepared by dissolving the copolymers and nylon-6 in sulfuric acid solution, precipitating in water and drying in vacuum.

The DSC measurements were carried out using a Perkin–Elmer DSC-7 at a heating rate of 20°C/min under $N_2$. An ultraviolet–visible (UV–visible) spectrophotometer (Model 756-MC from The Shanghai Analysis Instruments Factory, China) was used to study the solubility of the tri-block polymer solution in formic acid.
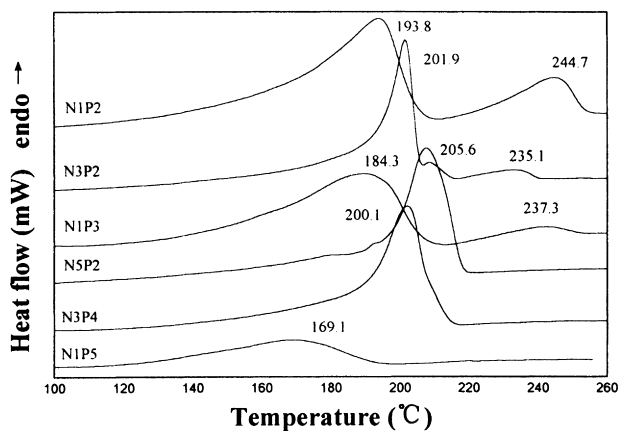


Fig. 2. DSC heating scans of the tri-block copolymers with different length of PPTA segment (20°C/min).

# 3. Results and discussion

## 3.1. Solubility of the model tri-block copolymers

It was observed that the tri-block copolymers could be dissolved or partly dissolved in formic acid, whereas the PPTA oligomer can only be dissolved in sulfuric acid. The light transmission properties of the copolymers in 1% (w/v) formic acid solution were determined using UV–visible spectrophotometry. The results are shown in Fig. 1, where the lower percentage of the relative light transmission indicates stronger light scatting owing to larger insoluble particles in the solution and thus poorer solubility.

It can be found that the solubility of the copolymers is strongly dependent on the molecular weight of the blocks and the relative length of the flexible and the rigid blocks. The specimen showing the best solubility is that with longest flexible blocks and shortest rigid block (N5P2). The size of the insoluble particles is estimated to be well below 400 nm based on the theory of light scatting and the experimental facts. For the specimens with shorter flexible blocks and longer rigid block, such as N1P4 and N1P3, poor solubility of the copolymer results in a cloudy solution. However, the solution cannot become clear even after several weeks, suggesting at least the partial solubility of the copolymers in formic acid. The length of the flexible block is seen to be the main factor to affect the solubility, and the length of the rigid-rod block influences the dispersion of insoluble particles.

Although one cannot simply conclude from these results that the rigid blocks are dispersed molecularly in the solution, the flexible polycaprolactam blocks bonded chemically to the ends of the rigid block can definitely reduce the tendency of self-aggregation of the rigid blocks to improve the solubility of the copolymers, resulting in smaller PPTA domains spreading in the solution. Since formic acid is a good solvent for nylon-6, it would be expected that the miscibility of the copolymers with nylon-6 can be consequently improved and similarly, the dispersion of the rigid-rod phase.

## 3.2. Meltability of the model tri-block copolymers

The thermogravimetric analysis results, not given here, showed that the introduction of polycaprolactam as flexible blocks to PPTA depresses only slightly the thermal stability of the component in the copolymers as compared to that of pure PPTA. Nevertheless, the thermal degradation temperature of the polycaprolactam blocks bonded to the rigid-rod is about 100°C higher in comparison to the corresponding polycaprolactam oligomers.

Fig. 2 displays the representative DSC heating curves for the tri-block copolymers. It is evident that all the copolymers obtained show meltability and definite melting peak(s) on the heating scans. The number of melting peaks and the melting temperature are seen to be again dependent on the
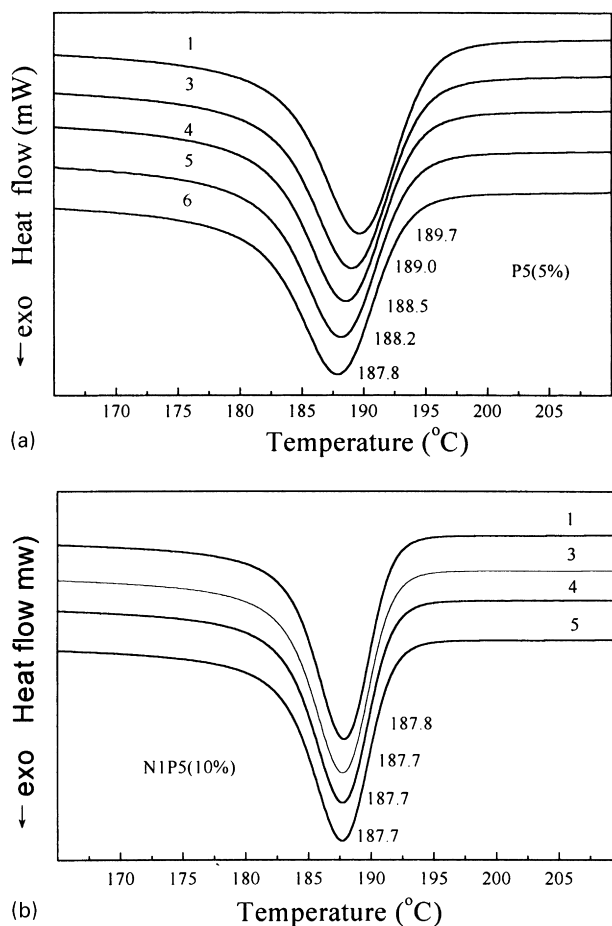
Fig. 3. (a) DSC cooling curves for blends of P5 (5%) with nylon-6 in the repeated heating–cooling cycles — the number indicates the *i*th cycle. (b) DSC cooling curves for blends of N1P5 (10%) with nylon-6 in the repeated heating–cooling cycles — the number indicates the *i*th cycle.

(see Table 1) in these copolymers and the fact that the size of insoluble particles, if these exist, is very small. In contrast, the specimens showing a double endotherm are those with larger insoluble rigid domains and higher rigid composition.

Pure PPTA has been found to be infusible until it decomposes and shows no endotherm in the DSC scan. It cannot therefore be firmly concluded at present that the second endotherm is due to the melting of the PPTA phase in the copolymer, and that the absence of the second endotherm results in the lack of insoluble PPTA domains in those specimens. On the other hand, the incorporation of flexible blocks into the copolymer can diminish the self-aggregation of the rigid blocks, leading to lower-order crystallites for the rigid phase, as discussed in the last section. Thus one cannot rule out the possibility of the formation of a less-ordered PPTA structure which would melt at lower temperature rather than being infusible. Although further investigation should be carried out in order to give a more confident answer, it is our belief that the melting of the second ordered structure should provide some PPTA blocks.

### 3.3. Phase stability of the nylon-6 blends with the model copolymers

Fig. 3 shows the DSC cooling thermograms of the nylon-6 blends containing PPTA oligomer (Fig. 3(a)) or the tri-block copolymer (Fig. 3(b)). For Fig.3(b), the mass of the rigid component is about 3% of the copolymer. The figure on each curve indicates the number of heating–cooling cycles that the specimen has undergone.

The main crystallization peak of pure nylon-6 used in this work is at 182.0°C, whereas both blends with PPTA oligomers and PPTA blocks are at 189.7–187.7°C, as seen in Fig. 3. As can be expected, the rigid PPTA domains may act as heterogeneous nuclei to promote the crystallization of the matrix upon cooling from the melt, elevating the onset and peak crystallization temperatures of nylon-6. By comparing Fig. 3(a) and (b), however, it can be found that this promotion of crystallization by the PPTA oligomers decreases as the number of heating–cooling cycles increases, while that of the tri-block copolymer remains unchanged.

The heterogeneous nucleation is well known to depend on the size and number of nuclei in the system. When the blends were heated and cooled repeatedly, the size and number of the PPTA nuclei would change if phase segregation of the rigid component occurred. In addition, the much sharper crystallization peak for the blends containing copolymers suggests that the size distribution of the nucleating PPTA domains is narrower. Obviously, the phase structure of the tri-block copolymers in the matrix is quite stable; indicating that the flexible polycaprolactam blocks bonded chemically to the rigid block can significantly prevent the tendency of self-aggregation of the rigid blocks, thus improving the dispersion of the copolymer. On the other hand, the motion and diffusion of the nylon-6 segments

molecular weight of the blocks and the relative length of the flexible and the rigid blocks.

It is observed that most of the copolymers exhibit a single well-profiled melting endotherm around 200°C. This peak can be attributed to the melting of the polycaprolactam blocks in the copolymer because it is located between the melting temperatures of nylon-6 and the corresponding polycaprolactam oligomers. On the other hand, the specimens showing two melting peaks are those with shorter flexible and rigid blocks, such as N1P2, N1P3 and N3P2. It should be pointed out that the position of the second endotherm is about 20–30°C higher than the melting temperature reported for nylon-6, indicating that in these samples there must exist a second ordered structure, which melts at a higher temperature than nylon-6 crystallites.

When examining Fig. 2 together with Fig. 1, it can be noticed that copolymers showing better solubility tend to be conducive to a narrower single endotherm. The absence of a second melting peak in these specimens might be explained by the fact that the mole ratio of the rigid phase is quite low

suffer the greater restraint from the binding to the rigid-rod as well as from the surrounding of the PPTA segments because of the strong hydrogen-bond interaction between the matrix and the reinforcing phase, and this will somehow hinder the rate of nucleation and crystallization of the matrix nylon-6. For the blends with the block copolymers, the interaction between nylon-6 and the block is stronger than that of blends with PPTA oligomers because of the existence of the nylon-6 blocks. So the effect described above is more obvious, leading to lower onset and peak crystallization temperatures on the DSC cooling curves, as can be noticed in Fig. 3(a) and (b).

## 4. Conclusions

The experimental results show that with the optimization and harmonization of the rigid and flexible blocks, the model tri-block copolymers designed as the dispersed component for melt-processable molecular composites exhibit unique solubility and meltability. The junction of flexible blocks to the ends of the rigid block enhances the interaction and miscibility between the reinforcing component and the matrix, and improves the dispersion of the rigid phase. The proposed approach to melt-processable molecular composites has been proven to be practicable by the preliminary study, and more investigations are being carried out in this laboratory to explore its further applications.

## Acknowledgements

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