

# Properties and Morphology of Poly(L-lactide)/Clay Composites According to the Clay Modification

Jae Hun Shim, Eung Soo Kim, Jung Hiuk Joo, Jin San Yoon

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

Received 26 September 2005; accepted 9 January 2006

DOI 10.1002/app.24900

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Montmorillonite (MMT) was modified with dodecylamine, 1,12-diaminododecane, and 1,11-aminoundecanoic acid to prepare CHMMT, NHMMT, and COMMT, respectively. The three clays were mixed with poly(L-lactide) (PLLA) with the aid of chloroform. Depending on the modifiers, PLLA/MMT composites exhibited different mechanical properties and morphology. A completely exfoli-

ated morphology was observed in the PLLA/COMMT composite (PLACO). The PLACO exhibited the best tensile properties among the tested composites because of the finest dispersion of the clay layers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4983–4988, 2006

**Key words:** nanocomposites; clay; polyesters

## INTRODUCTION

Composite materials are widely used in various fields, such as automotive, aeronautics, and communications. Depending on the composite nature and structure, mechanical properties were greatly improved and sometimes the price went down.

Recently, polymer/clay composites have attracted great interest from academia as well as industries because of the remarkable improvement of materials properties when compared with the mother polymer or the conventional micro- and macrocomposites.<sup>1–4</sup>

Nylon6/clay hybrids were developed at Toyota Central Research and Development Laboratories in 1986.<sup>5,6</sup> This is the first successful example of polymer/clay composite. The polar characteristics of nylon6 facilitated the dispersion of the clay layers and thereby enhancement of the mechanical properties was relatively easy to achieve.

However, usually the thermodynamics between polymer molecules in melt state and the silicate layers is not sufficiently favorable to expand the clay galleries large enough to have the exfoliation of the clay layers to take place.

A lot of studies have been devoted to developing the methods for the pretreatment of the clay to generate stronger interactions between the clay and the polymer matrix.<sup>7–9</sup>

Poly(L-lactide) (PLLA) is highlighted by scientists and engineers because of its biodegradability not

only for biomedical applications, but also for potential large-scale uses such as packaging and many consumer goods. PLLA is a linear aliphatic thermoplastic polyester, produced from renewable resources, with excellent properties comparable to many petroleum-based plastics.<sup>10,11</sup>

In this article, MMT was modified with dodecylamine, 1,12-diaminododecane, and 1,11-aminoundecanoic acid to prepare CHMMT, NHMMT, and COMMT, respectively. The modifiers have similar chain length, but different end group. The ester linkage of PLLA may interact differently with the end group depending on the modifier as shown in Scheme 1. Properties and morphology of the PLLA composites with the three different clays were explored.

## EXPERIMENTAL

### Materials

Na<sup>+</sup>-montmorillonite (NAMMT) was obtained from Southeastern Clay Products, Inc. (Gonzales, TX). The cation exchange capacity (CEC) of NAMMT was 92 mEq/g. Dodecylamine, 1,12-diaminododecane and 1,11-aminoundecanoic acid were purchased from Aldrich as reagent grade and used without further purification. The chloroform was purchased from Duksan Pure Chemical (Korea). Common reagents were used without further purification. The PLLA was supplied by Cargill Dow LLC (Minneapolis, MN), with a weight-average molecular weight of 250,000.

### Preparation of organophilic-MMTs and PLLA/organophilic-MMT hybrid

In a 1000 mL reactor, 20 g of the NAMMT was dispersed in 1 L of distilled water. The temperature

Correspondence to: J. S. Yoon (jsyoon@inha.ac.kr).  
Contract grant sponsor: Inha University.



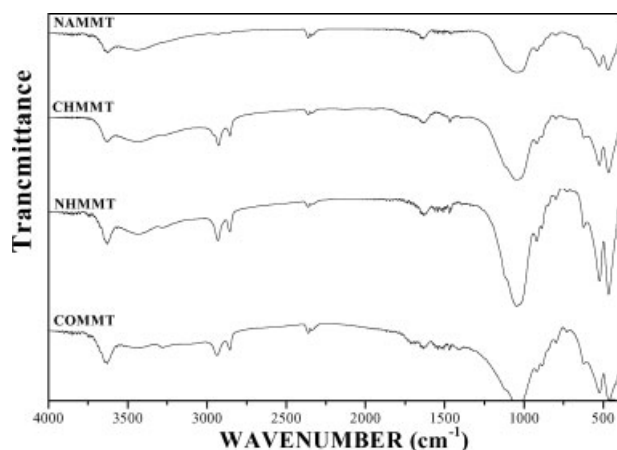


Figure 1 IR spectrum of clay and modified clays.

perature for 12 h. The product was poured into a large amount of methanol. The products were dried in convection oven at 60°C for 48 h, and in vacuum oven for 2 weeks. The dried hybrids were then converted into sheets with a thickness of 0.1–0.3 mm by pressing with  $\sim 2$  MPa at 170°C for 1 min.

### Characterization methods

The Fourier transformed infrared (FTIR) spectrum was recorded on a Perkin–Elmer Spectrum 2000 explore over a wavenumber range of 4000–400  $\text{cm}^{-1}$ . The variation of the interlayer distance of MMT in the nanocomposites was studied by means of wide angle X-ray scattering (WAXS) using a Rigaku DMAX 2500. The  $\text{CuK}\alpha$  radiation source was operated at 40 kV and 40 mA. Patterns were recorded by monitoring those diffractions appeared in the  $2\theta$  range from 2 to 10° with a scanning rate of 2°/min. The tensile properties of the composites was measured with an universal testing machine (UTM), (Hounsfield H 10KS-0061). Specimens were prepared according to ASTM D638. The cross-head speed was 5 mm/min. The results of five specimens were averaged. The morphological aspects of the composite have been examined by using transmission electron microscopy (TEM) to determine the internal micro-morphology. A Philips CM200 (TEM), with an acceleration voltage of 120 kV, was used. SEM (S-4200, Hitach, Japan) was used to observe the fractured surface morphology. Specimens were fractured while immersed in liquid nitrogen.

## RESULTS AND DISCUSSION

The organo-modification of MMT is an important step for the preparation of high-performance polymer/MMT composites. Figure 1 shows FTIR spectra of NAMMT, CHMMT, NHMMT, and COMMT. The

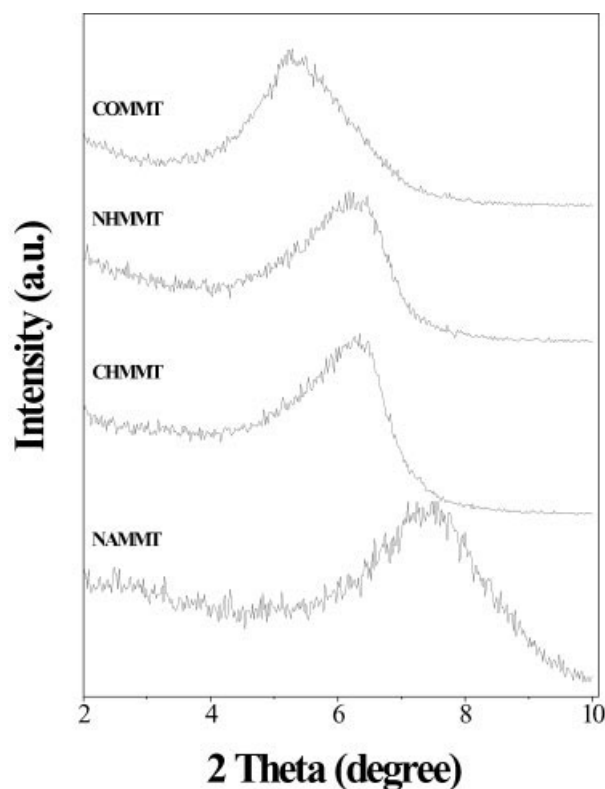


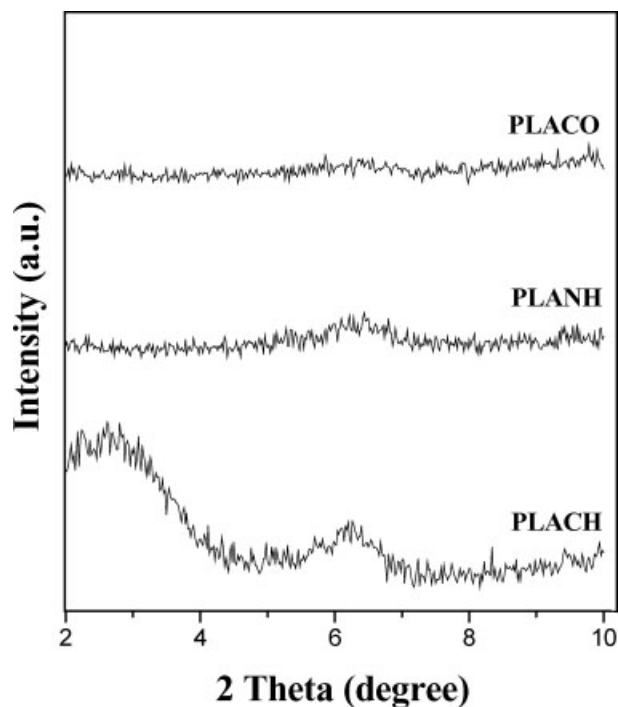
Figure 2 XRD patterns of pristine clay and organo-modified clays.

absorption characteristic band of NAMMT appears at 1030  $\text{cm}^{-1}$ . CHMMT exhibits the characteristic band of C–H stretching at 2923 and 2851  $\text{cm}^{-1}$ .<sup>12</sup> The peak at 1558  $\text{cm}^{-1}$  corresponds to  $-\text{NH}_2$  scissoring of NHMMT.<sup>13</sup> The carboxylic groups of COMMT display their characteristic absorption bands at 1710  $\text{cm}^{-1}$  for the C=O stretching and at 1418  $\text{cm}^{-1}$  for the in-plane O–H bending.<sup>13</sup> The FTIR results confirm that the MMT was modified successfully by the organic substances.

Intercalation of the organic substances into the interlayer spacing of the MMT was examined by using XRD as shown in Figure 2. The basal spacing of the MMT was calculated from the Bragg's equation, and the results are summarized in Table I. The interlayer spacing was enlarged from  $d = 1.18$  nm to  $d = 1.39$ , to  $d = 1.42$  and to  $d = 1.67$  nm as a result of the treatment with dodecylamine, 1,12-diaminododecane, and 1,11-aminoundecanoic acid, respectively.

TABLE I  
The Analysis of XRD Patterns of the Clay and Organo-Modified Clays

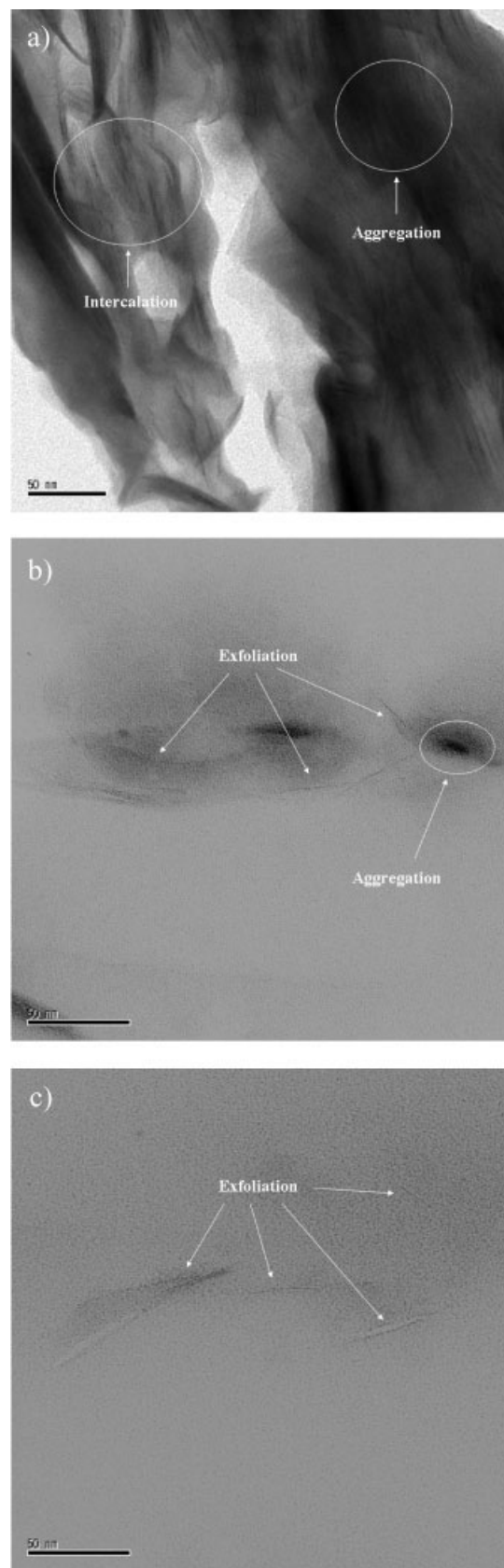
Clay	$2\theta$ (°)	$d_{001}$ (nm)
NAMMT	7.51	1.18
CHMMT	6.34	1.39
NHMMT	6.18	1.42
COMMT	5.28	1.67



**Figure 3** XRD patterns of PLACH, PLANH and PLACO composites.

It has been widely accepted that the basal spacing enlargement of the MMT depends strongly on the amine compounds used for the modification. The longer the chain length of the amine compound, the higher the  $d$ -spacing. It is to be noted that the  $d$ -spacing of COMMT was larger than that of CHMMT despite the fact that the chain length of 1,11-aminoundecanoic acid was similar to that of dodecylamine. This can be attributed in part to the hydrogen bond between the carboxylic end group and the amine group, and more free 1,11-aminoundecanoic acid molecules can enter into the interlayer spacing to enlarge the  $d$ -spacing due to the hydrogen bond. The carboxylic group of the former which is bulkier than the methyl group of the latter may be another reason for the larger  $d$ -spacing. Aminoundecanoic acid molecules are believed to lie more perpendicular to the clay platelets than dodecylamine and 1,12-diaminododecane, because the two different end groups of aminoundecanoic acid are pulled more strongly by both ionic bonding force and hydrogen interaction with the silicate layers. The perpendicular conformation of the surfactant molecules should also contribute to the  $d$ -spacing enlargement.<sup>15,16</sup>

CHMMT, NHMMT, and COMMT were mixed with PLLA to fabricate PLACH, PLANH, and PLACO, respectively. Figure 3 shows the XRD spectra of the three composites. In case of PLACH, a diffraction peak is observed at  $2\theta = 2.60^\circ$  (3.39 nm), corresponding to the (001) plane of the stacked and intercalated



**Figure 4** TEM images of (a) PLACH, (b) PLANH and (c) PLACO.



**TABLE II**  
**The Thermal and Mechanical Properties of Neat PLLA, PLACH, PLANH, and PLACO composites**

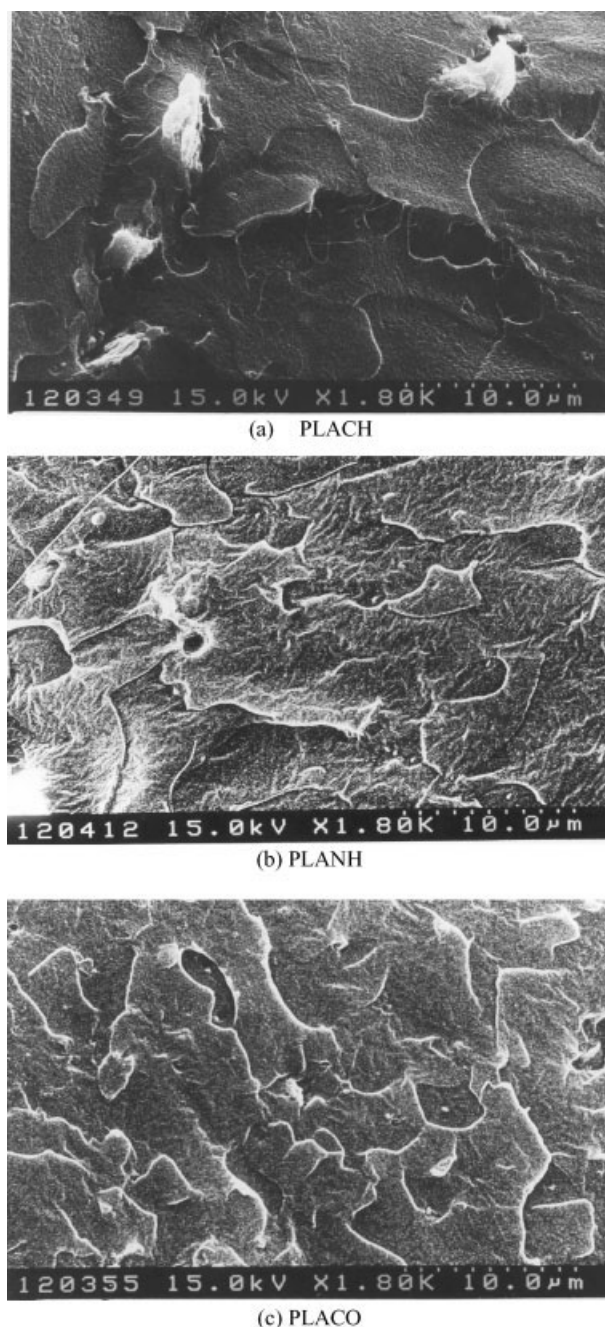
Composites	$T_g$ (°C)	$T_m$ (°C)	$\Delta H$ (J/g)	Young's modulus (MPa)	Tensile strength (MPa)
PLLA	57.5	154.5	36.0	$2.16 \pm 0.02^a$	$32.4 \pm 3.1^a$
PLACH	58.8	154.1	34.7	$2.40 \pm 0.02$	$32.4 \pm 1.3$
PLANH	58.7	153.7	36.1	$2.44 \pm 0.03$	$32.9 \pm 4.9$
PLACO	59.0	154.2	36.7	$2.53 \pm 0.05$	$42.3 \pm 3.6$

<sup>a</sup> Values are mean  $\pm$  standard deviation.

silicate layers dispersed in the PLLA matrix. The small additional peak at  $2\theta = 6.18^\circ$  was ascribed to the aggregated clay layers. Similarly, PLANH exhibited a small peak at  $2\theta = 6.20^\circ$ , indicating that PLANH possessed exfoliated morphology with some aggregates. In marked contrast, no peaks were observed in the XRD spectrum of PLACO, revealing that COMMT layers were completely exfoliated in the PLLA matrix without discernible aggregates.

The TEM images of the three composites are demonstrated in Figure 4. Figure 4(a) displays that the clay layers were intercalated with a lot of aggregates in the PLACH. The dark lines correspond to the cross section of the clay sheet about 1 nm thick and the gap between two adjacent lines is the interlayer spacing or gallery. The measured distance between the two adjacent lines, i.e., the interlayer spacing of intercalated tactoids, obtained from the TEM results, is consistent with those from the XRD data. Figure 4(b) visualizes the TEM image of the PLANH. The nanometer-range intercalated clay tactoids are not seen indicating that the clay layers were exfoliated. However, some aggregates of the clay layers are also observed in the PLANH. Figure 4(c) corresponding to the PLACO composite shows disordered and exfoliated platelets of the clay layers without discernible aggregates. The TEM observations in Figure 4 are in good agreement with the corresponding XRD results. According to the SEM images of the fractured surfaces in Figure 5, aggregates of the clay layers are also seen in PLACH, while they are not seen in PLACO. It is worth noting here that an exfoliated morphology can be obtained for PLLA/MMT composites even in the absence of a chemical reaction between PLLA and MMT.

Table II summarizes the glass transition ( $T_g$ ), melting peak temperature ( $T_m$ ) and heat of fusion of the neat PLLA and the PLLA/MMT hybrids.  $T_g$  of the hybrids was slightly higher than that of the neat PLLA, indicating that the segmental motion of the PLLA chains became restricted in the composites, similarly to the case of polystyrene/MMT composites.<sup>14</sup> However, the different degree of interaction between PLLA and the clays was not clearly



**Figure 5** SEM images of (a) PLACH, (b) PLANH, and (c) PLACO.

expressed by the  $T_g$  increase, because all the hybrids exhibited similar  $T_g$ s.  $T_m$  of PLLA did not change appreciably after the compounding of PLLA with the different clays. The heat of fusion of PLLA/clay hybrids was also nearly independent of the clay modification methods. It should be noted here that  $T_m$  did not depend strongly upon the kind of clay modifiers. This behavior is contrary to the expectation, because the exfoliated part of the clay in PLLA/clay nanocomposites could serve as a nucleating agent for crystallization, while the aggregated part disturbed the crystallization of the PLLA matrix.

Mechanical properties of the PLLA compounded with the different clays are summarized in Table II. Tensile modulus of the PLLA/MMT composites was higher than that of the neat PLLA. Tensile strength of the PLLA/MMT composites was also higher than that of the neat PLLA, and the PLACO exhibited the highest tensile strength among the PLLA/MMT composites. The finest dispersion of the clay layers in the PLACO is thought to be responsible for the best tensile properties.

### CONCLUSIONS

$\text{Na}^+$ -montmorillonite was modified with dodecylamine, 1,12-diaminododecane and 1,11-aminoundecanoic acid to prepare CHMMT, NHMMT, and COMMT, respectively. When PLLA was compounded with the three clays with the aid of chloroform, the degree of dispersion of the clay layers increased in the order of CHMMT < NHMMT < COMMT. Owing to the finest dispersion and exfoliation of the clay layers, the PLLA/COMMT composite exhibited the best mechanical properties among the tested

composites. To our best knowledge, this study reports for the first time that a completely exfoliated morphology of PLLA/MMT composite can be obtained even in the absence of chemical reaction between MMT and PLLA.

### References

1. Giannelis, E. P. *Chem Mater* 1990, 2, 627.
2. Alexandre, M.; Dubois, P. *Mater Sci Eng Rep* 2000, 28, 1.
3. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
4. Golden, J. H.; Deng, H. B.; Disalvo, F. J.; Frechet, J. M. J.; Thompson, P. M. *Science* 1995, 268, 1463.
5. Laus, M.; Francescangeli, O.; Sandrolini, F. *J Mater Res* 1997, 12, 3134.
6. Okada, A.; Usuki, A. *Mater Sci Eng C* 1995, 3, 109.
7. Kawasumi, M. *J Polym Sci Part A: Polym Chem* 2004, 42, 819.
8. Wu, S. H.; Wang, F. Y.; Ma, C. C. M.; Chang, W. C.; Kuo, C. T.; Kuan, H. C.; Chen, W. J. *Mater Lett* 2001, 49, 327.
9. Tanaka, G.; Goettler, L. A. *Polymer* 2002, 43, 541.
10. Ray, S. S.; Maiti, P.; Okamoto, M.; Yamada, K.; Ueda, K. *Macromolecules* 2002, 35, 3104.
11. Perego, G.; Cella, G. D.; Bastioli, C. *J Appl Polym Sci* 1996, 59, 37.
12. Arroyo, M.; López-Manchado, M. A.; Herrero, B. *Polymer* 2003, 44, 2447.
13. Smith, B. *Infrared Spectral Interpretation, a Systematic Approach*; CRC Press: Boca Raton, FL, 1999.
14. Chen, G.; Liu, S. H.; Chen, S. J.; Qi, Z. N. *Macromol Chem Phys* 2001, 202, 1189.
15. Chen, G. X.; Kim, H. S.; Shim, J. H.; Yoon, J. S. *Macromolecules* 2005, 38, 3738.
16. Lee, J. H.; Park, T. G.; Park, H. S.; Lee, D. S.; Lee, Y. K.; Yoon, S. C.; Nam, J. D. *Biomaterials* 2003, 24, 2773.
17. McNally, T.; Murphy, W. R.; Lew, C. Y.; Turner, R. J.; Brennan, G. P. *Polymer* 2003, 44, 2761.
18. Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978.
19. Gelfer, M. Y.; Song, H. H.; Liu, L.; Hsiao, B. S.; Chu, B.; Rafailovich, M.; Si, M.; Zaitsev, V. *J Polym Sci Part B: Polym Phys* 2003, 41, 44.