Preparation and Characterization of Polyamide 66/Montmorillonite Nanocomposites with Methyl Methacrylate as Cointercalation Agent

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ABSTRACT: This study reports a simple and low-cost preparation method for nearly exfoliated polyamide 66 (PA66)/montmorillonite (MMT) nanocomposites. Polymerizable methyl methacrylate (MMA) is used as cointercalation agent to take advantages of both *in-situ* polymerization and melt mixing. Two preparation approaches, either direct melt compounding or dilution from a master-batch, are investigated. The nano-scale dispersion of organo-MMT (OMMT) in PA66 is revealed by X-ray diffraction and transmission electron microscopy. PA66/MMT nanocomposites having superior mechanical properties and heat distortion temperature (HDT) can be obtained by either of the two preparation approaches on condition that excess MMA, which is on the surface of PA66/OMMT is removed by ventilation before melt compounding. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1–6, 2008

Key words: polyamide 66; montmorillonite; nanocomposites; MMA

INTRODUCTION

Polymer/clay nanocomposites have attracted increasing attention due to their academic and industrial interests ever since the first industrial report of nylon 6/montmorillonite (MMT) nanocomposites from Toyota.[1] By adding just a small amount of clay (2–5 wt %), the properties of the composite materials could by improved significantly, especially mechanical, thermal and barrier properties. Polyamide 66 (PA66) is an important engineering plastic. In recent few years, considerable research has been devoted to the preparation of PA66/clay nanocomposites.[2–19] High level of exfoliation was achieved mainly by three methods: (1) use of specially made organo-MMT (OMMT),[2] (2) treatment of OMMT by a cointercalation agent[3–12] such as epoxy resin[3–5] or aminoundecanoic acid,[6] (3) dilution from a PA6/OMMT master-batch.[13] When commercial OMMTs were used to prepare PA66/MMT nanocomposites, the level of exfoliation was rather limited, therefore, searching for simple and efficient preparation methods is still of high interest.

It is well-known that there are mainly three methods for preparing polymer/clay nanocomposites: melt mixing, *in-situ* polymerization, and solution polymerization. Melt process is the most utilized preparation method, since it approaches industrial compounding process, and has many advantages such as simple equipment, less pollution, etc. However, from the kinetic point of view, macromolecules have a size much bigger than small molecules, and thus difficult to diffuse into clay galleries. In *in-situ* polymerization, the monomer diffuses into clay galleries and polymerizes in clay galleries, and thus exfoliated structure could be easily obtained.

MMA is one of the most commonly used vinyl monomers with low toxicity. Exfoliated PMMA/clay nanocomposites have been obtained by various types of *in-situ* polymerizations such as bulk,[20] emulsion, and suspension techniques.[21] Since MMA can diffuse into clay galleries and also thermal polymerize in the absence of an initiator, it can help to increase basal spacing of clay and polymerize during melt compounding. Therefore, in this work, MMA is used as a cointercalation agent for preparation of nearly exfoliated PA66/MMT nanocomposites to take advantages of both *in-situ* polymerization and melt mixing. The dispersion of OMMT in PA66 is evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mechanical properties and heat distortion temperature (HDT) of PA66/MMT nanocomposites are also investigated.

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TABLE I
Summary of Sample Codzes and Preparation Conditions

Sample code	Approach	Notes
PA66/OMMT0	Direct melt compounding	No MMA
DM-ND	Direct melt compounding	PA66/OMMT/MMA mixture is not dried
DM-D	Direct melt compounding	PA66/OMMT/MMA mixture is dried
F-MB1	Dilution from master batch1	In preparation of MB1, PA66/OMMT/MMA mixture is not dried
F-MB2	Dilution from master batch2	In preparation of MB2, PA66/OMMT/MMA mixture is dried

EXPERIMENTAL

Materials

PA66 used in this study was Zytel 101L (Dupont) and the filler employed was NB-901 (Huate Group, China), which is a MMT modified with tallow quaternary ammonium to increase the domain spacing of Na^+-MMT. The cation exchange capacity of NB901 is 95 meq/100 g, and methyl methacrylate (MMA) was of analytically grade (Yili, China).

Preparation of PA66/MMT nanocomposites

A TE-34 twin-screw extruder (Keya, China) having screw diameter of 34 mm and L/D of 28 was used for melt compounding. The screw speed was maintained at 120 rpm. The barrel temperature was set to 250–260–260–265–265–240°C from hopper to die. PA66/MMT nanocomposites having 5 wt % of OMMT and 5 wt % of MMA were prepared by either direct melt compounding or dilution from master-batches having 10 wt % of OMMT and 10 wt % of MMA. The first approach was coded as ''DM,'' and the second as ''F-MB'' (Table I). For the first approach, the mixture of PA66/OMMT/MMA was melt compounded either shortly (1 h) after mixing (i.e., not dried, coded as ''DM-ND''), or after drying in a ventilated oven at room temperature (r.t.) for 5 h followed by 1 h of storage (coded as ''DM-D''). For the second approach, the nanocomposites were coded as ''F-MB1'' and ''F-MB2,'' where MB1 was prepared with undried mixture of PA66/OMMT/MMA and MB2 prepared with the dried mixture.

For comparison, PA66/MMT nanocomposites without the use of MMA were prepared by direct melt compounding, and coded as ''PA66/OMMT0.''

The extrudates were injection molded into tensile bars using a ZT-630 injector (Zhenda, China) with a barrel temperature of 260°C for measurement of mechanical properties and HDT.

Characterization

The morphology of the nanocomposites was examined using XRD and TEM. XRD patterns were obtained on injection-molded Izod bars except for the two samples of master-batches where films pressed at 280°C were analyzed, using a BRUKER D8-Advance diffractometer connected to a computer. The diffraction scans were collected at 1.5–10° using a scanning speed of 1°/min. TEM was performed on a Cambridge S250MK3 using an accelerating voltage of 200 KV. For TEM examinations, ultra-thin specimens with a thickness of about 50 nm were cut from the middle section of the injection-molded bars. Cutting operations were carried out using a Reichert Ultracut S microtome under cryogenic conditions, and the film was retrieved onto copper grids.

Tensile tests and also flexural tests were carried out with a GT-TCS 2000 machine (Gotech), according to ASTM D638 and ASTM D790, at a crosshead speed of 50 mm/min and 5 min/mm, respectively. Data from five measurements were averaged for each formulation. Izod impact tests were carried out on notched specimens using a GT-7045-I Izod impact tester (Gotech), according to ASTM D256, and data from seven measurements were averaged. The HDTs were measured on GT-HV2000 computer HDT/vicat tester (Gotech) following the procedure described in ASTM 648. Two specimens were used for each formulation. Prior to mechanical and HDT testing, all sample bars were dried in a vacuum oven at 110°C.

Dynamic mechanical analysis (DMA) was carried out on a DMA 2980 from TA instruments. The storage modulus E' and loss modulus E'' were determined at 1 Hz in the temperature range between −100 and +150°C. T_g was defined as the maximum of loss modulus E'' at the α transition.

RESULTS AND DISCUSSION

Intercalation of OMMT by MMA

The fact that exfoliated PMMA/clay can be prepared via *in-situ* bulk polymerization[20] using organophilic clay containing polymerizable groups makes us think that MMA is likely to be able to diffuse into organo-clay galleries quite easily even just after mixing at r.t. To verify this point, the mixture of OMMT and MMA was analyzed by XRD after different time intervals and with or without removal of excess MMA, which is on the surface of OMMT (Fig. 1).

The XRD pattern of commercial OMMT (curve a) shows a broad peak centered at $2\theta = 4.3°$, corresponding to a basal spacing of 2 nm as calculated from Bragg equation. When the mixture was analyzed shortly after mixing (1 h), a main reflection at 2.7° (corresponding to a basal spacing of 3.3 nm) along with one large shoulder-type peak at about 4°, and a minor reflection at 5.3° appeared (curve b). The minor peak at 5.3° indicates that there is a small part of OMMT having smaller intercalation extent. It can be clearly seen that OMMT is further intercalated by MMA, as evidenced by the shift of the main part of OMMT, and there is probably a small part of OMMT not intercalated by MMA. After storing for 6 h, the mixture shows a single broad peak at 4°,which corresponds to a basal spacing of 2.2 nm (curve c), indicating a more homogenized diffusion state of MMA in OMMT. It seems that the mixture of OMMT and MMA stabilizes with time, some MMA diffuses out from OMMT galleries containing a high level of MMA, which was forced into the galleries during mixing, and some diffuses into the OMMT galleries containing less or no MMA. When the mixture of OMMT and MMA is dried in a ventilated oven at r.t. for 5 h followed by 1 h of storage, MMA on the surface of MMT is removed, the XRD pattern (curve d) is similar to that of the sample without drying (curve c). This suggests that drying does not decrease the basal spacing and only MMA on the surface of OMMT is removed.

Since the interior of OMMT is organophilic, it seems reasonable to see the diffusion of MMA into OMMT galleries and consequently an increase of the basal spacing. This proves that MMA can be used as a cointercalation agent to further increase the basal spacing of OMMT.

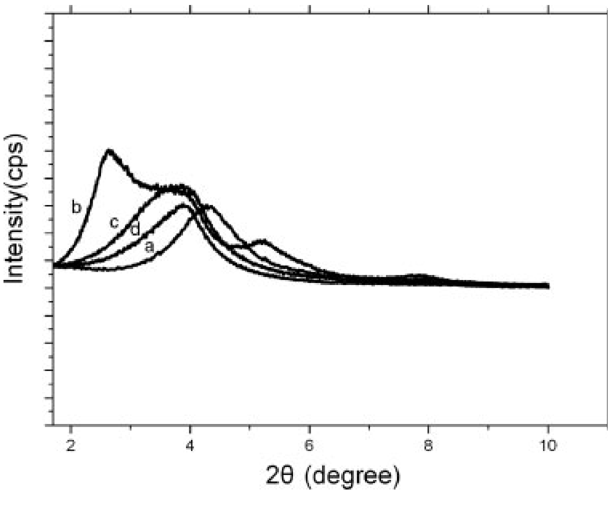

Figure 1 XRD patterns of (a) OMMT and OMMT/MMA 1 : 1 mixture after (b) 1 h of storage, (c) 6 h of storage, and (d) 5 h of ventilation plus 1 h of storage.

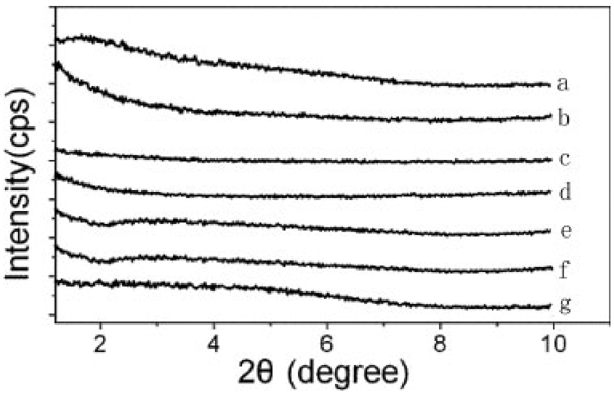

Figure 2 XRD patterns of PA66/MMT nanocomposites: (a) PA66/OMMT0, (b) MB1, (c) MB2, (d) DM-ND, (e) F-MB1, (f) DM-D, and (g) F-MB2.

The dispersion state of OMMT in master-batches and nanocomposites prepared via different ways

A combination of XRD analysis and TEM observation was used to evaluate the dispersion of OMMT in the two master-batches having 10 wt % of OMMT (MB1 and MB2) and nanocomposites containing 5 wt % of OMMT prepared by either direct melt compounding (DM-ND and DM-D) or dilution from master-batches (F-MB1 and F-MB2). For comparison, PA66/MMT nanocomposites having 5 wt % of OMMT prepared without the use of MMA (sample PA66/OMMT0) was also analyzed.

Figure 2 shows XRD patterns of the samples mentioned above. The PA66/OMMT0 nanocomposites prepared without MMA (curve a) exhibits a broad peak at 1.5°, indicating that the OMMT is in intercalated state with various degrees of intercalation. All the other nanocomposites, which have 5 wt % of MMA in their preparation, show featureless patterns, suggesting possible formation of exfoliated clay structure.

Figure 3 shows TEM photomicrographs of all the samples in discussion. In the nanocomposite prepared without MMA [Fig. 3(a)], the dispersion of OMMT is not good, and the OMMT exists mainly as tactoids. This is in agreement with the XRD pattern. In MB1, the master batch prepared without drying of surface MMA, clay layers disperse almost homogeneously and a nearly exfoliated structure is observed. As to MB2, the master-batch prepared with dried mixture of PA66/OMMT/MMA, some stacks containing a few layers were observed besides the exfoliated individual layers, suggesting a mixed structure of intercalation and exfoliated. Therefore, MB2 has a lower degree of exfoliation than MB1, and the removal of surface MMA has some negative effect on exfoliation of OMMT layers at such high OMMT loading (10 wt %). In all the nanocomposites having 5 wt % of OMMT and 5 wt % of MMA,

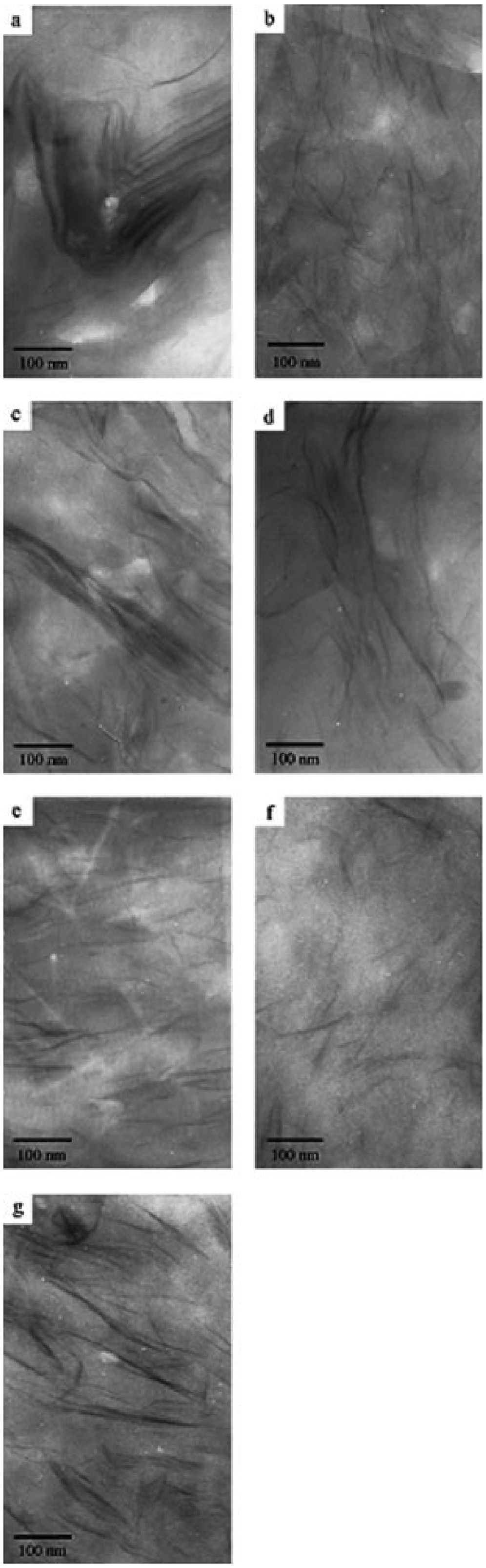

Figure 3 Photomicrographs of PA66/MMT nanocomposites: (a) PA66/OMMT0, (b) MB1, (c) MB2, (d) DM-ND, (e) F-MB1, (f) DM-D, and (g) F-MB2.

whatever the way of preparation [Fig. 3(d–g)], a nearly exfoliated structure is observed. The fact that F-MB2 has a better exfoliated structure than MB2 reveals that further processing and dilution can improve the extent of exfoliation.

Summarizing XRD and TEM results, nearly exfoliated PA66/OMMT nanocomposites having 5 wt % of OMMT can be prepared by either direct melt compounding or dilution from master-batches having 10 wt % of OMMT, no matter how the mixture of PA66/OMMT/MMA is handled (dried or not). The achievement of nearly exfoliated structure by the use of MMA can be explained by diffusion of MMA into OMMT galleries at the mixing stage and the formation of hydrogen bonding between MMA and PA66. As revealed by XRD patterns, MMA can diffuse into OMMT galleries and consequently increases basal spacing. The increased basal spacing is advantageous to the diffusion of PA66 into OMMT galleries. Furthermore, MMA can attract PA66 through formation of hydrogen bonding between C=O of MMA and NH of PA66.

Mechanical properties and heat distortion temperature

Mechanical properties and HDT of PA66 and PA66/OMMT nanocomposites prepared via different ways are listed in Table II.

The tensile strength and flexural strength of the nanocomposite prepared without the use of MMA (PA66/OMMT0) do not increase compared with that of neat PA66 due to poor dispersion of OMMT in PA66 matrix as demonstrated by XRD and TEM, while the impact strength decreases sharply due to incorporation of rigid OMMT. For nanocomposites prepared with cointercalation of MMA (the other four samples), it seems that when the mixture of PA66/OMMT/MMA is dried in the initial preparation (DM-D and F-MB2), no matter which approach it is, direct melt compounding or dilution from a master-batch, the nanocomposite has a substantial increase (16–23%) in tensile strength and a slight increase in flexural strength (2–9%) compared with neat PA66 and that prepared without the use of MMA, showing strong reinforcing effect attributed to nano-scale dispersion of OMMT in PA66 matrix. The impact strength is about the same value as the nanocomposite prepared without the use of MMA and much smaller than that of neat PA66. The increment of tensile strength and the decreasing tendency of toughness are similar to those found in other reports[8,11–13] involving PA66/MMT nanocomposites where either specially made OMMT or master-batch of PA6/OMMT is used in their preparations. A survey of literature has shown that only PA66/MMT nanocomposites prepared with epoxy resin as co-

TABLE II
Mechanical Properties and HDT of PA66 and PA66/MMT Nanocomposites

Sample code	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength[a] (J/M)	HDT(°C)
PA66	70.9 ± 0.2	2842 ± 92	〈5	111.2 ± 0.5	2603 ± 35	28.2 ± 0.7	113.0 ± 1.3
PA66/OMMT0	71.5 ± 2.4	3708 ± 157	〈5	106.4 ± 2.2	2876 ± 16	15.3 ± 0.2	136.5 ± 1.7
DM-ND	72.3 ± 1.6	3573 ± 81	〈5	113.1 ± 1.5	2807 ± 42	21.9 ± 1.5	133.7 ± 1.6
DM-D	86.9 ± 0.4	4032 ± 32	〈5	117.7 ± 1.8	2922 ± 32	13.0 ± 2.5	140.9 ± 1.2
F-MB1	72.7 ± 1.6	3676 ± 174	〈5	114.7 ± 0.5	2850 ± 13	22.2 ± 1.2	135.4 ± 1.1
F-MB2	82.2 ± 1.2	4613 ± 63	〈5	121.3 ± 1.2	3074 ± 24	15.5 ± 2.9	138.1 ± 1.3

[a] Notched Izod impact strength.

intercalation agent[3,4] can have simultaneous increase in both strength and toughness due to presumably strong interaction among the epoxy resin, OMMT and PA66. When the mixture of PA66/OMMT/MMA is used without drying (DM-ND and F-MB1), the values of tensile and flexural strength are lower than those of nanocomposites prepared with dried mixture of PA66/OMMT/MMA (DM-D and F-MD2), while those of impact strength increase significantly (but still lower than that of neat PA66). In these cases, although the dispersion of OMMT is good, it is possible that excess MMA, which is on the surface of OMMT polymerizes into PMMA during melt compounding, which plays the role of plasticizer, i.e., lowers strength and increases toughness. The plasticizing effect of PMMA in the PA66/MMT nanocomposites is further evidenced by DMA. A 5°C decrease of T_g was found when the nanocomposite DM-ND (with undried mixture of PA66/OMMT/MMA) was compared with DM-D (with dried mixture of PA66/OMMT/MMA), and the storage modulus E' of the former is smaller than that of the latter in all the tested temperature range.

The tensile modulus and flexural modulus of the PA66/MMT nanocomposites are all higher (26–62% and 8–18% increment, respectively) than neat PA66 due to the incorporation of mineral filler OMMT, which has a modulus considerably higher than that of PA66. The nanocomposites (DM-D and F-MB2) prepared with dried mixture of PA66/OMMT/MMA have higher tensile and flexural moduli than those prepared with undried mixture of PA66/OMMT/MMA due to removal of excess MMA. It is noted that all the nanocomposites prepared in this work show brittle fracture in tensile tests when measured at dry state. The elongation at break is less than 5% for all the nanocomposites.

HDT is an important parameter for engineering plastics. All the PA66/MMT nanocomposites prepared in this work have increased HDT values compared with neat PA66. The increment of 21–28°C is attributed to incorporation of rigid OMMT. The dispersion state of OMMT has little effect on HDT. The nanocomposites prepared with dried mixture of PA66/OMMT/MMA have the highest HDT values, which are 25–28°C higher than that of neat PA66.

The initial attention of drying the mixture of PA66/OMMT/MMA is to transform the mixture into easily handled form. Since MMA is a liquid, the mixture of PA66/OMMT/MMA looks like a paste, and can not be fed into the extruder smoothly. After drying in a ventilated oven at r.t., the excess MMA on the surface of PA66/OMMT is removed, yielding a solid-like mixture, which can be handled routinely. In this work, we found that removal of surface MMA does not affect exfoliation degree of OMMT in PA66 and is beneficial to the increase of strength and modulus.

CONCLUSIONS

The use of MMA can help to prepare nearly exfoliated PA66/MMT nanocomposites. MMA can diffuse into OMMT galleries and attract PA66 molecules through hydrogen bonding.

Removal of excess MMA, which is on the surface of PA66/OMMT by ventilation can improve the strength and modulus significantly. Otherwise, excess MMA could polymerize into PMMA acting as plasticizer and consequently lowering the strength and modulus of the nanocomposites.

PA66/MMT nanocomposites having superior mechanical properties and HDT can be prepared by either direct melt compounding or dilution from a master-batch. The latter facilitates large scale application of this MMA-mediated exfoliation method.

References

1. Okada, A.; Kawasumi, M.; Kurauchi, T. Polym prepr 1987, 28, 447.
2. Vlasveld, D. P. N.; Vaidya, S. G.; Berseec, H. E. N.; Picken, S. J. Polymer 2005, 46, 3452.
3. Gyoo, P. M.; Venkataramani, S.; Kim, S. C. J Appl Polym Sci 2006, 101, 1711.
4. Liu, X. H.; Wu, Q. J. Macromol Mater Eng 2002, 3, 287.
5. Liu, X. H.; Wu, Q. J.; Berglund, L. A. Polymer 2002, 43, 4967.
6. Han, B.; Ji, G.; Wu, S. S.; Shen, J. Eur Polym J 2003, 39, 1641.
7. Kang, X.; He, S. Q.; Zhu, C. S.; Wang, L. Y.; Lu, L. Y.; Guo, J. G. J Appl Polym Sci 2005, 95, 756.

8. Zhu, C. S.; Kang, X.; He, S. Q.; Wang, L. Y.; Lu, L. Y. Chin J Polym Sci 2002, 20, 551.
9. Lu, Y. L.; Zhang, Y.; Zhang, G. B.; Yang, M. S.; Yan, S. K.; Shen, D. Y. Polymer 2004, 45, 8999.
10. Yu, Z. Z.; Yang, M. S.; Zhang, Q. X.; Zhao, C. G.; Mai, Y. W. J Polym Sci Part B: Polym Phys 2003, 41, 1234.
11. Yu, Z. Z.; Yan, C.; Yang, M. S.; Mai, Y. W. Polym Int 2004, 53, 1093.
12. Hao, X. Y.; Gai, G. S.; Liu, J. P.; Yang, Y. F.; Zhang, Y. H.; Nan, C. W. Mater Chem Phys 2006, 96, 34.
13. Gonza′lez, I.; Eguiaza′bal, J. I.; Naza′bal, J. Polymer 2005, 46, 2978.
14. Vrria, F.; Paul, D. R. Polymer 2004, 45, 8501.
15. Qin, H. L.; Su, Q. S.; Zhang, S. M. Polymer 2003, 44, 7533.
16. Lu, Y. L.; Zhang, G. B.; Feng, M.; Zhang, Y.; Yang, M. S.; Shen, D. Y. Polym Sci Part B: Polym Phys 2003, 41, 2313.
17. Ristolainen, N.; Heikkila, P.; Harlin, A. Macramol Mater Eng 2006, 291, 114.
18. Nair, S. V.; Goettler, L. A.; Lysek, B. A. Polym Eng Sci 2002, 42, 1872.
19. Dasari, A.; Yu, Z. Z.; Mai, Y. W. Polymer 2005, 46, 5986.
20. Zeng, C. C.; Lee, L. J. Macromolecules 2001, 34, 4098.
21. Huang, X. Y.; Brittain, W. J. Macromolecules 2001, 34, 3255.