Mechanical, Thermal, and Morphological Properties of Bismaleimide/Unsaturated Polyester Copolymers

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ABSTRACT: An unsaturated polyester (UP) resin was modified by the addition of a thermosetting bismaleimide (BMD) as a second coreactive monomer. The copolymers were characterized in terms of mechanical, thermal, and morphological properties by tensile, bend, and impact testing; thermogravimetric analysis; heat deforming temperature analysis; dynamic mechanical analysis; and scanning electron microscopy. In addition, Fourier transform infrared spectroscopy of modified resin indicated that crosslinking networks were formed between BMD and UP. The properties of the modified resins were compared with those of unmodified resins. The results indicate that the addition of BMD not only improved the thermal decomposition temperature and heat deforming temperature but also caused small changes in the mechanical properties. The effect of the construct of BMD and the reactions among BMD, UP, and styrene were analyzed. The results show that BMD has great potential to improve the properties of UP. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 593–598, 2006

Key words: copolymerization; polyesters; mechanical properties; modification

INTRODUCTION

In recent years, thermosetting materials have received increasing attention in industry. Unsaturated polyester (UP) resins are one of the most widely used thermosetting materials because they are relatively inexpensive and offer advantages such as being light in weight and possessing reasonably good mechanical properties. UPs have a leading role in the development of fiberglass-reinforced products, having tremendous versatility and very low costs. The use of UPs in bulk and sheet-molding compounds results in composite materials that have high strengths, dimensional stability, and very good surface qualities.[1–7] They have many applications in automotive, aircraft, electrical, and appliance components as substitutes for traditional materials. However, the mechanical properties and heat resistance of composite materials are low; thus, modification of UP resins are necessary.

To improve the ultimate properties of UP resins, a second component can be added. In this study, bismaleimide (BMD) was used as the second reactive part. The choice of the BMD was made because of its very high rigidity and high glass-transition temperature. BMD resins are considered a class of high-temperature thermosetting addition-type polyimides, and they are widely used as matrix resins for advanced composites in the electronic and aerospace industries. In addition, another advantage is their reactive maleimide end groups, which are thermally polymerizable without the elimination of volatile byproducts that cause voids in high crosslinked polymeric materials.[8–14] However, modified resins have high rigidity, heat resistance, and a high crosslinking density of the network due to the introduction of BMD. As a result of the high rigidity and heat resistance of BMD resin, styrene of the UP resin and BMD copolymerize through an alternating mechanism in solution,[15,16] sequentially introducing the concerned performance of BMD. So the rigidity and heat resistance of the UP resin can be improved.

In this article, the modification of UP resin with BMD is presented. The mechanical, thermal, and morphological properties were studied. In this investigation, we attempted to improve both the toughness and thermal behavior of the UP resin through the formation of an intercrosslinked network with BMD. The properties of the modified resins were compared with those of the unmodified resins. The results indicate that the addition of BMD to the UP resin improved its properties.

EXPERIMENTAL

Materials

The UP resin used in this study was an uncured UP (General Purpose Resin 196s), which was supplied by

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Tianjin Synthetic Material Factory (Tianjin, China). The resin contained 35% styrene. The acid number of the prepolymer, defined as the number of milligrams of KOH required for the titration of 1 g of prepolymer was 16.5–25.5. The viscosity was 0.23–0.47 Pa·s/25°C. The BMD resin used was 4,4′-bismaleimido-diphenyl-methane from Tiancheng Chemical Corp. (Ningbo, China) Methyl ethyl ketone peroxide and cobalt naphthenate were bought from Tianjin Synthetic Material Factory.

Preparation procedure

A typical copolymer (BUP5) was prepared as follows: 3.0 g of BMD was dissolved in 60 g of the UP resin at room temperature with continuous stirring, and the reactive mixture was heated to 90°C under nitrogen. A homogeneous, transparent solution was obtained. Then, the temperature was lowered to 25°C. The accelerant, cobalt naphthenate (0.5 wt %), and 1 wt % of the radical initiator, methyl ethyl ketone peroxide, were added in turn with vigorous mechanical stirring. The solution was then poured into molds for solidification. In this way, five BMD/UP copolymers containing 1, 2, 5, 8, and 10 wt %BMD were obtained; these modified resins were named according to their different BMD contents: BUP1, BUP2, BUP5, BUP8, and BUP10, respectively.

Characterization

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were determined on a Vector-22 FTIR spectrometer (Bruker, Germany) with KBr pellets.

Mechanical tests

Tensile strength testing was performed with a CMT-6104 electronic tensile tester (Shenzhen, Guangdong Province, China) with a computer controlling the system. The size of the dumbbell-shaped samples was 14 × 3.3 × 3.6 mm^3. The tests were conducted at an extension rate of 20 mm/min.

Bend strength testing was also carried out at room temperature in the CMT-6104 tester. A fixed rate of 2 mm/min was used in all cases, and the results were taken as the average of five tests. Samples were used according to Chinese standard GB/T2570-1995.

Impact strength was carried out on a XCJ-40 Charpy impact tester (Chengde, Hebei Province, China). Samples were cut according to Chinese standard GB/T2571-1995.

Thermal analysis

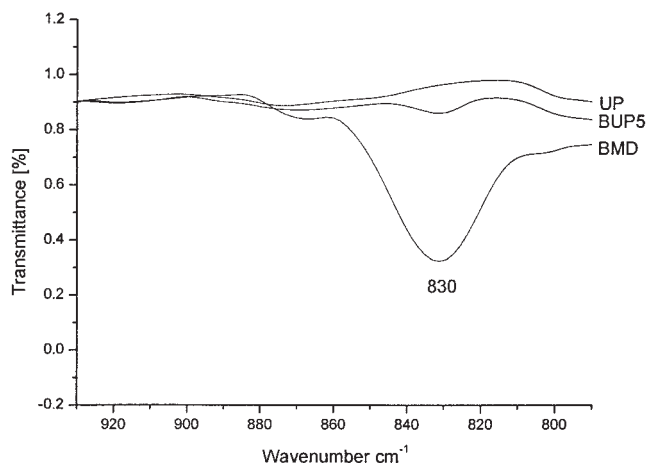Thermogravimetric analysis (TGA) was carried out with a DuPont TA Instruments SDT-2960 differential

Figure 1 FTIR spectra of the UP resin, BMD, and BUP5.

scanning calorimeter. The samples were gradually heated to 800°C in N$_2$ at a rate of 20°C/min.

Heat deforming temperature (HDT) experiments were recorded with a XWB-300F HDT Vicat temperature tester (Chengde, Hebei Province, China) at a heating rate of 120°C/h. Methyl silicone oil was applied as the heating medium. Samples were used according to Chinese standard GB1634-79.

Dynamic mechanical analysis (DMA)

DMA experiments were carried out on compression-molded polymer bars in a Netzsch DMA 242C (Selb, Germany) at a constant frequency of 5 Hz from room temperature to 200°C at a heating rate of 5°C/min in the three-point tensile mode. Temperature calibration was carried out with water and indium. The size of the samples was 30 × 6.1 × 3.6 mm^3.

Scanning electron microscopy (SEM)

SEM experiments were carried out in a Philips XL30 (Eindhoven, The Netherlands). The fractured surfaces of the samples were coated with a thin layer of gold *in vacuo* before SEM observations.

RESULTS AND DISCUSSION

FTIR analysis

With FTIR spectroscopy to trace the reaction of UP/BMD, the changed form of the characteristic functional groups was observed intuitively. Figure 1 shows the FTIR spectra of the UP resin, BMD monomer, and BUP5 in the range 930–790 cm^{-1}. BMD presented a typical absorption at 830 cm^{-1}; this peak was assigned to out-of-plane blending of the —C=C— group.[17,18] In the spectra of BUP5, a doublet band at 830 cm^{-1} was visible, whereas in the spectrum
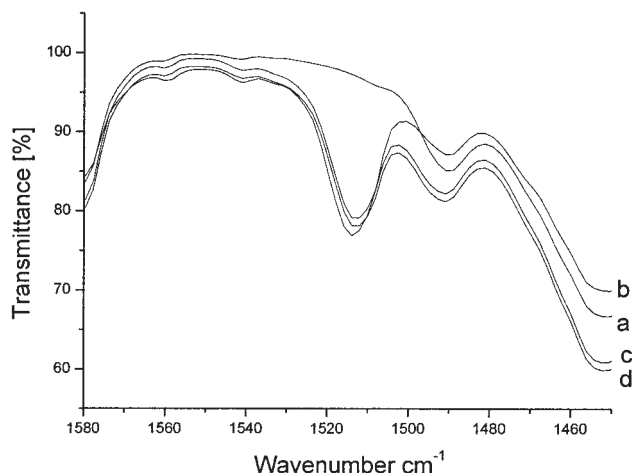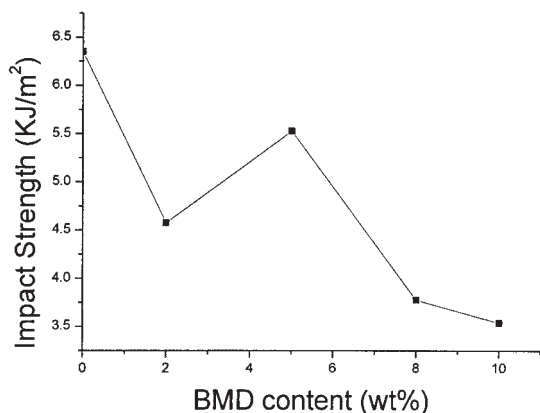
Figure 2 FTIR spectra of (a) the UP resin,(b) BUP5, (c) BUP8, and (d) BUP10.

Figure 4 Influence of BMD content on tensile strength.

of the unmodified resin, this band was not present. In this representation, UP and BMD were involved in the crosslinking process.
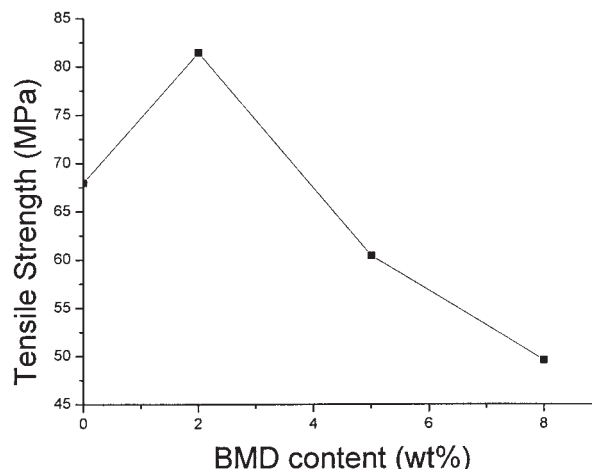
Because of the low BMD content in the copolymer, this peak had a relatively low intensity. Another confirmation of the crosslinked reaction of BMD and UP resin is shown in Figure 2. In this representation, the imide group presented a typical absorption at 1512 cm^{-1}.[19] This absorption was clearly detected in the spectrum of the BMD/UP copolymer, whereas the neat UP resin did not have this band. Moreover, as shown in Figure 2, the intensity of this peak gradually increased with increasing concentration in the resin, which indicated the copolymerization of BMD and UP resin during the reaction.

Mechanical properties

Impact strength and tensile strength as a function of BMD content in the BMD/UP copolymers are reported in Figures 3 and 4, respectively. The tensile

strength of BUP2 was highest, which was higher than that of the neat UP resin. Although the maximum impact strength was found for BUP5, the impact strength of the modified UP resin was lower than that of the neat resin. Figure 5 shows bend strength as a function of BMD content in the BMD/UP copolymers; a similar trend was found as with the impact strength curve. When the BMD content was 5 wt %, the bend strength was highest, which was higher than that of the neat UP resin. The bend strength value of BUP5 was about 22 MPa higher than that of UP. The results indicate that the addition of BMD made small changes in the mechanical properties of UP.

To explain the changes in the mechanical properties, we need to set about the principle of the polymerization. BMD accelerated the curing reactions of the UP matrix, causing the system to crosslink; thus, an inter-crosslinked polymer network was obtained. The presence of the BMD monomer within this network structure had two effects. First, it increased the crosslinking density because the BMD was tetrafunctional,

Figure 3 Influence of BMD content on impact strength.
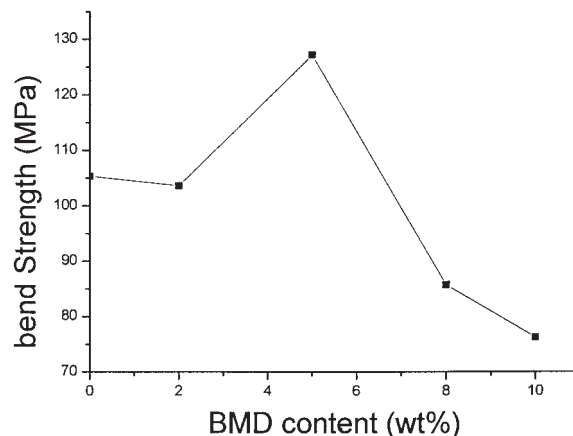
Figure 5 Influence of BMD content on bend strength.

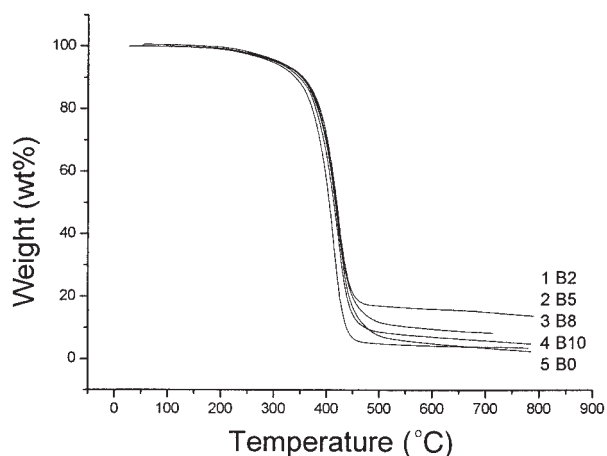**Figure 6** TGA curves of UP and the modified resins.

Figure 7 DTG curves of UP and the modified resins.

whereas styrene was bifunctional. In fact, a single BMD unit could link four polyester chains, whereas a styrene unit could link only two; Second, it increased the overall rigidity of the network because the BMD unit was considerably stiffer than the styrene unit.

The bend strength and impact strength showed maximum improvement at a BMD content of 5%, whereas the tensile strength was maximal at a BMD content of 2%. This seemed rather unexpected. It can be explained by the fact that the bend strength and impact strength were more affected by the crosslinking density, but the tensile strength was more affected by the length of molecular chain. A crosslinking reaction between double bonds may arise when there are many unsaturated bonds in the system, whereas the molecular chain cannot linearly increase. BMD was tetrafunctional, whereas styrene was bifunctional, which increased the chance of crosslinking reaction between double bonds. So the tensile strength of the copolymers decreased with the addition of BMD, and the maximum tensile strength was found in BUP2.

Thermal properties

TGA

BMDs are monomers typically used in the preparation of high-temperature polymers; thus, one of our most important intentions of the addition of BMD was in-

creased heat resistance of the UP resin. Figure 6 shows the TGA curves for UP and the modified resins, whereas the data for the resins are listed in Table I.

Figure 7 shows the DTG curves for UP and the modified resins, whereas the data for the resins are listed in Table II. As shown in Figures 6 and 7, the addition of BMD improved the thermal decomposition temperature and HDT of the UP resin.

The data in Table I indicate the temperature at which 5 wt % degradation occurred (T_{d5}) and the temperature at which 50 wt % degradation occurred (T_{d50}). T_{d5} represents the onset of the degradation, whereas T_{d50} also provides some information on the course of the degradation. Table II shows the temperature of the maximum rate of weight loss (T_{max}) of UP and the modified resins. It was obvious that the modified resins showed higher heat resistance than the neat UP. The addition of BMD could play a more effective role in improvement of the UP resin. The T_{max} value of the modified resins was about 13°C higher than that of UP. The delay in degradation was mainly due to the thermally stable aromatic–heterocyclic structure of BMD and the formation of an inter-crosslinking network. The results confirmed that the addition of BMD remarkably improved the thermal stability of the UP resin.

HDT

The effects of BMD content on HDT are reported in Table III. In this representation, HDT of the modified

TABLE I
Thermal Decomposition Temperatures of UP and the Modified Resins

	Content of BMD (%)				
	0	2	5	8	10
T_{d5} (°C)	300.2	301.7	304.7	307.8	309.3
T_{d50} (°C)	402.5	408.6	408.6	413.2	411.6

TABLE II
T_{max} Values of UP and the Modified Resins

	Content of BMD (%)				
	0	2	5	8	10
T_{max} (°C)	412.2	413.8	420.3	423.6	425.2

TABLE III
Influence of BMD Content on HDT

	Content of BMD (%)				
	0	2	5	8	10
HDT (°C)	54	74.3	69.1	79.9	72.3

resins were all higher than that of neat UP. When the BMD content was 8 wt %, HDT was highest, which was 26°C higher than that of UP. Although content of BMD was up to 10 wt %, HDT decreased little; this may have been due to the bad dispersion of BMD at high BMD contents. Because of the high rigidity and high glass-transition temperature of BMD, the addition of BMD to UP resin not only improved its thermal decomposition temperature and HDT but also made small changes to its mechanical properties. So the rigidity and heat resistance of the UP resin were improved.

DMA

The tensile storage modulus (E') and the loss tangent (tan δ) curves as a function of temperature for the neat UP resin and BUP5 copolymer are reported in Figure 8. Over the temperature range investigated, E' of the UP resin showed a gradual and continuous decrease in the range from 20 to 60°C. At this point, a sudden drop was observed that corresponded to the onset of large-scale molecular mobility. A similar trend was found for the BUP5 copolymer, with the difference being that the E' values were lower in the copolymer in the range 20–40°C, with E' starting to drop at higher temperatures, whereas at high temperatures, the E' values of UP and the BUP5 copolymer were mainly consistent. As shown in Figure 8, the glass-transition temperature of the BUP5 copolymer was

slightly higher than that of the neat UP resin. Other information was gained by inspection of the tan δ curves; one loss peak was observed in the transition region of both the UP resin and the BUP5 copolymer. This indicated that BMD/UP copolymer system formed a homogeneous phase, not phase separation; thus, this did not benefit the improvement of the mechanical properties. These results indicate that BMD and the UP resin dissolved each other especially. On the other hand, styrene interacted with both BMD and UP, which resulted in a network structure.

SEM

Figure 9 shows the SEM observation of the fracture surface of UP and the BMD/UP copolymers with different BMD contents. It was obvious that the morphological structure of the modified resins was greatly changed because of the addition of BMD. For the neat UP resin [Fig. 9(a)], the fracture surface was clear and sharp, typical of a brittle material, although for the BMD/UP copolymer with 2 wt % BMD [Fig. 9(b)], the fracture surface was rough and rugged. The SEM photograph of BUP5 is shown in Figure 9(c). The fracture surface clearly appeared with a ligament and drawbench shape. As shown in Figure 9(c), the extent and branch of crack were also observed; this benefited the increase in impact strength. The presence of BMD forced the crack to progress along a more tortuous path, which increased the fracture surface area and toughness of the materials; thus, the mechanical properties were improved with the addition of BMD. In the SEM photograph of BUP10 [Fig. 9(d)], a wavy shape and a little stripe could be seen. Compared to Figure 9(c), the toughness of the copolymer with 10 wt % BMD was obviously reduced; this resulted in a decrease in the impact strength of BUP10. This may have been due to the bad dispersion of BMD at high BMD
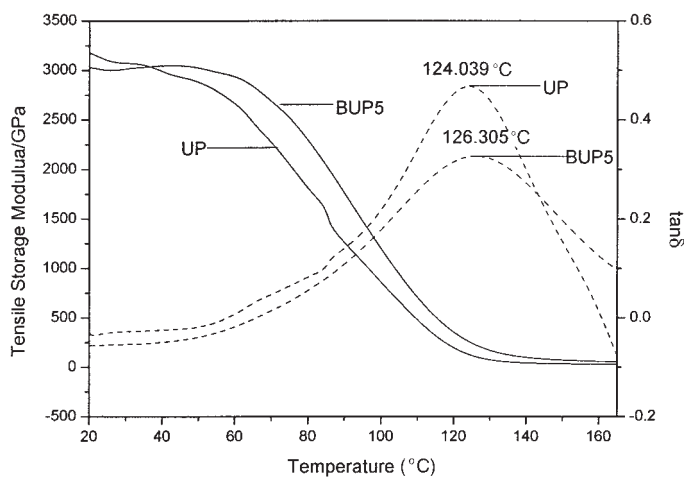
Figure 8 DMA curves of the UP resin and BUP5.
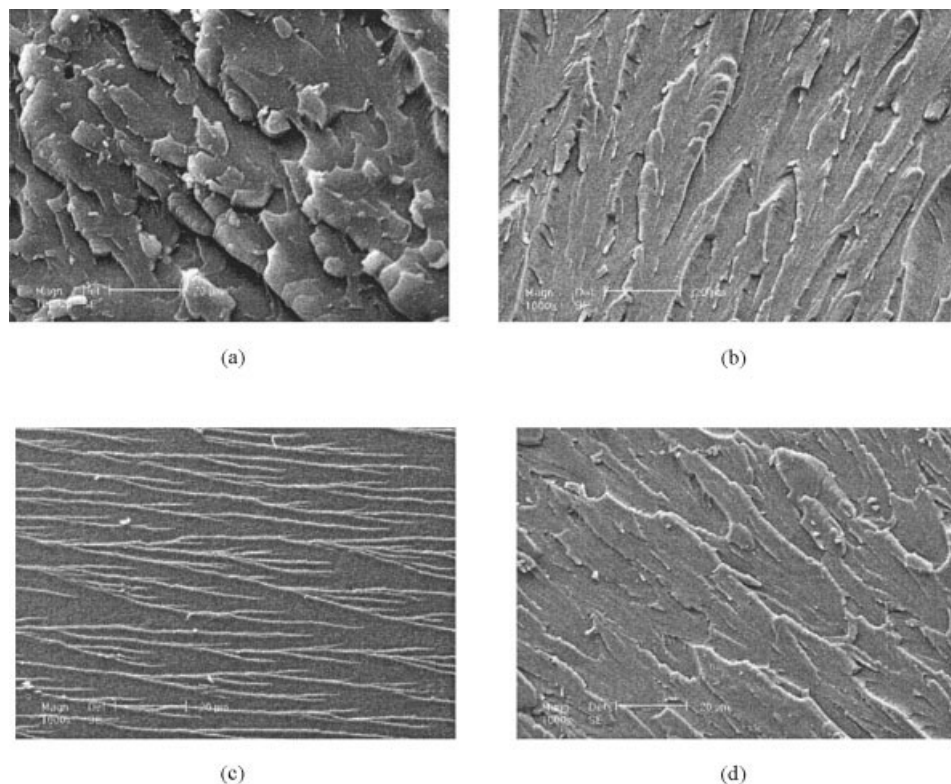
Figure 9   SEM photos (1000×) of the impact fracture of (a) UP, (b) BUP2, (c) BUP5, and (d) BUP10.

contents. These observations were in agreement with the previous data for the mechanical properties.

CONCLUSIONS

In this study, a system consisting of a UP and a thermosetting BMD resin was investigated. BMD was readily dissolved in the UP; furthermore, styrene of the UP resin and BMD copolymerized through an alternating mechanism in solution, sequentially introducing the concerned performance of BMD. Because of the high rigidity and high glass-transition temperature of BMD, the addition of BMD to the UP resin not only improved its properties but also accelerated the polymerization process. Most of the thermal properties of the modified resins were far higher than that of the neat UP resin; the mechanical properties were changed little in the copolymers.

References

 1. Burn, R. B. Polyester Molding Compounds; Marcel Dekker: New York, 1982.
 2. Hietalathti, K.; Root, A.; Skrifvars, M.; Sundholm, F. J Appl Polym Sci 1997, 65, 77.
 3. Martuscelli, E.; Musto, P.; Ragosta, G.; Scarinzi, G.; Bertotti, E. J Polym Sci Part B: Polym Phys 1993, 31, 619.
 4. Bellenger, V.; Mortaigne, D.; Grenier-Loustalot, M. F.; Verdu, J. J Appl Polym Sci 1992, 44, 643.
 5. Chen, J. S.; Yu, T. L. J Appl Polym Sci 1998, 69, 871.
 6. Yang, Y. S.; Pascault, J. P. J Appl Polym Sci 1997, 64, 133.
 7. Yang, Y. S.; Pascault, J. P. J Appl Polym Sci 1997, 64, 147.
 8. Boey, F. Y. C.; Song, X. L.; Yue, C. Y.; Zhao, Q. J Polym Sci Part A: Polym Chem 2000, 38, 907.
 9. Morgan, R. J.; Shin, E. E.; Rosenberg, B.; Jurek, A. Polymer 1997, 38, 639.
10. Liu, Y. L.; Chen, Y. J. Polymer 2004, 45, 1797.
11. Dinakaran, K.; Alagar, M.; Suresh, K. R. Eur Polym J 2003, 39, 2225.
12. Mai, K. C.; Huang, J. W.; Zeng, H. M. J Appl Polym Sci 1997, 66, 1965.
13. Yuan, Q. L.; Huang, F. R.; Jiao, Y. S. J Appl Polym Sci 1996, 62, 459.
14. Sasuga, T.; Hagiwara, M. Polymer 1986, 27, 681.
15. He, J. D.; Wang, J.; Li, S. D. Acta Polym Sinica 2000, 5, 559.
16. Barrales-Rienda, J. M. J Macromol Sci Chem 1977, 11, 267.
17. Colthup, N. B.; Daly, L. H.; Wiberley, S. E. Introduction to Infrared and Raman Spectroscopy; Academic: San Diego, 1990.
18. Yang, Y. S.; Lee, L. J. Macromolecules 1987, 20, 1490.
19. Awdzik, B. G.; Matynia, T.; Chmielewska, E. J Appl Polym Sci 2001, 82, 2003.