

*Dedicated to the memory of  
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

## FeS<sub>2</sub>/POLYIMIDE COMPOSITE FILMS. SYNTHESIS AND CHARACTERIZATION

Ion SAVA\*

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Vodă 41A, Iași 700487, Roumania

*Received May 19, 2009*

A series of FeS<sub>2</sub>/polyimide composite films with different FeS<sub>2</sub> content have been synthesized by incorporating FeS<sub>2</sub> microparticles with a diameter of 2-5 μm into polyamic acid, followed by stepwise thermal imidization process. The incorporation of FeS<sub>2</sub> slightly increases the glass transition temperature of the composite polyimide films, while the thermal degradation temperature of composite decreases with increasing FeS<sub>2</sub> content.

### INTRODUCTION

The development of high performance polymers has been the focus of attention for over 50 years being of fundamental importance in the aerospace and electronic industries, medicine, communications and in applications that demand service at enhanced temperatures with maintaining their structural integrity as well as excellent combination of chemical, physical and mechanical properties. Some of the important polymers in this respect are polyamides, polyimides and polyoxadiazoles.<sup>1-4</sup>

Aromatic polyimides are a special class of high performance polymers known for their outstanding thermal stability in air and good physico-mechanical properties at high temperature.<sup>5-9</sup> Particularly interesting is the potential use of polyimides in micro electro mechanical systems (MEMS) devices since they possess both the chemical and thermal stability necessary to withstand conventional MEMS processing. However, most of polyimides are insoluble and infusible, and therefore, difficult to process. In some applications, the properties of polyimides do not always meet the requirements for optimum performance. For example, the high resistivity of polyimide, which is useful in a lot of electrical

applications, provides no benefit in static charge dissipation and in production of thin-film resistive heaters. One approach to make polyimides suitable for such applications is to obtain polyimide composites. For these specific applications a great deal of researches have been devoted to the synthesis of modified polyimides and polyimide composite materials that exhibit unique physical properties. Incorporating inorganic materials into polyimide materials is a useful strategy to improve their properties. Many inorganic materials as hybrid element- or dispersed phase-embedded polyimide matrices have been extensively studied such as silica/PI, silica-alumina/PI, TiO<sub>2</sub>/PI, ZnO/PI, Cr<sub>2</sub>O<sub>3</sub>/PI, Fe<sub>2</sub>O<sub>3</sub>/PI, Barium and Titanium oxide/PI, ZnS/PI.<sup>10-20</sup> Magnetic polymer composites prepared from polymer matrices and magnetic powder, combine the favorable properties of magnetic material with the easy processing of the polymer.<sup>21-23</sup>

The goal of the present work is to obtain polyimide composite films by incorporating high dispersed FeS<sub>2</sub> microparticle into benzophenontetracarboxylic dianhydride/2,6-bis(3-aminophenoxy)benzotrile as a thermostable host polymer. The structure, morphology and thermal, physical properties have been investigated.

\* Corresponding author: isava@icmpp.ro

## RESULTS AND DISCUSSION

FeS<sub>2</sub>/polyimide composite films have been obtained by mixing the corresponding polyamic acid, previously obtained by the polycondensation reaction of benzophenonetetracarboxylic dianhydride (BTDA) and 2,6-bis(3-aminophenoxy)benzotrile, with magnetic powder of pyrite; then the homogeneous solution was cast onto a glass plate and heated in order to perform the cyclization to imide structure. For comparison we used a pure polyimide film (**PI**) and FeS<sub>2</sub>/composite polyimide films with 10% pyrite (**PI-10**) and 20% pyrite (**PI-20**).

The FTIR spectra of pure polyimide and FeS<sub>2</sub>/polyimide composites have shown the characteristic absorption peaks of imide groups at 1780 (C=O symmetric stretching), 1719 (C=O asymmetric stretching), 1368 (C-N stretching), 1098 and 715 cm<sup>-1</sup>. The characteristic absorption peak of poly(amidic acid) at 3450 cm<sup>-1</sup> disappeared almost completely and the characteristic absorption peak at 1670 cm<sup>-1</sup> (C=O from polyamic acid) is overlapped with C=O from BTDA (Figure 1). The introduction of pyrite powder in the polyamic acid does not affect the imidization process.

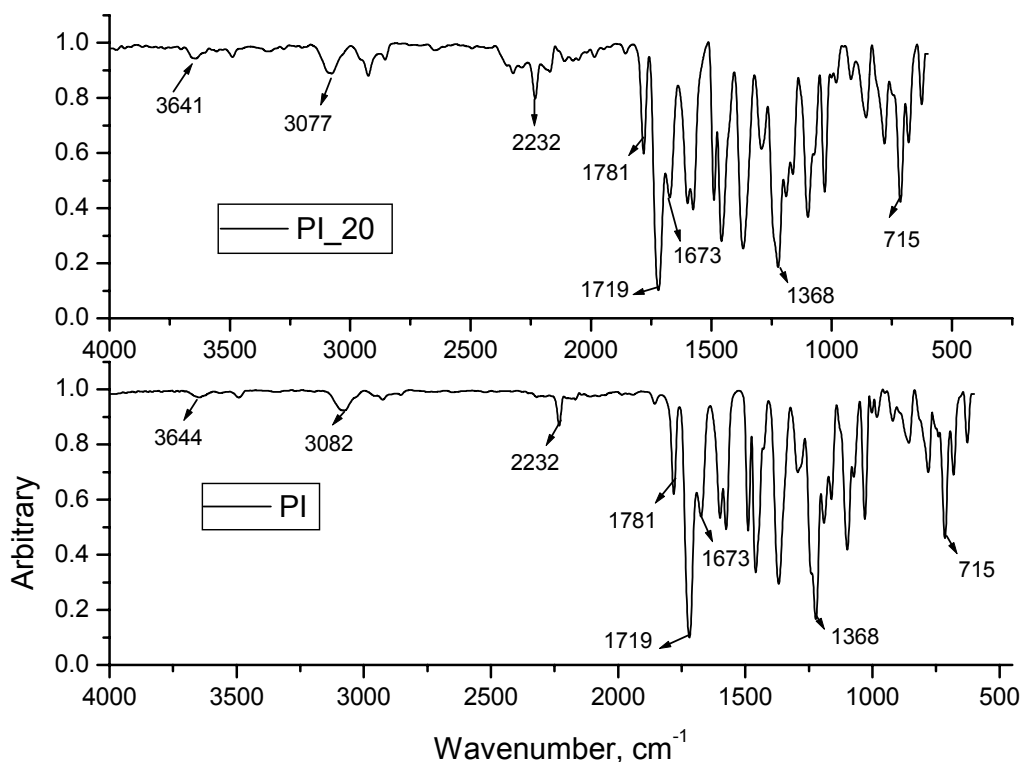


Fig. 1 – FTIR spectra of pure polyimide film (**PI**) and FeS<sub>2</sub>/ polyimide composite film (**PI-20**).

The thermal stability of the polymers were determined using thermogravimetric analysis under nitrogen. The temperatures of weight loss for the pure polyimide and FeS<sub>2</sub>/polyimide composite films are given in Table 1. The decomposition temperature of the polyimide composite films decreases with increasing FeS<sub>2</sub> content from 512°C for pure polyimide to 465°C for polyimide with 20% FeS<sub>2</sub>. The decreasing in thermal stability of the composite films can probably attributed to metal-catalyzed oxidative degradation of the composite films.<sup>7, 20</sup> However, the polyimide/FeS<sub>2</sub> composites may be considered to exhibit high thermal stability.

The thermal transition behaviour of the pure polyimide and FeS<sub>2</sub>/polyimide composite films

was studied using dynamic mechanical analysis. The effects of temperature and content of metallic powder of pyrite on the storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of the pure polyimide (**PI**), polyimide with 10% (**PI-10**) and 20% (**PI-20**) pyrite at a frequency of 1 Hz are seen in figure 2. All the curves show three distinct regions (figure 2a): a glassy high modulus region where the segmental mobility is restricted, a transition zone where a substantial decrease of the storage modulus with increasing temperature occurs and a short rubbery plateau, where the storage modulus remains constant, around 10<sup>6</sup> Pa.

Table 1  
Thermal analysis of **PI**, **PI-10** and **PI-20** films

Polymer	T <sub>5</sub> (°C)	T <sub>10</sub> (°C)	W <sub>500</sub> (%)	T <sub>max</sub> (°C)	W <sub>tmax</sub> (%)	Tg(°C) from tan δ DMA
<b>PI</b>	512	545	4	555	19.4	155
<b>PI-10</b>	480	525	7	535	23.3	170
<b>PI-20</b>	465	500	10	520	27.5	178

T<sub>5</sub> = temperature of 5% weight loss (from TGA curve); T<sub>10</sub> = temperature of 10% weight loss (from TGA curve); W<sub>500</sub> = weight loss at 500 C (from TGA curve); T<sub>max</sub> = temperature of the maximum speed of decomposition; W<sub>tmax</sub> = weight loss at T<sub>max</sub> (from TGA curve).

The **PI** film shows a high modulus,  $1.9 \cdot 10^9$  Pa, below its glass transition temperature (T<sub>g</sub>), followed by a drastic drop in magnitude around 130°C which is the onset of the glass transition. The severe decrease in modulus with temperature indicates distinct transition from glassy to rubbery state. The temperature at which E' starts to decrease rapidly corresponds to the glass transition

temperature. The E' values of the **PI-10** and **PI-20** slightly decrease with the increasing of the content of pyrite being  $1.31 \cdot 10^9$  Pa and  $0.85 \cdot 10^9$  Pa, respectively. In the same time the onset of the glass transition temperature increases with increasing pyrite content being 152°C for **PI-10** and 158°C for **PI-20**.

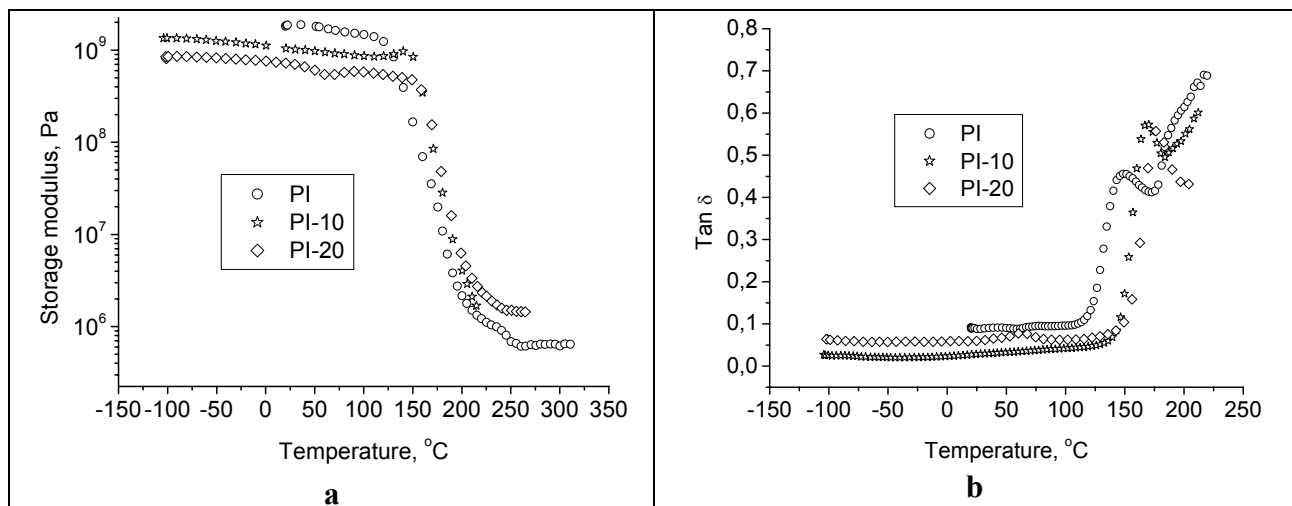


Fig. 2 – Temperature dependence of the storage modulus (a) and tan δ for polymers **PI**, **PI-10** and **PI-20**.

The variation of loss tangent (tan δ) with temperature for the pure polyimide and composite polyimide films confirms information about the main relaxation processes in these compounds (figure 2b), obtaining by analyzing the variation of E' with temperature. One can be seen that as the temperature increases, tan δ goes through a maximum near T<sub>g</sub> in the transition region. Micro-Brownian motion of molecular segments begins at T<sub>g</sub> where short range diffusion can take place. The tan δ values are low below T<sub>g</sub> because the thermal energy is insufficient to cause rotational and transitional motions of the segments.<sup>24,25</sup> The peak

of tan δ for pure **PI** is noticed at 155°C due to the α transition arising from the segmental motion. In the same manner the composite polyimide films **PI-10** and **PI-20** show the glass transition temperatures at 170°C and 178°C, respectively.

Transmission electron microscopy micrograph for **PI-20** shows that the pyrite particles are uniformly dispersed in the polyimide matrix and remain at their original size of 2-5 μm in diameter with a very few aggregates. This fact maintains the mechanical and thermal properties of composite films at high values and lead to some new characteristics useful in some microelectronic applications.

A preliminary research study has been done for determination of displacement of a membrane based on these polyimides under direct current at voltage of 460 V. Voltage control was obtained by using a voltage source that can generate a voltage up to 500 V. The displacements for pure polyimide film used in a polymeric membrane were around 1200 nm. The inclusion of the pyrite powder in the polyimide matrix leads to breakdown of the membrane at the same voltage. These results can be the start points for further interesting investigations.

## EXPERIMENTAL

### Materials

2,6-Dichlorobenzonitrile (Fluka), 3-aminophenol 99% (Aldrich), anhydrous potassium carbonate (Fluka) were used as received. N-methyl 2-pyrrolidone 99% (Aldrich) was distilled under vacuum over phosphorous pentoxide before use. Benzophenonetetracarboxylic dianhydride (Fluka) was recrystallized from acetic anhydride. Pyrite was obtained as wastes from burning of pyrite ores to produce sulfuric acid. The granulometric distribution of pyrite ash particles, performed with vibrating sieves, was in the range of 0–125  $\mu\text{m}$ .

### Synthesis of 2,6-bis(3-aminophenoxy)benzonitrile

2,6-Bis(3-aminophenoxy)benzonitrile was obtained by nucleophilic displacement reaction of 2,6-dichlorobenzonitrile with 3-aminophenol by a method reported in the literature,<sup>26</sup> as shown in Scheme 1. Melting point 121–123°C.

### Preparation of the polyimide/composite films

The polymer precursor, poly(amidic acid) was synthesized by the reaction of the benzophenonetetracarboxylic dianhydride and 2,6-bis(3-aminophenoxy)benzonitrile in NMP in 15% solids concentration under nitrogen atmosphere. In a typical

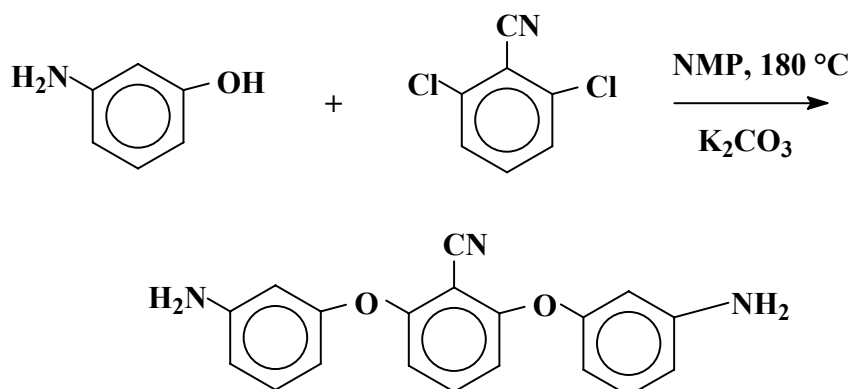
synthesis, 2,6-bis(3-aminophenoxy)benzonitrile was dissolved in NMP, and a equimolecular amount of BTDA was added under stirring. Stirring was continued at room temperature for 4 h, resulting in a viscous yellow solution. These preliminary steps and the subsequent conversion of the resulting materials to polyimide/composite films are shown in scheme 2.

The desired amount of  $\text{FeS}_2$  particles was added to poly(amidic acid) solution and the mixture was stirred for 1 h at room temperature. The  $\text{FeS}_2$ /polyimide composite films were prepared by casting the homogeneous viscous solution onto a glass plate. The films were cured on a hot plate at 60°C for 4 h and then a stepwise thermal imidization process (30 min at each of the following temperatures 100, 150, 200°C, and finally at 220°C for 1 h) was carried out.

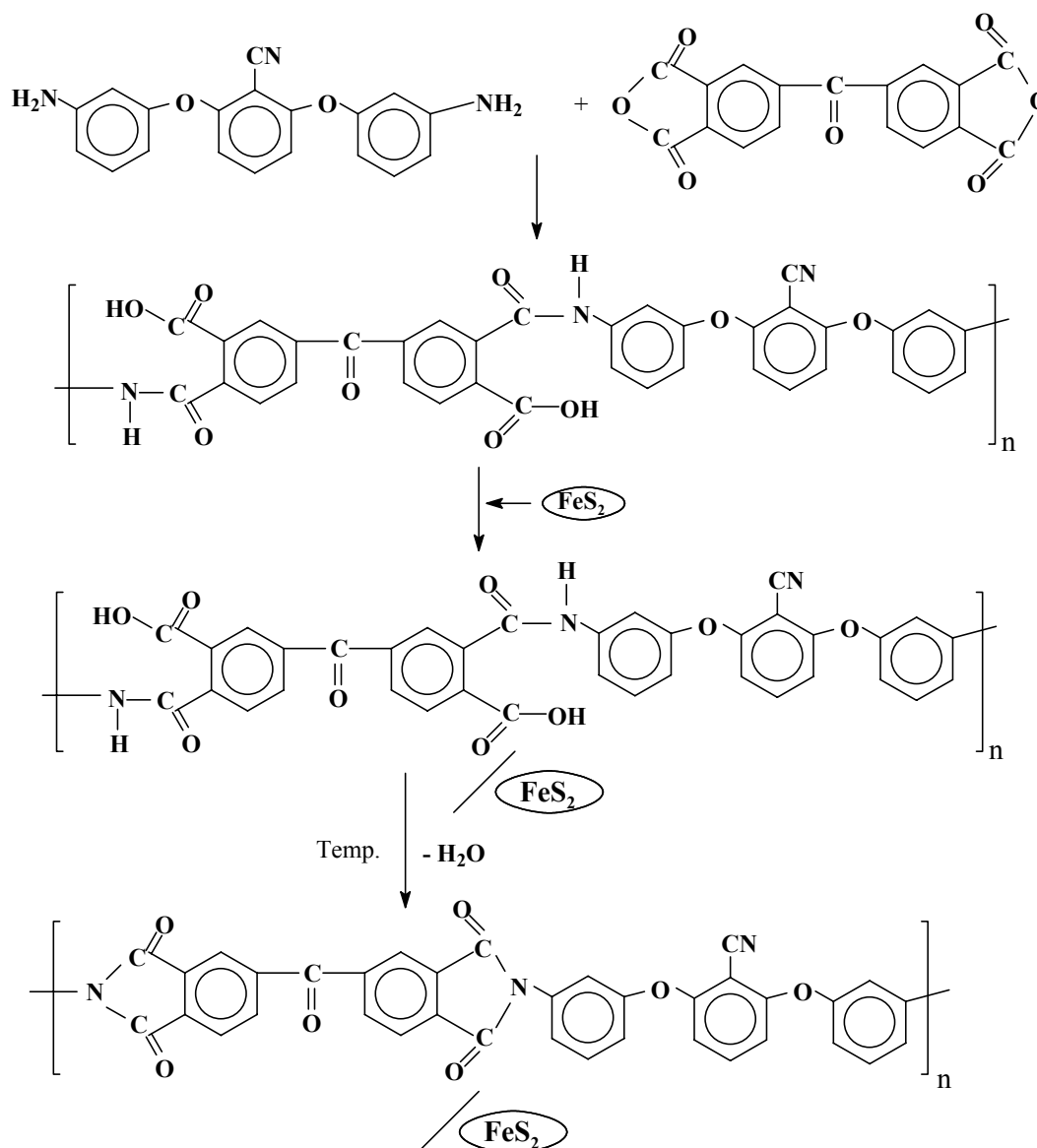
### Measurements

Fourier transform infrared (FTIR) spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company) spectrometer with a resolution of 0.5  $\text{cm}^{-1}$ . The thermogravimetric analysis (TGA) of the polymers was performed with a Mettler 681e instrument, operating at a heating rate of 15°C/min, in nitrogen. Glass transition temperature of the polymers was determined with a Mettler differential scanning calorimeter DSC 12E.

DMA experiments were performed by using a PerkinElmer Diamond apparatus provided with a standard tension attachment. The apparatus was heated at 2°C/min, in a nitrogen atmosphere, up to a temperature higher than that corresponding to glass transition. The films 10 x 10 x 0.20 (mm x mm x mm) were longitudinally deformed by a small sinusoidal stress, at a frequency of 1 Hz, and the resulted strain was measured. Transmission electron microscopy (TEM) was carried out using a JEOL-2021 microscope. The study of the displacement of the polymer membrane based on these polyimides was performed by using an experimental setup, based on Michelson type interferometer using AGILENT 5529 system equipped with temperature, humidity and pressure sensors.<sup>27, 28</sup>



Scheme 1 – Synthesis of 2,6-bis(3-aminophenoxy)benzonitrile.

Scheme 2 – Synthesis of FeS<sub>2</sub>/polyimide composite.

## CONCLUSIONS

Polyimide/pyrite composite films with good mechanical and thermal properties have been prepared by blending pyrite microparticles and polyamic acid followed by heating for removing the solvent and thermal cyclization to imide structure. The introduction of pyrite particles in a polyimide matrix enhances the glass transition temperature and improves the mechanical properties of the composite. The DMA thermograms show that the glass transition temperature slightly increases while the storage modulus decreases with increasing pyrite content in the composite.

The pure polyimide film can be used in the obtaining of membranes which under a direct

current of 460 V can produce a nanodisplacement up to 1200 nm. The polymeric membranes could be used in different linear actuators.

*Acknowledgements.* The author appreciates the help of Mariana Cristea's group for the DMA measurements and for the commentary on the results.

## REFERENCES

1. J. Preston, Aromatic polyamides, In: Encyclopedia of polymer science and engineering, HF Mark, NM Bikales, CG Overberger, G. Menges, Editors. New York, Wiley, 1988, Vol 11, 381-409.
2. B. Silion, Polyimides and other heteroaromatic polymers, In: Comprehensive polymer science, G Allen, Editor, Oxford, Pergamon Press, 1989, vol 5, p 499-532.

3. P.E. Cassidy, T.M. Aminabhavi and V.S. Reddy, Heat resistant polymers, In: Kirk-Othmer encyclopedia of chemical technology, JI Kroschwitz, Editor, New York, Wiley, 1994, 2 nd edition, vol 12, p. 1045-1070.
4. B. Schulz, M. Brumă and L. Brehmer, *Adv. Mater.*, **1997**, *9*, 601-613.
5. C. E. Sroog, *Prog. Polym. Sci.*, **1991**, *16*, 561-694.
6. M. Sato, "Polyimides", In: Handbook of Thermoplastics, O Olabisi, Editor, New York, Marcel Dekker, 1997, p. 665-669.
7. P. M. Hergenrother, *High Perform. Polym.*, **2003**, *15*, 3-45.
8. M. Brumă, E. Hamciuc, I. Sava, C. Hamciuc, M. D. Iosip and J. Robison, *Rev. Roum. Chim.*, **2003**, *48*, 629-638.
9. E. Hamciuc, M. Brumă, C. Hamciuc and R. Lungu, *Rev. Roum. Chim.*, **2006**, *51*, 765-771.
10. M. Nandi, J.A. Conklin, L. Jr. Salvati and A. Sen, *Chem Mater.*, **1991**, *3*, 201-206.
11. Z. Ahmad and J.E. Mark, *Chem Mater.*, **2001**, *13*, 3320-3330.
12. H.B. Park, J.H. Kim, J.K. Kim and Y.M. Lee, *Macromol Rapid Commun.*, **2002**, *23*, 544-550.
13. J. Zhong, M.Yhang, Q.Jiang S.T. Yeng, B. Cai and Q. Lei, *Mater Lett.*, **2006**, *60*, 585-589.
14. P.C. Chiang and W.T. Whang, *Polymer* **2003**, *44*, 2249-2254.
15. Y.J. Tong, Y.S. Li, F.C. Xie, and M.X. Ding, *Polym Int.*, **2000**, *49*, 1543-1547.
16. S.C. Hsu, W.T. Whang, C.H. Hung, P.C. Chiang and Y.N. Hsiao, *Macromol Chem Phys.*, **2005**, *206*, 291-298.
17. M. Nandi, J.A. Conklin, L. Jr Salvati and A. Sen, *Chem Mater.*, **1990**, *2*, 772-776.
18. J.J. Bergmeister and L.T. Taylor, *Chem Mater.*, **1992**, *4*, 729-737.
19. Y. Tong, Y. Li, J. Liu and M. Ding, *J. Appl. Polym. Sci.*, **2002**, *83*, 1810-1816.
20. X. Lu, N. Lu, J. Gao, X. Jin and C. Lu, *Polym. Int.*, **2007**, *56*, 601-605.
21. Z. Osawa, K. Kawauchi, M. Iwata and H. Harada, *J. Mater. Sci.*, **1988**, *23*, 2637-2644.
22. H. S. Gokturk, T. J. Fiske and D. M. Kaylon, *IEEE Trans. Magn.*, **1993**, *29*, 4170-4176.
23. J.G. Liu, Y. Nakamura, T. Ogura, Y. Shibasaki, S. Ando and M. Ueda, *Chem Mater.*, **2008**, *20*, 273-281.
24. C. Komalan, K.E. George, P.A.S. Kumar, K.T. Varughese and S.Thomas, *eXPRESS Polymer Letters*, **2007**, *1*, 641-653.
25. M. Cristea, D. Gheorghiu-Ioniță, M. Brumă and B. C. Simionescu, *J. Therm. Anal. Cal.*, **2008**, *93*, 63-68.
26. A. Saxena, P.V. Prabhakaran, V.L. Rao and K.N. Ninan, *Polym Int.*, **2005**, *54*, 544-552.
27. Agilent Technologies "Agilent 5529A/55292A Dynamic Calibrator, Measurement Reference Guide".
28. C. Hamciuc, E. Hamciuc, M. Ignat and G. Zărnescu, *High Perform. Polym.*, **2009**, *21*, 205-218.