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Non-isothermal crystallization kinetics of Poly(phenylene sulfide)/hyperbrtanched Poly(phenylene sulfide) blends

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Abstract: The non-isothermal crystallization behaviour of poly(phenylene sulfide) (PPS) in blends with hyperbranched poly(phenylene sulfide) (HPPS) was studied by means of differential scanning calorimetry (DSC). It was observed that the PPS crystallization temperature was found to decrease upon addition of the HPPS. It suggested that the crystallizability was reduced. The Ozawa equation was valid not only for neat PPS, but also for the blends. A notable reduction in Avrami exponents for the PPS/HPPS blend systems suggested that the nucleated process leads to rod-shaped growth with thermal nucleation. The cooling crystallization function, which represents the rate of non-isothermal crystallization, was found to decrease with increase in HPPS content. The Ea value increases with the increase in HPPS content. Our results indicated that crystallization of the PPS was hampered by content of hyperbranched poly(phenylene sulfide).

Introduction

The study of non-isothermal crystallization of polymers is of great technological significance, since most practical processing techniques proceed under non-isothermal conditions. Moreover, from a scientific point of view, non-isothermal experiments may mean a great deal in view of the understanding of the crystallization behavior of polymers, because the more used isothermal methods are often restricted to narrow temperature ranges [1].

The crystallization behaviour of neat PPS [2], of PPS filled with solid fillers [3-5] and of PPS blended with thermoplastic polymers [6, 7] has been studied extensively by isothermal methods. The nonisothermal crystallization kinetics of PPS was studied by Lopez and Wilkes [8]. They have found that the Avrami exponents, determined by the Ozawa equation from non-isothermal measurements, are in good agreement with those achieved by isothermal methods.

Dendritic polymers, including dendrimers and hyperbranched polymers, are known to have special properties defined by their three dimensional structure and the large number of functional groups. Dendritic polymers are currently compared with conventional linear thermoplastics in order to evaluate unusual properties [9]. In 1992, Kim and Webster firstly reported blending of hyperbranched polyphenylene with linear polystyrene [10]. In recent years various blends between dendritic polyesters and linear polymers have been described, and advantages for processing of the materials due to the dendritic component have been mentioned [11-16].

However, one could not find articles in the literature that discussed isothermal or non-isothermal crystallization kinetics about blends of linear and hyperbranched polymer.

In this work, we attempted to prepare blends of hyperbranched poly(phenylene sulfide)(HPPS) with a commercially available linear poly(phenylene sulfide)(PPS), on the nonisothermal crystallization kinetics by differential scanning calorimetry (DSC) data, adopting the Ozawa equation.

Results and Discussion

Non-isothermal crystallization behaviour of PPS/HPPS blends

All samples were investigated by differential scanning calorimetry (DSC) to see changes in the melting and crystallization behaviour. The DSC thermograms obtained at a cooling rate of 10 ^{0}C /min for neat PPS, PPS/HPPS (95/5) and PPS/HPPS(80/20) blends are shown in Figure1. The exothermic crystallization peaks were monomodal and their shapes indicate that secondary crystallization did not play an important role in these blends. Also observed was the fact that the pure PPS exotherm was much sharper than that of PPS/HPPS blends and located at a higher temperature with respect to the latter.

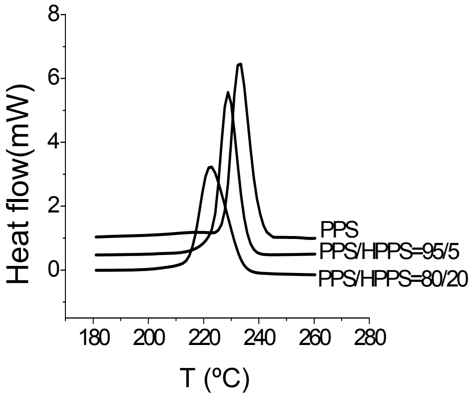

Fig.1. DSC. cooling traces of PPS and PPS/HPPS blends, recorded at 10 ^{0}C/min.

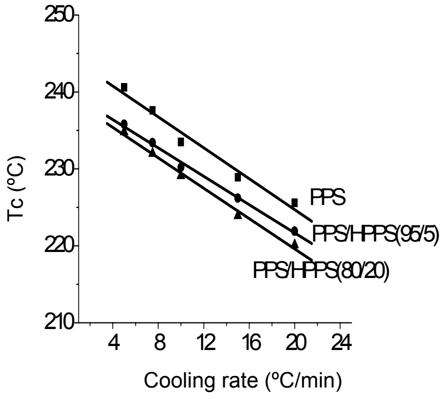

Fig. 2. Plot of Tc as a function of cooling rates corresponding to PPS and PPS/HPPS blends.

The crystallization temperature T_c, the melt temperature T_m, the degree of supercooling (T_m-T_c) and the (T_{co}-T_c) of the PPS and the PPS/HPPS blends at different cooling rates were presented in Table 1. It was observed that the Tc shifted to lower (Figure 2) values indicating reduced crystallizability of the PPS as the HPPS content [19].

Tab. 1. Thermal characteristics of PPS/HPPS blends.

	Cooling rate(^{0}C/ min)	T_c(^{0}C)	T_{co}(^{0}C)	T_m(^{0}C)	T_{co}-T_c (^{0}C)	T_m-T_c (^{0}C)
PPS	5	240.6	246.8	286.9	6.2	46.3
	7.5	237.6	244.2	287.5	6.6	49.9
	10	233.5	240.3	286.6	6.8	53.1
	15	228.9	237.1	285.7	8.2	56.8
	20	225.6	235.1	286.5	9.6	61.1
PPS/HPPS 95/5	5	235.8	242.2	286.1	6.4	50.3
	7.5	233.4	240.2	286.0	6.8	52.6
	10	229.2	236.7	285.6	7.5	56.4
	15	226.2	234.9	285.8	8.7	59.6
	20	221.9	232.2	285.5	10.2	63.6
PPS/HPPS 80/20	5	234.8	241.3	284.4	6.5	49.6
	7.5	232.0	239.4	285.0	7.4	53.0
	10	228.1	235.7	284.0	7.7	55.9
	15	223.9	232.8	284.2	8.9	60.4
	20	220.1	229.8	284.4	9.7	64.3

The crystallization temperature T_c, the melt temperature T_m, the degree of supercooling (T_m-T_c) and the (T_{co}-T_c) of the PPS and the PPS/HPPS blends at different cooling rates were presented in Table 1. It was observed that the Tc shifted to lower (Figure 2) values indicating reduced crystallizability of the PPS as the HPPS content [19].

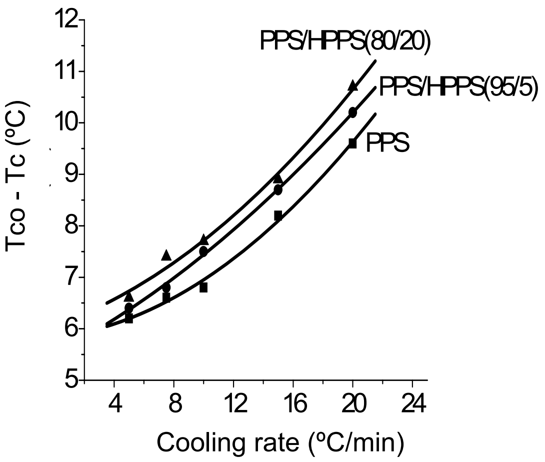

Fig. 3. Plot of (T_{co}-T_c) as a function of cooling rates corresponding to PPS and PPS/HPPS blends.

The crystallization temperature decreased on increasing the cooling rate, as could be expected for the polymer crystallization controlled by nucleation [20]. The value (T_{co}-T_c) could be used as a measure for the crystallization rate (Figure 3). The value (T_{co}-T_c) increasing reflected a decrease of the non-isothermal crystallization rate by the presence of HPPS [21]. The degree of supercooling (T_m-T_c) required for the crystallization in the PPS/HPPS blends was higher compared to that required for pure PPS (Figure 4). The increasing in the degree of supercooling could be attributed to cumber nucleation process in the presence of solidified [22].

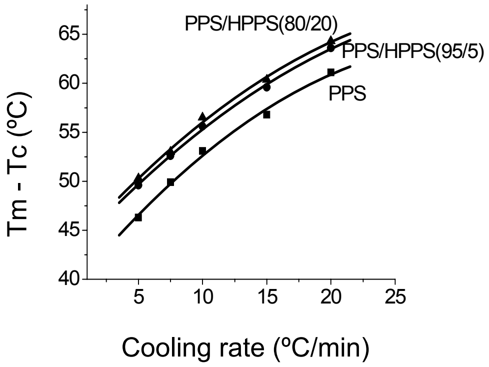

Fig. 4. Plot of (T_m-T_c) as a function of cooling rates corresponding to PPS and PPS/HPPS blends.

All those mean that the hyperbranched polymer did not act as nucleation agent and that crystallization of the blends were hampered by content of hyperbranched polymer.

Non-isothermal crystallization kinetics of PPS/HPPS blends

The overall non-isothermal crystallization kinetics of PPS and PPS/HPPS blends was studied using the Ozawa equation:

$$\ln\{-\ln[1 - X(T)]\} = \ln F(T) - n\ln\varphi$$

Where X(T) is the volume fraction of material crystallized at temperature T. φ is the constant cooling rate. n is the Avrami exponent, which depend on the nucleation density and the spherulitic radial growth rate, for both instantaneous and sporadic nucleation. F(T) is the cooling crystallization function. The amorphous fractions [1 - X(T)] is plotted as function of temperature for the different cooling rates as shown in Figure 5 for pure PPS, Figure 6 for PPS/HPPS(95/5), Figure 7 for PPS/HPPS(80/20). Values of the amorphous fraction at a given temperature were taken from these plots at each cooling rate. Then, the double logarithm of the reciprocal amorphous fractions ln{-ln[1-X(T)]} at constant temperature was plotted as a function of the cooling rate. If the Ozawa equation was valid, the curve corresponding to each temperature should be a straight line. The slope provided the Avrami exponent and the intercept determines the value of the cooling crystallization function. As in Figure 5, 6, 7 all the curves of amorphous fraction versus temperature had approximately the same shape. This would indicate that only the retardation effect of cooling rate on the crystallization was observed in these cures.

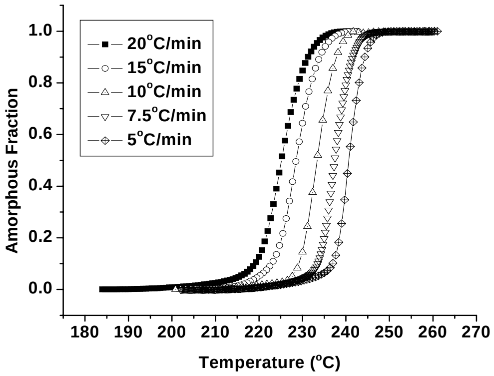

Fig. 5. Plot of amorphous fraction as a function of temperature for pure PPS crystallized non-isothermally at various cooling rates.

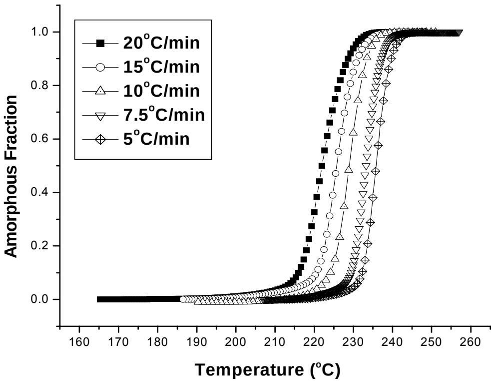

Fig. 6. Plot of amorphous fraction as a function of temperature for PPS/HPPS(95/5) crystallized non-isothermally at various cooling rates.

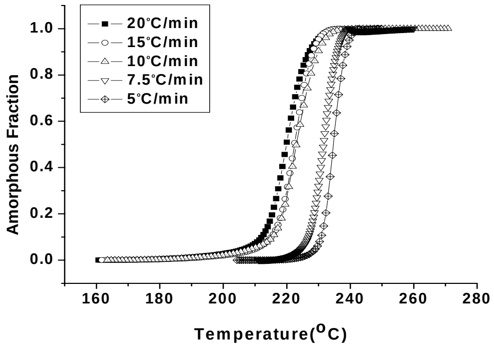

Fig. 7. Plot of amorphous fraction as a function of temperature for PPS/HPPS(80/20) crystallized non-isothermally at various cooling rates.

The Ozawa plots could be obtained by plotting the double logarithm of the reciprocal amorphous fractions against cooling rate, for different temperatures, as shown in Figures 8, 9 and 10, respectively for PPS, PPS/HPPS (95/5) and PPS/HPPS (80/20) blend. It could be seen that these plots as well as those of all other blends studied represent straight lines, which mean that the Ozawa equation described the non-isothermal crystallization behaviour of the blends investigated satisfactorily.

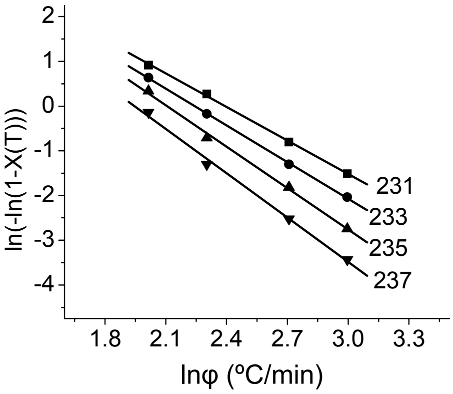

Fig. 8. Plot of ln{-ln[1-X(T)]} vs. lnφ at various temperatures corresponding to pure PPS.

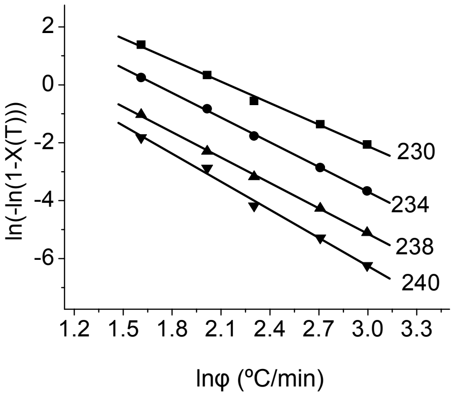

Fig. 9. Plot of ln{-ln[1-X(T)]} vs. lnφ at various temperatures corresponding to PPS/HPPS(95/5).

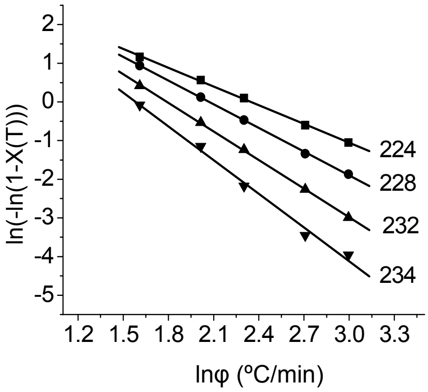

Fig. 10. Plot of ln{-ln[1-X(T)]} vs. lnφ at various temperatures corresponding to PPS/HPPS(80/20).

The intercept of the Ozawa plots gave the cooling crystallization function F(T), which represented the rate of non-isothermal crystallization [8, 20 ,23] . The plot of cooling crystallization function against temperature was presented in Figure 11. The function decreased with the increase in temperature or increase in HPPS content. The F(T) values measured for the blends were of the same order of magnitude as those obtained for pure PPS. The values measured were in good agreement with those given by Ozawa [8] for PET, Kozlowski [23] for nylon, Elder and Wlochowicz [24] for PP and Lopez and Wilkes [20] for PPS.

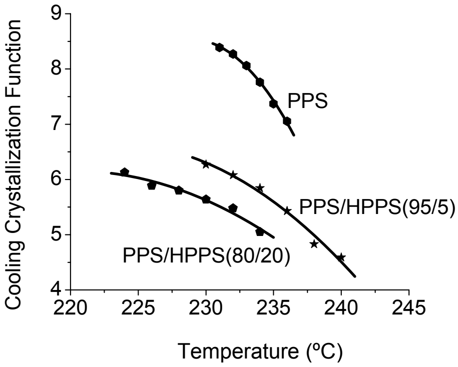

Fig. 11. Plot of the cooling crystallization function as a function of temperature corresponding to PPS and PPS/HPPS blends.

The Avrami exponents obtained were plotted against temperature in Fig. 12. PPS gave a value of 3.1, suggested that the nucleated process lead to Ozawa plots of non-isothermal crystallization for neat PPS a spherulitic growth with thermal nucleation [25, 26].

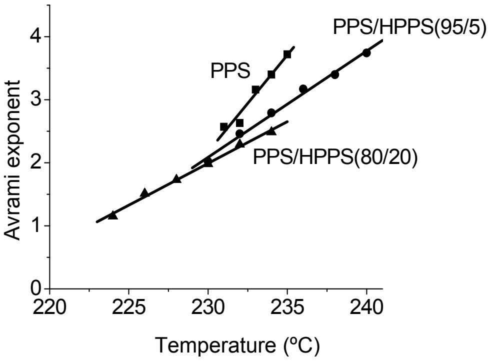

Fig. 12. Plot of the Avrami exponent as a function of temperature corresponding to PPS and PPS/HPPS blends.

In the case of PPS/HPPS blend systems, however, the Avrami exponent decreased with the HPPS content increase. Two factors might lower the value of Avrami exponent: (1) the fast crystallization rate of the blend systems at lower temperatures prevented the spherulite from developing into three dimensional crystallites [20]; (2) the growth site impingement, truncation of spherulites, impurity segregation and slightly slow secondary crystallization [20, 24, 27] might change the crystallization mechanism if the crystalline weight fraction is higher than 0.5. However, at higher crystallization temperatures, e.g. 235 °C, the Avrami exponent of blends becomes approximately 3 because the predetermined nuclei grow into three-dimensional spherulites before cooling [28]. This finding showed that the type of nucleation and the geometry of crystal growth markedly changed in the presence of blends. The deviation of Avrami exponent n could be attributed to factors such as time-dependent nucleation, variant growth rate constant as well as a combination of homogeneous and heterogeneous nucleation. However, in general, it was difficult to elucidate the growth of geometry and the type of nucleation solely from the value of n.

Non-isothermal crystallization activation energy of PPS/HPPS blends

The activation energy of nonisothermal crystallization can be determined by the Kissinger equation:

$d\ln(Q/T_c^2)/d(1/T_c) = -Ea/R$

Where Ea is the activation energy. R is the universal gas constant. Q is the cooling rate. T_c, is the crystallization temperature. Figure13 show the plots of $\ln(Q/T_c^2)$ versus $(1/T_c)$. The activation energies Ea obtained from the slope of the plots were 41.34kJ/mol for PPS, 45.22kJ/mol for PPS/HPPS(95/5) and 46.77kJ/mol for PPS/HPPS(80/20) blends respectively. The Ea value increased with the increasing in HPPS content. It clarified that the addition of HPPS caused the crystallizability of the PPS/HPPS blends to reduce.

In this work, we prepared blends of hyperbranched poly(phenylene sulfide) with a linear poly(phenylene sulfide), which with some structural similarity and a high concentration of chlorine end group, are able to promote strong interactions with the linear polymer. It was suggested that the addition of HPPS caused more steric hindrance, thereby decreasing the transportation ability of polymer chains.

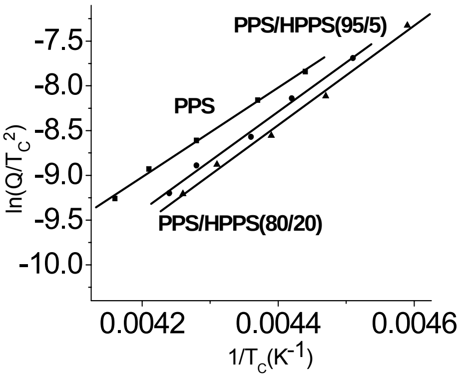

Fig. 13. Plot of $\ln(Q/T_c^2)$ vs. 1/Tc corresponding to PPS and PPS/HPPS blends.

Conclusions

The basic thermal properties of PPS and PPS/HPPS blends were studied using DSC. The DSC thermograms of PPS and PPS/HPPS blends shown that .the crystallization temperature (T_c) shifted to lower values, the value (T_{co}-T_c) increased, the degree of supercooling (T_m-T_c) increased by content of hyperbranched polymer. These indicated that the crystallizability reduced and the non-isothermal crystallization rate decreased. The nonisothermal crystallization processes of PPS and PPS/HPPS blends were described by the method developed by Ozawa. It was shown that the Ozawa equation was valid not only for neat PPS, but also for the PPS/HPPS blends. A notable reduction in Avrami exponent (n) for the PPS/HPPS blend systems suggested that the type of nucleation and the geometry of crystal growth changed in the presence of HPPS. The cooling crystallization function (F(T)), which represented the rate of non-isothermal crystallization, decreased with the increase in HPPS content. The Ea value increased with the increase in HPPS content.

It was concluded that the crystallization of the blends was hampered by content of hyperbranched poly(phenylene sulfide).

Experimental

Materials

The PPS used was commercial grade (M_w about 50000) manufactured by Sicuan huatuo Co. HPPS was synthesized in our laboratory (M_w about 22100, MD above 3.1). The molecular masses and molecular mass distribution of polymer were determined by GPC against polystyrene standards. DSC analysis of the above synthesized HPPS samples was done. The HPPS samples were found to be completely lacking in crystallinity: if the polymer samples were heated to 350 ^{0}C, then slowly cooled back to room temperature, no crystallization was observed and no T_m was observed up to 350 ^{0}C.

Synthesis procedure of HPPS

The synthesis procedure of HPPS in this work was similar to that in Hanson's work [17] and Hewen Liu's work [18]. To improve monomer conversion, we decreased reaction temperature and NMP was used as the reaction medium. A 250ml three-neck flask was charged with 80 ml NMP, 10 g 2,4-dichlorlbenzenthiol and 5.6 g KOH. The mixture was stirred under pure N_2 and was heated and maintained 10 h. The reactions were then cooled and diluted with an equal volume of water and poured into 300 ml 10% HCl solution. The resulting precipitate was vacuum-dried at 80 ^{0}C and then dissolved with vigorous stirring in a minimal amount of THF. The THF solution was added drop wise to hexanes with vigorous stirring over a period of 2 h. This precipitate was then filtered, washed with hexanes, and dried thoroughly under vacuum. The product was obtained as yellow powder. The mechanism of the synthesis of HPPS is illustrated in Scheme 1. FTIR (KBr): 3051, 1565, 1449, 1365, 1095, 1029, 868, 810cm^{-1} and ^{1}H NMR(CD_3Cl) 7.47, 7.43, 7.39, 7.37, 7.26, 7.22ppm, which have similar characteristics to those obtained in Hanson's work [17] and Hewen Liu's work [18]. In the AB2 systems, the degree of branching determined by NMR is usually about 50%-60% [29-31]. However, for the hyperbranched PPS, the degree of branching could not be determined from its 1H NMR spectrum because the chemical shifts of the aromatic protons were not well resolved for this determination [17, 18, 32].

Blends Preparation

Two kinds of blends were prepared, all based on weight fraction; the PPS/HPPS ratios were 95/5 and 80/20 respectively. All polymers were kept in vacuum oven at

80°C for 12 h before processing. Blends of PPS and HPPS were prepared using a twin-screw extruder (DACA Co. American). The melt mixing temperature was 300 °C and the screw speed was 75 rpm. The final mixing time was chosen as 10 min for all blends, which was well after the torque had reached a minimum plateau value. All blends were cooled rapidly in air after the extrusion process.

Thermal analysis

The measurement of samples was performed using a DSC (Modulated DSC 2910, TA Inc. American). The sample crystallizations were performed at constant cooling rate after being held in the molten state at 320 °C for 5 min to destroy any residual nuclei. The crystallization exotherms were recorded at selected cooling rates: 5, 7.5, 10, 15, 20 ^{0}C/min under N_2 atmosphere.

The crystallization temperature (T_c) and melt temperature (T_m) were determined from the peak maxim of the DSC thermograms. The crystallization onset temperature (T_{co}) was the temperature at the intercept of the tangents at the baseline and the high temperature side of the exotherm.

Acknowledgements

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References

[1] Minkova, L. I.; Magagnini, P. L. *Polymer* **1995**, 36, 2059.
[2] Lopez, L. C.; Wilkes, G. L. *Polymer* **1988**, 29, 106.
[3] Nadkarni, V. M.; Jog, J. P. *J. Appl. Polym. Sci.* **1985**, 30, 997.
[4] Desio, G. P.; Rebenfeld, L. *J. Appl. Polym. Sci.*, **1990**, 39,825.
[5] Song, S. S.; White, L. J.; Cakmak, M. *Polym. Eng. Sci.* **1990**, 30, 994.
[6] Nadkarni, V. M.; Shingankuli, V. L.; Jog, J. P. *Int. Polym.Process.* **1987**, 2, 53.
[7] Shingankuli, V. L.; Jog, J. P.; Nadkarni, V. M. *J. Appl Polym. Sci.* **1988**, 36, 335.
[8] Ozawa, T. *Polymer* **1971**, 12, 150.
[9] Voit, B.; Beyerlein, D.; Eichhorn, K.J.; Grundke, K.; Schmaljohann, D.; Loontjens, T. *Chem Eng Technol* **2002**; 25, 704.
[10] Kim, Y. H.; Webster, O.W. *Macromolecules* **1992**, 25, 5561.
[11] Massa, D. J.; Shriner, K. A.; Turner, S. R.; Voit, B. I. *Macromolecules* **1995**, 28, 3214.
[12] Schmaljohann, D.; Potschke, P.; Hassler R.; Voit B. I.; Froehling P. E.; Mostert B. *Macromolecules* **1999**, 32, 6333.
[13] Jang, J.; Oh, J.H.; Moon, S.I. *Macromolecules* **2000**, 33, 1864.
[14] Zuideveld, M.; Gottschalk, C.; Kropfinger, H.; Thomann, R.; Rusu, M.; Frey, H. *Polymer* **2006**, 47, 3740.
[15] Huber, T.; Potschke, P.; Pompe, G.; Häβler, R.; Voit, B.; Grutke, S.; Gruber, F. *Macromol. Mater. Eng.* **2000**, 280/281, 33.
[16] Monticelli, O.; Oliva, D.; Russo, S.; Clausnitzer, C.; Potschke, P.; Voit, B. *Macromol. Mater. Eng.* **2003**, 288, 318.
[17] Alfredo, M.; James, E.H.; Julianne, G. *Chem. Mater.* **2005**, 17, 1812.
[18] Ranglei, X.; Hewen, L.; Wenfang, S. *J. Poly. Sci. Part B: Polymer Physics,* **2006**, 44, 826
[19]; Bulakh, N.; Jog, J.P.; Nadkarni, V.M. *J. Macromol. Sci-Phys,* B32(3), **1993**, 275.

[20] Lopez, L. C.; Wilkes, G. L. *Polymer* **1989**, 30, 882.
[21] Monticelli, O.; Oliva, D.; Russo, S.; Clausnitzer, C.; Potschke, P.; Voit, B. *Macromol. Mater. Eng.* **2003**, 288, 318.
[22] Kancheng, M. *J. Appl. Polym. Sci.*, **2000**, 78, 1579.
[23] Kozlowski, W. *J. Polym. Sci. C* **1970**, 38, 47.
[24] Elder, M.; Wlochowicz, A. *Polymer* **1983**, 24, 1593.
[25] Day, M.; Suprunchuk, T.; Cooney, J. D.; Wiles, D. M. *J. Appl. Polym. Sci.* **1988**, 36, 1097.
[26] Kumar, S.; Anderson, D. P.; Adams, W. W. *Polymer* **1986**,27, 329.
[27] Cebe, P.; Hong, S. D. *Polymer* **1986**, 27, 1183.
[28] Gopakumar, T. G.; Ghadage, R. S.; Ponrathnam, S.; Rajan, C. R. *Polymer* **1997**,38,2209
[29] Kim, Y.H.; Webster, O.W. *Macromolecules* **1992**, 25,5561.
[30] Turner, S.R.; Walter, F.; Voit, B.I.; Mourey, T.H. *Macromolecules* **1994**, 27,1611.
[31] Feast, W.J.; Stainton, N.M. *J Mater Chem* **1995**, 5, 405.
[32] Uhrich, K.E; Hawker, C.J.; Fréchet, J.M. *Macromolecules* **1992**, 25, 4583.