Modification of Poly(propylene) by Grafted Polyester-Amide-Based Dendritic Nanostructures with the Aim of Improving Its Dyeability

Morteza Ganjaee Sari,[1] Siamak Moradian,[1] Saeed Bastani,[2] Norbert Stribeck[3]

[1]Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, P.O. 15875-4413, Tehran, Iran
[2]Department of Surface Coating and Corrosion, Institute for Color Science and Technology, P.O. 1668814811 Tehran, Iran
[3]Department of Chemistry, Institute of Technical and Macromolecular Chemistry, Hamburg University, Hamburg, Germany

ABSTRACT: Fiber-graded poly(propylene) was modified by polyester-amide-based dendritic nanostructures with the aim of improving its dyeability. Two different dendritic polymers were used and the dendritic nanostructures were formed *in situ* via reactive blending with maleic anhydride-modified poly(propylene). Samples were chosen exploiting a 4-component mixture design. Thermal, morphological, and rheological characterizations showed domains with different size and distribution were formed and primary properties of the dendritics determined the characteristics of the resulted domains. Morphological parameters were quantified by digital analysis of scanning electron microscope images. Thermal and rheological behavior also demonstrated good agreements with the inferred morphology of the formed dendritic domains. The modified samples were then dyed with dispersed dyestuffs. A variety of substantivities were obtained, and some of the modified samples showed a significant enhancement in dyeing properties. A predictive model was developed for K/S ratio, where K and S are absorption and scattering coefficients of the Kubelka-Munk one constant theory, respectively. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2449–2462, 2012

Key words: poly(propylene) PP; dendrimers; hyperbranched; dyes/pigments

INTRODUCTION

Poly(propylene) (PP) is a thermoplastic polymer that is widely used in different application fields regarding its outstanding and desirable physical, mechanical, and thermal properties.[1] Poly(propylene) possesses combination of some useful and advantageous properties such as relatively high stiffness, high melting point, high tensile strength, low density, relatively good resistance to impact, good rot resistance, easy processability, almost zero water adsorption, good antistatic character as well as wide availability, low cost, and excellent resistance to chemicals.[2–4] Despite all these desired properties and vast fields of applications, poly(propylene) fibers are almost always described as nontextile fibers because they cannot be dyed through an aqueous bath. Some intrinsic properties of poly(propylene) such as hydrophobicity, nonpolar structure, high crystallinity, and stereo regularity in its isotactic form (which is incidentally responsible for the good physical properties of the material) make poly(propylene) very hard to be dyed.[5] Possessing the shape of globular core-shell micelles that are covalently bonded to each other, enables dendritic polymers to have a stable structure and render them suitable species for dispersing molecules with differing nature in solutions or polymer blends.[6] They can be modified by grafting hydrophobic groups on their surfaces through which the micellar properties can be manipulated. On the other hand, as all dendritic polymers have a large number of functional groups either inside or on the surface further modifying reactions are possible.[7] Using dendritic polymers as hosts for dye molecules has been investigated by a few researches[3,8] and the obtained results demonstrated significant enhancement in dyeing properties of poly(propylene) although further investigation appears to be necessary on the effects of dendritic polymers on structural, morphological, rheological, etc., characteristics of dendritically blended poly(propylene). In this study, poly(propylene) was modified with the intention of improving its dyeability using dendritic polymers via an approach in which the surface modification and

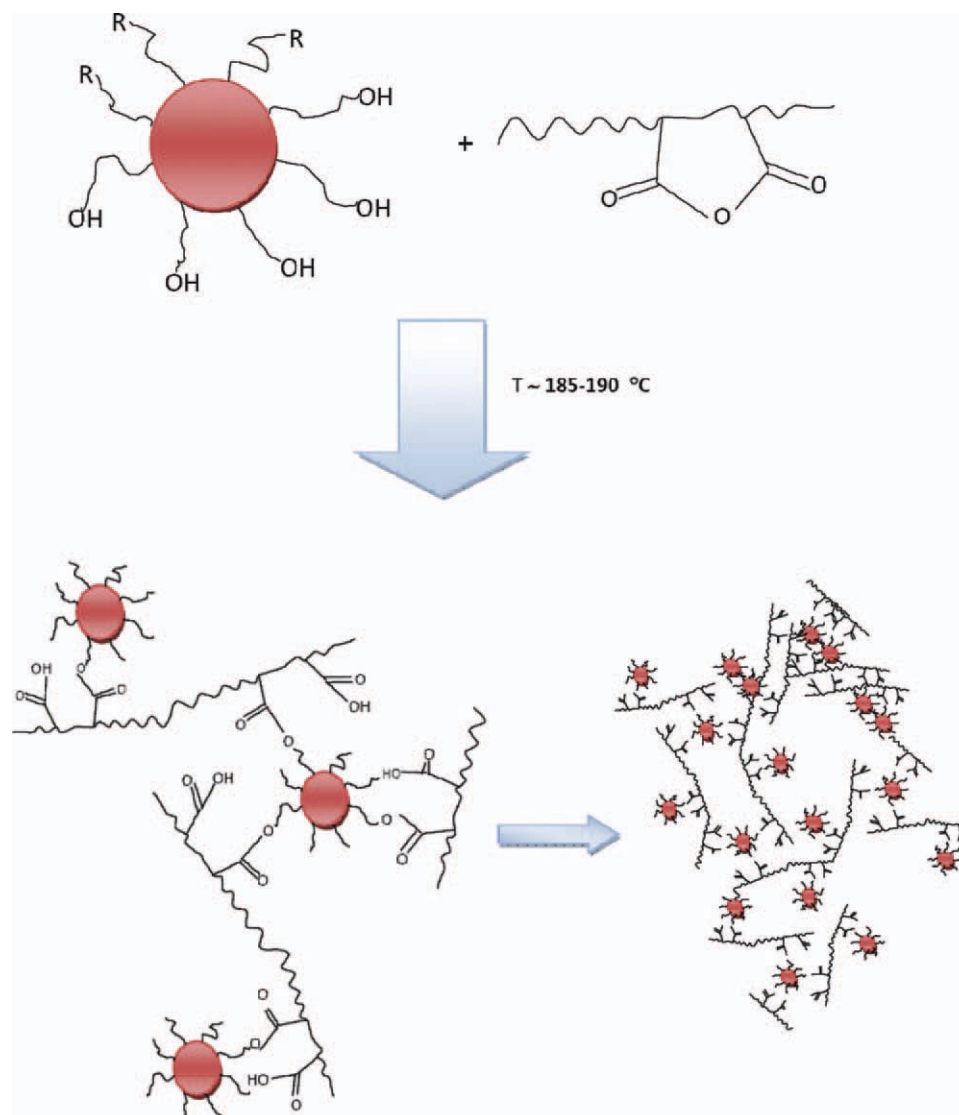*Correspondence to:* S. Moradian (moradian@aut.ac.ir).

Figure 1 Schematic reactions of hydroxyl end-groups of dendritic polymers with maleic anhydride groups on maleic anhydride modified poly(propylene) chains, R can be either hydrophobic groups (e.g., Stearate) or hydrophilic ones (e.g., OH). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grafting of dendritics onto the main matrix chains were performed simultaneously. In this approach, a simultaneous modification and *in situ* grafting of dendritic polymers on the main matrix, causes the hydrophilic hydroxyl groups of the dendritic polymers to be replaced by hydrophobic poly(propylene) chains by the aid of an intermediate reagent (i.e., maleic anhydride modified poly(propylene)) through which a more even distribution of guest domains is expected. These simultaneous modification and grafting are schematically demonstrated in Figure 1. The hydroxyl groups of the dendritic polymer have the ability of opening the anhydride groups on modified maleated poly(propylene) chains and are grafted on them.[9–12] The effects of these *in situ* formed cross-linked structures on thermal and morphological properties as well as rheological charac-

teristics were investigated preceding dyeability properties assessments. Moreover, to study the effect of hydrophobicity of dendritics and consequently their distribution in the matrix on the mentioned properties, two different kinds of dendritic polymer with differing surface properties were used. Third generation dendritics are recommended for enhancements of dye uptake of hydrophobic fibers. Amongst such a generation, dendritic polymers with partial polar structures (i.e., carbonyl and nitrogen group in the interior and hydroxyl groups on the periphery) in addition to availability as a mass produced product make them more appropriate as dyeabiliy-promoters. The possibility of replacing or reacting their periphery hydroxyl groups other more desirable groups or compounds is another advantageous property of these dendritics. These properties as
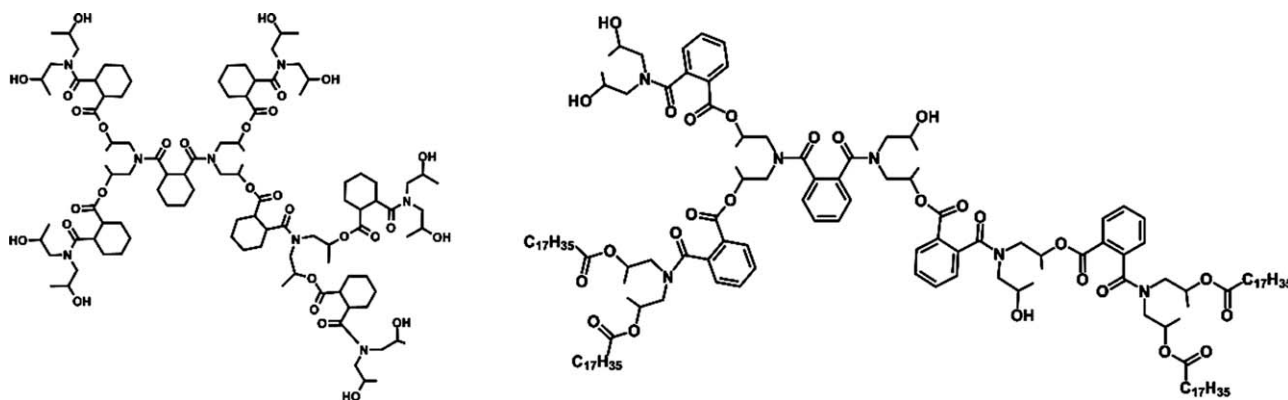
Figure 2 Schematic structures of PH (named H1500 in the DSM data sheet) (left) and PS (named PS2550 in the DSM data sheet) (right).

well as specific recommendations of the manufacturer for their use as dye uptake enhancers were the criteria for their selection. Disperse dyestuffs are the only class of nonionized polar structures designed for dyeing of hydrophobic polyester fibers from aqueous media. Such dyestuffs are generally smaller than most dyestuffs which is a prerequisite for diffusion of dyestuffs into matrices. Affinity (i.e., the thermodynamic equivalence of substantivity) to a modified partially polar polypropylene matrix, is through nonionic Van der Waals forces by a solid solution mechanism. Due to their small size, disperse dyestuffs tend not to aggregate which in turn leads to almost mono molecular absorption giving economically viable highly bright shades on such matrices. The use of disperse dyestuffs on polypropylene modified by dendritics polymers has the added advantage of being entrapped within domains or micellar structures containing dendritics polymers which will lead better fastnesses.

EXPERIMENTAL

Materials

Poly(propylene) granules used in this study, were purchased from Arak Petrochemical Company (APC) (Arak, Iran). This grade, under the trade name of V30S (designated as PP), was a fiber graded with good fluidity and is highly recommended for spinning applications. Two different kinds of dendritic polymers based on a polyester-amide, namely H1500 (designated as PH) having only hydrophilic hydroxyl end groups and PS2550 (designated as PS) having both hydrophobic stearate and hydrophilic hydroxyl end groups, were kindly supplied by DSM Hybrane Company (Geleen, Netherlands) and used. Figure 2 shows schematic structures of these two polymers. Maleic anhydride chemically modified poly(propylene) was obtained from DuPont Packaging and Industrial Polymers Company (Delaware, USA) under the

trade name of DuPont TM Fusabond® P MD353D (designated as PM). This chemically modified poly (propylene) has been categorized to "very high" maleic anhydride graft levels. The quantitative amount of grafting is not available in the company's data sheet but according to authors' preliminary measurements, the grafting percentage was determined as 1.5% which is in good agreement with the value 1.4% given in the U.S. Patent 7138454. Three different disperse dyestuffs (i.e., CI Disperse Blue 60, CI Disperse Yellow 211, and CI Disperse Red 324) were selected for the dyeing process. Other materials and additives used in washing, dyeing, and reduction clearing processes were all commercial brands.

Experimental design and samples' compositions

To obtain optimum proportions of different components (i.e., PP, PS, PH, and PM) an experimental mixture design was exploited. In this design, a four-component special cubic Scheffe model was used. The general polynomial function for this model is given in Eq. (1)[13–15]

$$E(Y) = \sum_{i=0}^{4} \beta_i X_i + \sum \sum_{i<j}^{4} \beta_{ij} X_i X_j$$
$$+ \sum \sum_{i<j<k} \sum_{}^{4} \beta_{ijk} X_i X_j X_k \quad (1)$$

where $E(Y)$ is the response of a specific property, βs are coefficients which determine the impacts of different components on a specific property, and Xs are the amounts of each components. The expanded model is shown in Eq. (2).

$$E(Y) = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2$$
$$+ \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4$$
$$+ \beta_{34} X_3 X_4 + \beta_{123} X_1 X_2 X_3 + \beta_{124} X_1 X_2 X_4$$
$$+ \beta_{134} X_1 X_3 X_4 + + \beta_{234} X_2 X_3 X_4 \quad (2)$$

TABLE I
Blends Compositions of the Simplex Lattice Special Cubic Scheffe Model

Blends compositions	X_1 (PP)	X_2 (PS)	X_3 (PH)	X_4 (PM)	Response
Sa1 = PP	100.00	0.00	0.00	0.00	Y_1
Sa2 = PP/PS (90 : 10)	90.00	10.00	0.00	0.00	Y_2
Sa3 = PP/PH (90 : 10)	90.00	0.00	10.00	0.00	Y_3
Sa4 = PP/PM (90 : 10)	90.00	0.00	0.00	10.00	Y_4
Sa5 = PP/PS (95 : 5)	95.00	5.00	0.00	0.00	Y_{12}
Sa6 = PP/PH (95 : 5)	95.00	0.00	5.00	0.00	Y_{13}
Sa7 = PP/PM (95 : 5)	95.00	0.00	0.00	5.00	Y_{14}
Sa8 = PP/PS/PH (90 : 5 : 5)	90.00	5.00	5.00	0.00	Y_{23}
Sa9 = PP/PS/PM (90 : 5 : 5)	90.00	5.00	0.00	5.00	Y_{24}
Sa10 = PP/PH/PM (90 : 5 : 5)	90.00	0.00	5.00	5.00	Y_{34}
Sa11 = PP/PS/PH (93.3 : 3.3 : 3.3)	93.33	3.33	3.33	0.00	Y_{123}
Sa12 = PP/PS/PM (93.3 : 3.3 : 3.3)	93.33	3.33	0.00	3.33	Y_{124}
Sa13 = PP/PH/PM (93.3 : 3.3 : 3.3)	93.33	0.00	3.33	3.33	Y_{134}
Sa14 = PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3)	90.00	3.33	3.33	3.33	Y_{234}
Sa15 = PP/PS/PH/PM (92.5 : 2.5 : 2.5 : 2.5)	92.50	2.50	2.50	2.50	Y_{1234}
Sa16 = PP/PS/PH/PM (96.25 : 1.25 : 1.25 : 1.25)	96.25	1.25	1.25	1.25	Y_{11234}
Sa17 = PP/PS/PH/PM (91.25 : 6.25 : 1.25 : 1.25)	91.25	6.25	1.25	1.25	Y_{12234}
Sa18 = PP/PS/PH/PM (91.25 : 1.25 : 6.25 : 1.25)	91.25	1.25	6.25	1.25	Y_{12334}
Sa19 = PP/PS/PH/PM (91.25 : 1.25 : 1.25 : 6.25)	91.25	1.25	1.25	6.25	Y_{12344}

In which:

$$\beta_1 = Y_1, \beta_2 = Y_2, \beta_3 = Y_3, \beta_4 = Y_4,$$

$$\beta_{12} = 4Y_{12} - 2(Y_1 + Y_2), \beta_{13} = 4Y_{13} - 2(Y_1 + Y_3),$$

$$\beta_{14} = 4Y_{14} - 2(Y_1 + Y_4), \beta_{23} = 4Y_{23} - 2(Y_2 + Y_3),$$

$$\beta_{24} = 4Y_{24} - 2(Y_2 + Y_4), \beta_{34} = 4Y_{34} - 2(Y_3 + Y_4),$$

$$\beta_{123} = 27Y_{123} - 12(Y_{12} + Y_{13} + Y_{23}) + 3(Y_1 + Y_2 + Y_3),$$

$$\beta_{124} = 27Y_{124} - 12(Y_{12} + Y_{14} + Y_{24}) + 3(Y_1 + Y_2 + Y_4),$$

$$\beta_{134} = 27Y_{134} - 12(Y_{13} + Y_{14} + Y_{34}) + 3(Y_1 + Y_3 + Y_4),$$

$$\beta_{234} = 27Y_{234} - 12(Y_{23} + Y_{24} + Y_{34}) + 3(Y_2 + Y_3 + Y_4).$$

The lower and upper bounds of each component used in this study (90 < PP < 100, 0 < PS < 10, 0 < PH < 10, 0 < PM < 10) satisfy $L_i \leq X_i \leq U_i$ condition so they are single-component constraints and since the following criterion has been met for the mentioned bounds, therefore, they are inconsistent constraints and accordingly a Simplex Lattice Design can be used.[13–15]

$$U_i + \sum_{j=1}^{4} L_j > \text{Total} \quad \text{or} \quad L_i + \sum_{j=1}^{4} U_j < \text{Total} \quad (3)$$

The compositions of the proposed experimental design are given in Table I and the imaginary space for such a design is a simulated tetrahedron. It must be noted that these compositions have been designed for 0.1 kg total blend. The first fourteen blends (i.e., Sa1 to Sa14) are necessary to develop the model equation and the last four blends (i.e., Sa15 to Sa19) are test points to examine the precision and accuracy of the model equation's predicted values of a certain property for various compositions of

the four components.[13–15] The whole experimental design process was performed by the aid of Minitab version 15 software.

Samples blending

To blend different compositions of the materials, a Brabender Plasticorder internal mixer model W50 equipped with a Banbury type rotor design, was used. Blending temperature was kept at 200°C, and the rotor speed was adjusted to 100 rpm. Blending was continued till the rotor torque reached a constant value plus an additional time of approximately 2 min for reassurance that the mixing process was complete. The overall duration of the mixing process was around 10 min. After discharging the material, they were broken into pieces using a breaker miller to make them ready for subsequent measurements and testing.

Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) measurements were performed using a DSC821 METTLER TOLEDO interfaced to a PC. A nitrogen flow was used to neutralize the environment. To remove the thermal history, samples underwent a heating and cooling process with a rate of 30°C/min and then a heating rate of 20°C/min was selected to heat the sample from 10°C to 200°C.

Morphology

To study the morphology of the samples a Philips XL30 scanning electron microscope (SEM technique) was used. A routine PVD process was applied to
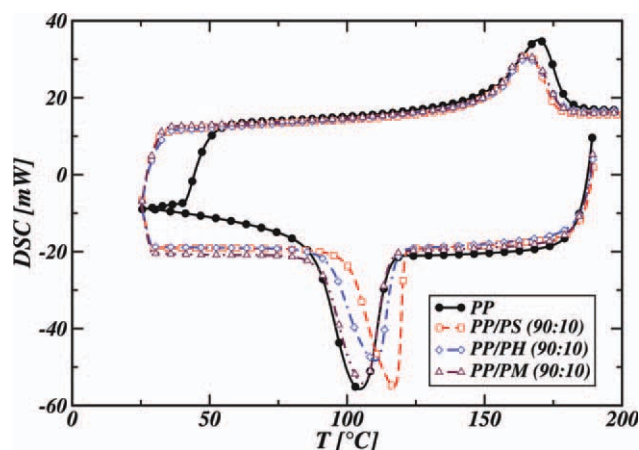
Figure 3 DSC thermographic diagrams of PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coat the samples with a thin layer of gold to make them conductive.

Rheology

Rheological behavior was performed on a MCR300 rheo-mechanical spectroscope equipped with an US200/32 accessory which provided a thermal chamber where the temperature could be precisely adjusted. The temperature was kept at 200°C which was the same as the mixing process temperature. Angular frequencies varied from 0.1 to 500 s^{-1}.

Dyeing properties

A dyeing process together with a consecutive reduction clear process was used on samples which were compressed to thin films with a thickness of ca. 100 µm. To produce these films, a laboratory compressing tool with a pressure of 100 bar at temperature of 200°C was used. A dye quantity of 1% o.w.f (i.e., on the weight of the blend) and a liquor-to-goods (L : G) ratio of 200 : 1 were selected to prepare the dyebath. To improve dye dispersion in the aqueous bath, 3% o.w.f of a commercial dispersing agent was added, and 3 % o.w.f of acetic acid was used to adjust pH in the acidic region of ca. 5. Before the dyeing process, to remove dirt and undesired materials from the surface of PP films, a pretreatment process using a nonionic detergent at 70°C, was performed for 20 min. Loosely attached dye molecules on the surface of the modified PP films were removed by a consecutive reduction clearing process using a nonionic detergent (2×10^{-6} kg/m^3), sodium hyposulfite (3×10^{-6} kg/m^3), and sodium hydroxide (2×10^{-6} kg/m^3). The process lasted for 20 min at a temperature of 70°C and liquid to good (L : G) ratio of 200 : 1. A Color Eye 9000 spectropho-

tometer was used to measure colorimetric parameters (i.e., reflectance data and color coordinates) in the wavelength range 360 to 780 nm. K/S coefficients obtained from the Kubelka-Munk one constant theory [Eq. (4)] were used as representative for dye absorption of the samples. To reduce errors, five measurements were carried out at different locations on each sample.

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S} \qquad (4)$$

where R is the measured reflectance at infinite thickness, K is the absorption coefficient, and S is the scattering coefficient of the Kubelka-Munk one constant theory.

RESULTS AND DISCUSSION

Degree of crystallization certainly has an impact on the mechanical properties that are matter of importance in fibers.[1] The first sample (i.e., PP) is pure poly(propylene) and the other samples either contain dendritic polymers (i.e., PP/PS (90 : 10) and PP/PH (90 : 10)) or maleic anhydride (i.e., PP/PM (90 : 10)) in their compositions. The respective thermographic diagrams for these four samples are illustrated in Figure 3. Degree of crystallinity was calculated on the basis that the heat of fusion for a fully crystalline poly(propylene) was 207.1×10^3 J/kg.[16–20] The unimodal melting peak shows that the related melting peaks for dendritic polymers and maleic modified PP are too small to be resolved by the DSC technique. In the literature,[21–23] different reasons for such a behavior are discussed, among which the amount of additives (being equal to or less than 10 weight percent) and the domain sizes (expected nanometric sizes) seem to be the most important ones. It can be seen from Table II that all three additives (i.e., the two dendritic polymers and maleic anhydride poly(propylene)) have a decreasing effect on

TABLE II
Melting and Crystallization Points, FWHM of the Melting Peaks and Crystallinity

Samples	T_m (°C)	T_c (°C)	FWHM (°C)	Crystallinity (%)
PP	169.46	104.487	26.35	50.62
PP/PS (90 : 10)	165.61	117.053	23.65	51
PP/PH (90 : 10)	165.3	110.325	23.65	46.42
PP/PM (90 : 10)	165.27	105.959	25.00	45.78
PP/PS (95 : 5)	169.75	108.5	27.02	49.61
PP/PH (95 : 5)	169.42	101.953	27.70	48.6
PP/PS/PM (90 : 5 : 5)	166.62	108.968	24.32	49.36
PP/PH/PM (90 : 5 : 5)	165.63	113.036	20.27	48.7

TABLE III
Measured and Calculated Heat of Fusion (H_f)

Samples	Calculated H_f (J/kg)	Measured H_f (J/kg)
PP[a]/PS[b] (95 : 5)	102.73×10^3	101.48×10^3
PP/PH[c] (95 : 5)	100.66×10^3	100.87×10^3
PP/PS/PM[d] (90 : 5 : 5)	102.22×10^3	98.55×10^3
PP/PH/PM (90 : 5 : 5)	100.85×10^3	97.95×10^3

[a] $H_f = 104.84 \times 10^3$ J/kg.
[b] $H_f = 37.63 \times 10^3$ J/kg.
[c] $H_f = 25.48 \times 10^3$ J/kg.
[d] $H_f = 46.32 \times 10^3$ J/kg.

the melting temperatures and the crystallite sizes (the latter was deduced from FWHM values of the melting peaks). Decreased melting points of the blends are due to the lower melting points of the additives compared to the neat poly(propylene). It is also evident from Table II that the more hydrophobic dendritic polymer (i.e., PS) has an insignificant effect on the degree of crystallinity; while the more hydrophilic dendritic polymer and the maleic anhydride modified poly(propylene) have clearly decreased the degree of crystallinity. In order to interpret such complex behaviors, the recrystallization temperature (i.e., T_c) of each sample must be considered. It is clear that T_c for PP/PS (90 : 10) is a little above 117°C which is 13°C higher than the T_c for the pure poly(propylene). This tends to suggest that this dendritic polymer is acting as a nucleating agent forming smaller sized crystallites which is estimated from its lower FWHM value as well as its constant degree of crystallinity. This behavior however, is not seen for PP/PH (90 : 10); despite the fact that increased T_c alongside of decreased crystallite size has occurred, as the overall crystallinity has also decreased. Looking through the properties of the dendritic polymers such as molecular structure, shape, hydrophobicity, molecular size, symmetry, etc., makes it evident that it is more likely PH would disorder and change the crystalline configuration of the poly(propylene) matrix because it shows a lower endothermic melting peak and consequently a lower heat energy per unit mass. Assuming the same heat of fusion for both dendritic states, then it is clear that the degree of crystallinity for PH is approximately 12% lower than that for PS, and this could be the reason for the overall decrease in the crystallinity of PP/PH (90 : 10). The same reasoning justifies the lower crystallinity of PP/PM (90 : 10). To study the effect of grafting of the dendritic polymers on crystallinity and thermal behavior of blends of poly(propylene), two pairs of samples (i.e., PP/PS (95 : 5) and PP/PS/PM (90 : 5 : 5) and PP/PH (95 : 5) and PP/PH/PM (90 : 5 : 5)) were selected. According to Table II, there is no significant change in the melting

points of PP, PP/PS (95 : 5) or PP/PH (95 : 5). The decrease for PP/PS/PM (90 : 5 : 5) and PP/PH/PM (90 : 5 : 5) compared with PP must be related to the addition of maleic anhydride modified poly(propylene). However, the changes in recrystallization temperature, crystallite size, and the degree of crystallinity are not the same as for blends containing only a single additive. This is attributed to interactions between dendritic polymers and maleic anhydride modified poly(propylene). Similar complicated behavior is observed for other pairs of samples. Respecting these outcomes, it can clearly be concluded that these two dendritic polymers behave quite differently within the main poly(propylene) matrix whether acting as an individual additive or as a coadditive alongside of maleic anhydride modified poly(propylene). This suggests that there appears to be no linear correlation between the used amounts of combined additives and the thermal properties of the resultant blends. To clarify the interaction between the dendritic polymers and that of maleic anhydride modified poly(propylene), the measured heat of fusion for the pure poly(propylene) and the additives (i.e., PP, PS, PH, and PM) were compared with their calculated equivalents (assuming a linear correlation to exist). Table III shows the measured and the calculated heat of fusion (i.e., H_f) for the two selected pairs of samples. It is seen from Table III that as PP/PS (95 : 5) and PP/PH (95 : 5) contain no coupling agent, the linearly calculated heats of fusion are almost the same as the measured ones. However, on addition of the coupling agent (i.e., maleic anhydride modified poly(propylene) as in PP/PS/PM (90 : 5 : 5) and PP/PH/PM (90 : 5 : 5)), the linearly calculated heat of fusion deviates from their corresponding measured values. This indeed could be taken as an acceptable argument for the existence of interactions between the dendritic polymers' end groups and the maleic anhydride rings schematically shown in the introduction section. In fact, the decrease in heats of fusion for the latter two samples can be attributed to diffusion of dendritic domains into the crystalline regions and by so doing inhibit crystal growth.[21]

Figure 4 shows the SEM micrographic images of PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10), where there were no possibility of a reaction with the maleic anhydride groups. PP is pure poly(propylene) without any additives. As is seen, the SEM images show no phase separation for this sample; however, phase separation for PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10) can clearly be distinguished. To make the images comparable, an image analysis process was performed using an appropriate computer software (Digimizer version 3.4.1.0). Table IV shows the results of this analysis through which domains' sizes and
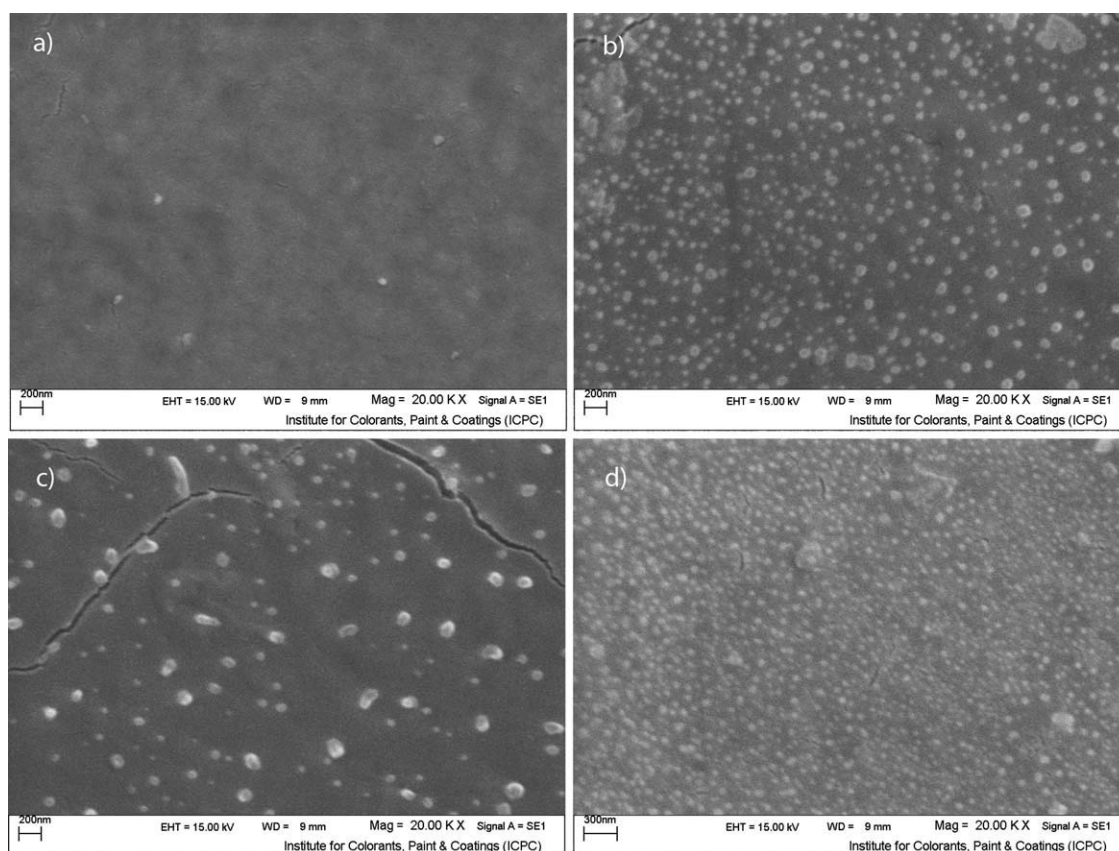
Figure 4 Scanning electron micrographs of PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10) (a to d respectively).

distributions (i.e., dendritic states) can be more easily investigated. The mean diameter of dendritic domains for PP/PS (90 : 10) and PP/PH (90 : 10) are ca. 42.1 nm and 51.1 nm, respectively. Standard deviation for PP/PS (90 : 10) is 10.4 nm, whereas it is 15.7 nm for PP/PH (90 : 10). Considering the structures of PS and PH, one can interpret as to why the domain size of PP/PH (90 : 10) is larger and also why it is less evenly distributed. Poly(propylene) matrix is intrinsically hydrophobic with a hydrocarbon backbone which possesses no polar or chemically active groups. However PH is a polyester amide hyperbranched with hydrophilic OH end-groups that makes it wholly different in nature compared to PP. Such dissimilarity can function as a driving force for making the hydrophilic hyperbranched polymer chains to aggregate and form larger domains in the main matrix. However, PS possesses hydrophobic stearic groups in its periphery which are more compatible in nature with PP and therefore smaller and more evenly distributed domains can be obtained during blending. PP/PM (90 : 10) contains PM (i.e., maleic anhydride modified poly(propylene)), whose backbone structure is almost similar to the main poly(propylene) matrix. One would expect smaller sized domains and more evenly distributed in the matrix. These expectations are clearly reflected, with

good agreements in Table IV (i.e., 34.6 nm mean diameter and 7.1 nm standard deviation). To study the effect of interactions of anhydride rings with hydroxyl end-group of dendritic polymers on domain size and distribution, three pairs of samples (i.e., PP/PS (95 : 5) and PP/PS/PM (90 : 5 : 5), PP/

TABLE IV
Image Analysis Results for PP, PP/PS (90 : 10), PP/PH (90 : 10), PP/PM (90 : 10), PP/PS (95 : 5) and PP/PS/PM (90 : 5 : 5), PP/PH (95 : 5) and PP/PH/PM (90 : 5 : 5) and PP/PS/PH (93.3 : 3.3 : 3.3) and PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3)

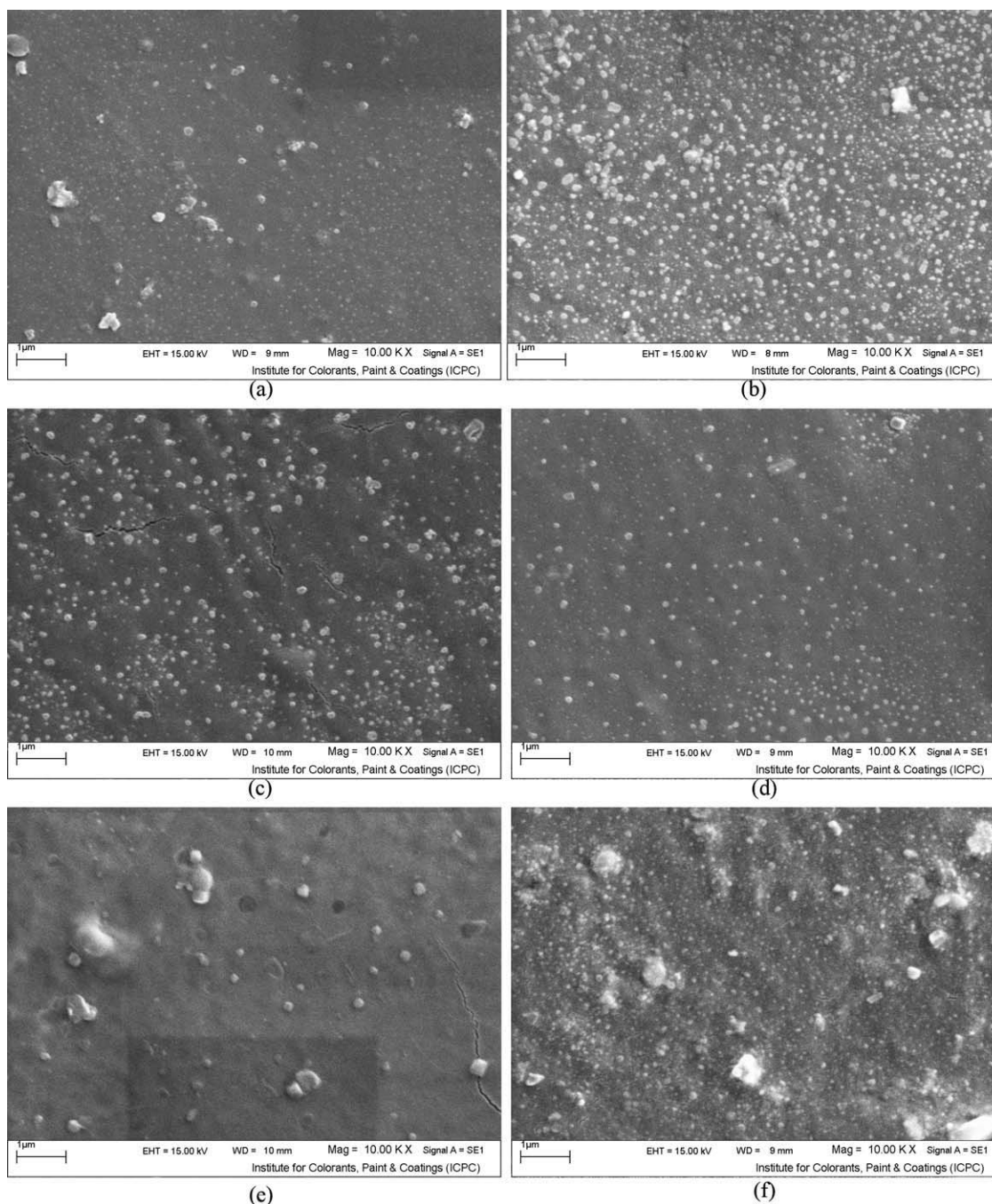| Sample	Mean particle diameters (nm)	Standard deviation (nm)	SD/Mean
PP	–	–	–
PP/PS (90 : 10)	42.1	10.4	0.25
PP/PH (90 : 10)	51.1	15.7	0.31
PP/PM (90 : 10)	34.6	7.1	0.21
PP/PS (95 : 5)	97.2	11.7	0.31
PP/PS/PM (90 : 5 : 5)	65.3	15.4	0.33
PP/PH (95 : 5)	62.8	32.1	0.26
PP/PH/PM (90 : 5 : 5)	40.3	11.7	0.44
PP/PS/PH (93.3 : 3.3 : 3.3)	112.6	58.3	0.52
PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3)	47.6	13.4	0.28

Figure 5 SEM images for PP/PS (95 : 5) and PP/PS/PM (90 : 5 : 5), PP/PH (95 : 5) and PP/PH/PM (90 : 5 : 5) and PP/PS/PH (93.3 : 3.3 : 3.3) and PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3) a to f respectively.

PH (95 : 5) and PP/PH/PM (90 : 5 : 5) and PP/PS/PH (93.3 : 3.3 : 3.3) and PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3)) were chosen. Figure 5 shows the SEM images of these three pairs in which the domain size and distribution can easily be compared. As it is clear, the dendritic domains in PP/PS (95 : 5), PP/PH (95 : 5) and PP/PS/PH (93.3 : 3.3 : 3.3) are aggregated, and their sizes are relatively large which indicate inappropriate distribution of dendritic domains. This aggregation was expected to take place in the absence of reaction between the anhydride rings and

OH groups as no grafting takes place. In other words, the aggregation of polar dendritic polymers with hydrophilic end groups within a hydrophobic poly(propylene) is rationally expected. According to Table IV, the mean domain size for PP/PS (95 : 5), PP/PH (95 : 5), and PP/PS/PH (93.3 : 3.3 : 3.3) are 97.2 nm, 62.8 nm, and 112.6 nm, respectively, and the respective values for the corresponding maleic containing samples (i.e., PP/PS/PM (90 : 5 : 5), PP/PH/PM (90 : 5 : 5), and PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3)) are 65.3 nm, 40.3 nm, and 47.6 nm showing
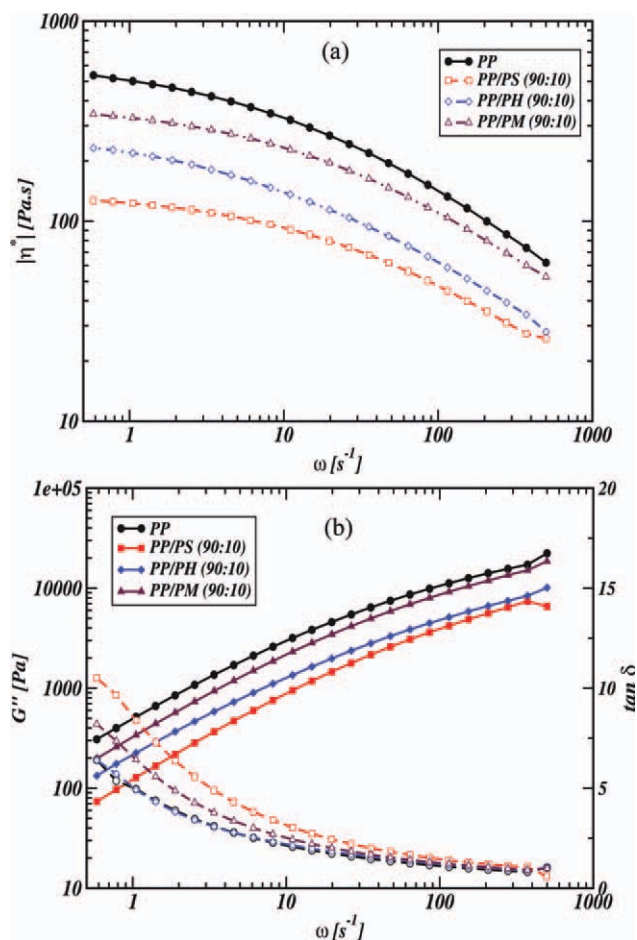
Figure 6 Complex viscosity (a) loss modulus and damping factor (b) for PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

smaller sized domains for the latter. This can be attributed to grafting of dendritic polymers onto the poly(propylene) chains of PM which would change their hydrophilic surface into a hydrophobic one thus enabling them to disperse more evenly in the main hydrophobic poly(propylene) matrix. The DSC results also showed lower degrees of crystallinity which was also attributed to the maleic interaction with dendritic end groups which enables them more easily to penetrate into the crystalline regions and hence disorganize the crystal growth in poly(propylene). It is clear here that at least the expected reduction in domain size and amelioration of domain distribution has occurred and such findings are in good agreement with the DSC results. Complementary investigation by the use of WAXS and SAXS measurements are currently being undertaken by the authors to elucidate the nano-structural changes of various samples.

Rheological behavior becomes a matter of importance when one studies extruding and spinning processes. Energy consumption of these processes greatly depends on properties such as viscosity which can easily be assessed by rheological studies. Rheological flow behavior is one of the most important characteristic of the macroscopic properties of fluids. In principle, it depends on (a) the molecular features, such as size, shape, density and flexibility and (b) the specific nature of the intermolecular interactions.[24] Additionally, a structural study of dendritic-grafted poly(propylene) as nano dispersions can also be performed by rheological experiments.[25] Such experiments were performed in dynamic (frequency sweep) mode in which the frequency of fixed deformation differ within a specific span. An important first step in performing dynamic rheological characterization is to determine the linear viscoelastic region of materials in which dynamic rheological parameters are independent of the applied strains.[26] Primary examinations showed that all samples demonstrate linear viscoelastic behavior in strain percents between 0.1% and 30%, therefore, to keep the substances in their linear viscoelastic region, the strain was kept at 10% where no nonlinear behaviors would be encountered. To determine the effect of each component (i.e., PS, PH, and PM) on the rheological properties, the first four samples were taken into consideration. Figure 6 illustrates complex viscosity, loss modulus and damping factor versus frequency of deformation for PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10). As is clear, adding 10 wt % of PS and PH as dendritic polymers to the linear poly(propylene) noticeably decreases the overall complex viscosity across the whole range of deformation frequencies compared with the bare poly(propylene). Such behavior of dendritic states (i.e., high decreasing effect on melt viscosity) has been investigated somehow extensively in various studies.[6,24–36] Earlier suggestions in this field declared that these polymers can act as "molecular ball-bearings" which lubricate the flow.[29] Others showed that such additives might be able to interrupt the local entanglement network of the matrix in which they were blended.[27] It has also been clarified that in general, smaller dendritic polymers (i.e., earlier generations) have greater impacts on reducing melt viscosity of their respective blends.[28] The neat dendritic polymers demonstrated that they themselves do not form any interconnected entanglements with each other and therefore they can probably produce free volumes in a linear polymer melt which make it easier for polymer chains to move about, hence reducing the viscosity.[29] The PP/PM (90 : 10) sample in which 10% of maleic anhydride modified poly(propylene) was added to the poly(propylene) matrix also showed decreased complex viscosity which is quite expected from the very high melt flow index of this material and the mixture rules of binary blends. It should be taken into
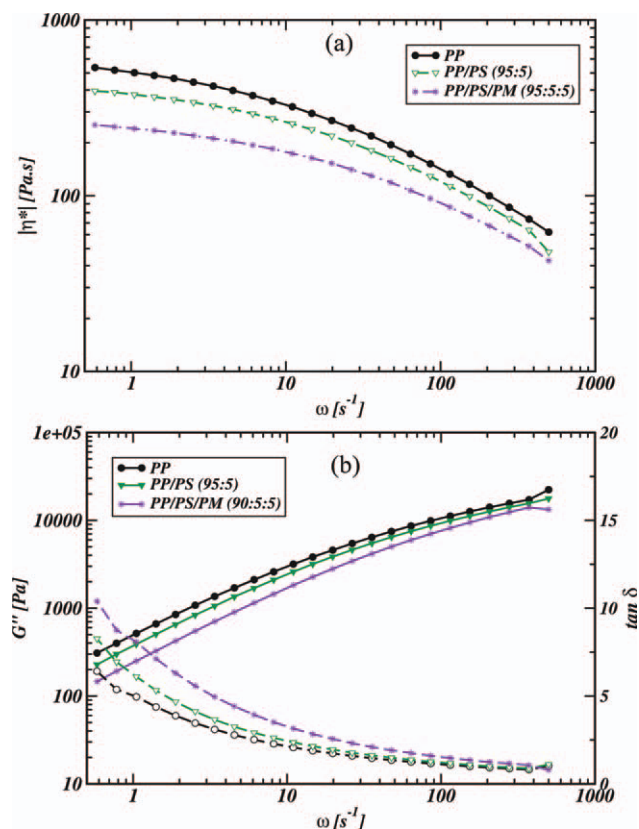
Figure 7 Complex viscosity (a) loss modulus and damping factor (b) for PP, PP/PS (95 : 5), and PP/PS/PM (90 : 5 : 5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

consideration that although this polymer has a smaller molecular weight compared neat poly(propylene) but it is still a linear polymer and acts quite differently from a dendritic one. So as can be seen from Figure 6(a), the viscosity has declined in PP/PM (90 : 10) but to a much lesser extent than the other two samples. Another important point disclosed in the viscosity diagrams is that identical amounts of the two mentioned dendritic polymers have different impacts on decreasing viscosity. PS which is the more hydrophobic of the two (calculated HLB is ca. 33.15) and has a molecular weight of 2500 decreases viscosity nearly an order of magnitude whilst PH with more hydrophilic properties (calculated HLB is ca. 72.95) and smaller molecular weight (1500) reduces viscosity to much lesser extent. This can be rationalized, as mentioned before, in terms of similarity in hydrophobic nature of PS and the main matrix which induces smaller aggregation and better distribution of dendritic domains. These findings were also confirmed by thermal and morphological studies. This suggests that larger proportions of PS can organize themselves along the main matrix and affect complex viscosity more than PH which is more hydrophilic

which consequently would form larger domains with broader distributions. The more liquid-like behavior of PP/PS (90 : 10) can be obtained from its loss modulus and damping factor diagrams of Figure 6(b). The ordonnance of loss modulus for these samples are PP > PP/PM (90 : 10) > PP/PH (90 : 10) > PP/PS (90 : 10). As is expected, samples with higher viscosities show larger moduli while the damping factor of PP/PS (90 : 10) has dominance almost over the entire range of angular frequencies. This can be an evidence for the fact that the dendritic domains with smaller sizes have a better distribution in the main matrix and ease the movement of poly(propylene) chains on each other which means more energy dissipation during deformation and smaller elastic energy to be stored. These deductions are in good agreement with the results from the thermal and the morphological studies. To study the effect of adding a coupling agent and the consequence of grafting dendritic polymers on their rheological behavior, as the aforesaid pairs were selected. Figure 7(a,b) show complex viscosity, loss modulus, and damping factor for PP, PP/PS (95 : 5), and PP/PS/PM (90 : 5 : 5). The latter has a minimum value for viscosity and a maximum value for damping factor. This reduction in viscosity values can be either attributed to the formation of crosslinked spherically shaped dendritic domains which was schematically demonstrated in Figure 1 or to the addition of 5% of PM. At lower frequencies the reduction in viscosity for PP/PS/PM (90 : 5 : 5) and PP/PS (95 : 5) compared with PP is about 53% and 27%, respectively, while the reduction in viscosity for PP/PM (95 : 5) (the diagram has not been given) which has only 5% of PM is only 13% which is smaller than the difference between the reduced viscosities of PP/PS/PM (90 : 5 : 5) and PP/PS (95 : 5). This suggests, as explained previously, that the formation of the mentioned domains is responsible for the decreased viscosity values and are good evidence that the expected crosslinked nano-structured domains have been formed via grafting and are distributed more evenly in the main poly(propylene) matrix. Anyhow such decreases in melt viscosity values are favorable as it lowers energy consumption during processing (i.e., in extruding or spinning). As mentioned before, the larger values of damping factor across the whole frequency span is an eloquence of a more liquid-like behavior which can be attributed to well-formed smaller shaped, uniformly distributed dendritic domains which ease the movement of long chains that in turn increase the proportion of dissipated energy during deformation. As morphological studies have indicated that the dendritic domains in PP/PS/PM (90 : 5 : 5) are smaller in size and have better distributions, then the rheological findings are in
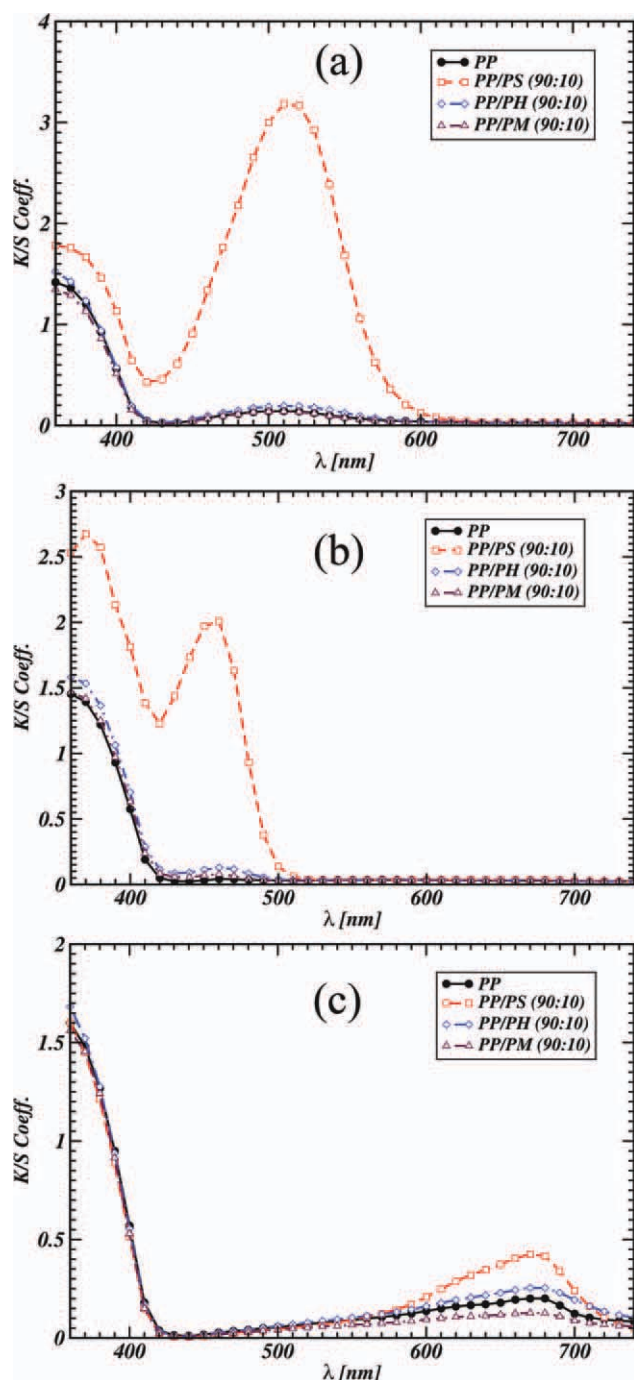
Figure 8 *K/S* coefficients for red- (a), yellow- (b), and blue- (c) dyed samples PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM (90 : 10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good agreement with the results from the morphological studies.

As mentioned previously, the main objective of reactive modification of poly(propylene) using dendritic polymers was to improve the dyeability of the resultant blend with the disperse dyestuffs. Figure 8 shows *K/S* coefficient versus wavelength for samples PP, PP/PS (90 : 10), PP/PH (90 : 10), and PP/PM

(90 : 10) dyed with red-, yellow-, and blue dyes. Wavelengths at which maximum absorption (i.e., λ_{max}) for red-, yellow-, and blue-dyed samples occurred at 510, 460, and 670 nm, respectively. It can be seen that PP shows almost no absorption peak and very small coefficients which of course was expected due to the absence of suitable reactive sites to provide enough affinity as a driving force to make dye molecules transfer through the aqueous bath into the hydrophobic matrix. There is also no considerable improvement in dye absorption for PP/PH (90 : 10) and PP/PM (90 : 10) compared with PP as the K/S coefficients are too small which are indicative of very low dye uptake. However, PP/PS (90 : 10) shows a significant increase in absorption especially for the red- and the yellow-dyed samples. In other words, these results underline the fact that PS has acted as an effective dyeability promoter while PH and PM could not significantly improve this property. In the case of PP/PM (90 : 10), maleic anhydride groups, as the only relatively reactive groups existing in the composition, do not provide sufficient affinity for dye molecules to be adsorbed on the surface of PP films. From the view point of crystallinity according to DSC results, PP/PM (90 : 10) has a lower degree of crystallinity which makes it more susceptible to be diffused by dye molecules although does not necessarily guarantee the adsorbance of dye molecules. The same behavior can be seen in PP/PH (90 : 10). Scrutinizing the molecular structure of PH and its HLB value, it is clearly more hydrophilic compared to PS which appears to be more capable of increasing surface energy and interacting with the polar disperse dye molecules. To rationalize poor dyeing behavior of this sample, authors are working on nanostructural parameters and dynamic mechanical properties and the
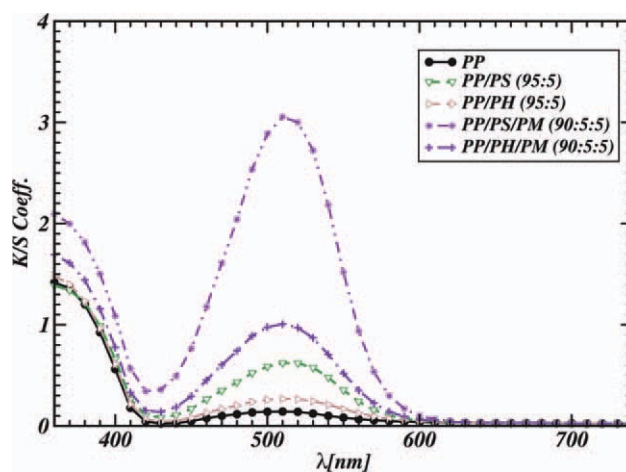

Figure 9 *K/S* coefficients for red-dyed PP, PP/PS (95 : 5), and PP/PS/PM (90 : 5 : 5) and PP/PH (95 : 5) and PP/PH/ PM (90 : 5 : 5) Samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
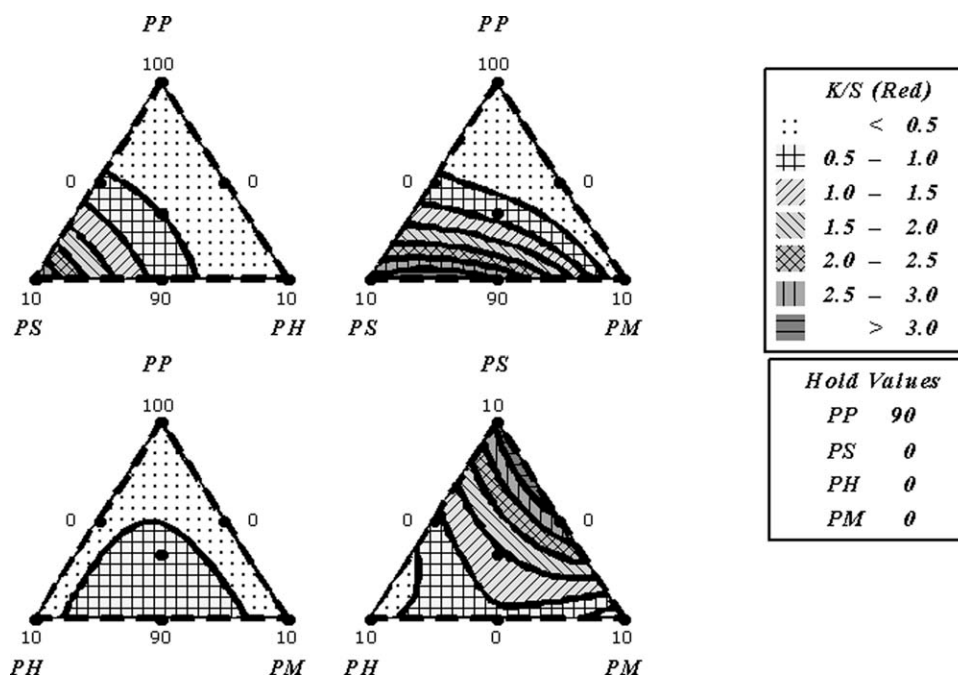
Figure 10 Contour plots of the developed predictive equation of K/S coefficients for the red-dyed samples.

influence of dendritic states on changing the glass transition temperature which may be responsible for the disability of PH to ameliorate dyeability of poly (propylene) blends. Preliminary studies show that PH is unable to decrease the glass transition temperature, while PS lowers it by as much as ca. 10°C. These studies also point to the fact that PH is capable of changing the crystallites' orientation to a lesser extent compared with PS. This behavior certainly affects the diffusion of dye molecules within the modified PP matrix. Thus, the higher dye uptake in the PS blends may be attributed to the ease of diffusion of dye molecules into the disoriented crystallites.[37] However, additional analyses such as SAXS, kinetic and thermodynamic studies which incidentally are being investigated by the authors currently, will be required to be able to confirm unequivocally the exact morphological state of such blends at nano-scale. Moreover, according to morphological assessments, better distribution of PS in PP matrix provides higher specific area for dye molecules to interact with functional groups. To study the impact of using maleic coupling agent and grafting reaction on dyeability, three pairs of samples (i.e., PP/PS (95 : 5) and PP/PS/PM (90 : 5 : 5), PP/PH (95 : 5) and PP/PH/PM (90 : 5 : 5) and PP/PS/PH (93.3 : 3.3 : 3.3) and PP/PS/PH/PM (90 : 3.3 : 3.3 : 3.3)) were selected. Figure 9 demonstrates K/S coefficient curves versus wavelength for the red-dyed first and second pairs of samples as well as for PP. Comparing PP/PS/PM (90 : 5 : 5) and PP/PS (95 : 5), clearly illustrates that the former has a higher value of K/S

coefficient which means a higher uptake of dye molecules has occurred. K/S coefficients for PP/PS/PM (90 : 5 : 5) are nearly as much as those for PP/PS (90 : 10) which contains twice as much PS in its composition. As was shown, PM does not in itself have a positive influence on enhancing the K/S coefficients, this is in fact an indication that the use of maleic modified poly(propylene) as a coupling agent for grafting dendritic polymers onto the poly(propylene), has a significant synergistic effect on promoting the dye-ability of the modified poly (propylene). Such improvement can be attributed to the expected three dimensional nanometric structures of dendritic domains explained before which establish desirable area and spaces for dye molecules. In addition as was seen in PP/PS (90 : 10), the more even distribution of dendritic domains, the higher K/S coefficient values will obtain and according to SEM images samples with better distribution show higher dyeability. These findings to a large extent certify the DSC and morphological studies. It is clear that the same trend is repeated for PP/PH/PM (90 : 5 : 5) compared with PP/PH (95 : 5) although the relative values of the K/S coefficients are considerably smaller than those for PP/ PS/PM (90 : 5 : 5). Such behavior is an eloquence of a considerably positive effect of the mentioned grafting reactions. PP/PS/PM (90 : 5 : 5) shows an increase of 387% (red-dyed), 237% (yellow-dyed), and 63% (blue-dyed) in K/S coefficient compared with PP/PS (95 : 5). This trend can also be seen in the other selected pairs and confirms the
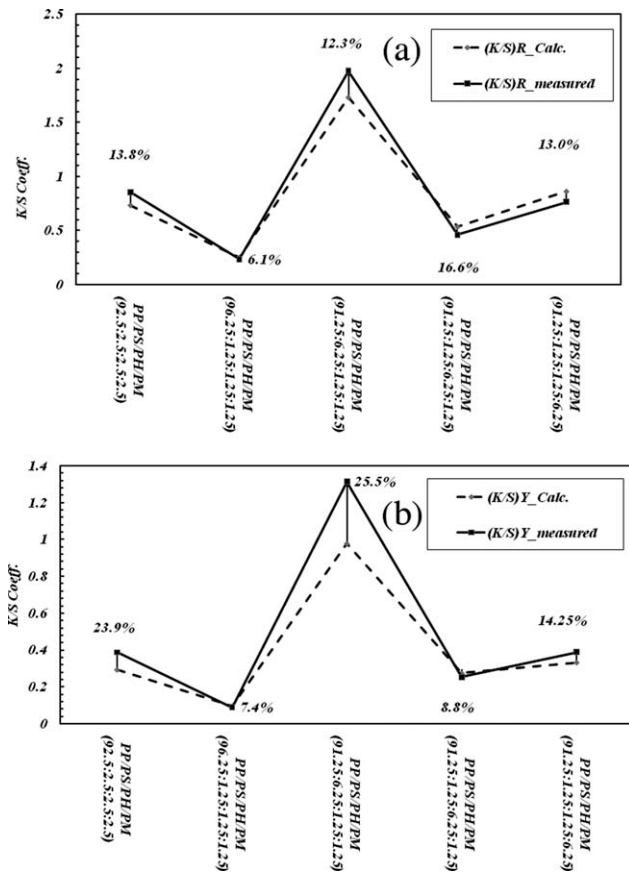
Figure 11 K/S coefficients (measured and calculated) for the test samples and the relative errors involved in the developed predictive equations for red- (a) and yellow- (b) dyed samples.

aforementioned findings. To quantify the effect of each component (i.e., PS, PH, and PM) and their synergistic or antagonistic effects on enhanced dye-ability, the maxima in K/S coefficients as a response and the amounts of components as independent variables were used to develop a predictive equation. As mentioned previously, special cubic Scheffe model was used and the last five samples were used as test points to determine the corresponding errors. Such predictive equations are as follows:

$$
\begin{aligned}
E(K/S)_{Red} =\ & 0.00176802\beta_1 + 3.91334\beta_2 - 0.50653\beta_3 \\
& - 0.212784\beta_4 - 0.040221\beta_{12} - 0.00565535\beta_{13} \\
& + 0.00220206\beta_{14} - 0.243416\beta_{23} + 1.22991\beta_{24} \\
& - 0.0591488\beta_{34} + 0.00235061\beta_{123} - 0.0130348\beta_{124} \\
& + 0.001044\beta_{134} - 0.00945468\beta_{234}
\end{aligned} \tag{5}
$$

$$
\begin{aligned}
E(K/S)_{Yellow} =\ & 0.000602924\beta_1 + 2.02237\beta_2 - 0.556663\beta_3 \\
& - 0.0758445\beta_4 - 0.0204552\beta_{12} - 0.00625303\beta_{13} \\
& + 0.000821037\beta_{14} - 0.278198\beta_{23} + 1.08027\beta_{24} \\
& + 0.255993\beta_{34} + 0.00291818\beta_{123} - 0.0117355\beta_{124} \\
& - 0.00269357\beta_{134} - 0.00639434\beta_{234}
\end{aligned} \tag{6}
$$

$$
\begin{aligned}
E(K/S)_{Blue} =\ & 0.0017923\beta_1 + 0.28663\beta_2 - 0.0859551\beta_3 \\
& + 0.293896\beta_4 + 0.00126595\beta_{12} - 0.00311273\beta_{13} \\
& - 0.00331299\beta_{14} - 0.0841469\beta_{23} + 0.133235\beta_{24} \\
& + 0.0877029\beta_{34} + 0.000955575\beta_{123} - 0.00135822\beta_{124} \\
& - 9.14 \times 10^{-4}\beta_{134} - 0.00546242\beta_{234}
\end{aligned} \tag{7}
$$

where

$$
\beta_1 = PP,\ \beta_2 = PS,\ \beta_3 = PH,\ \beta_4 = PM
$$
$$
\beta_{12} = PP \times PS,\ \beta_{13} = PP \times PH,\ \beta_{14} = PP \times PM,
$$
$$
\beta_{23} = PS \times PH,\ \beta_{24} = PS \times PM,\ \beta_{34} = PH \times PM,
$$
$$
\beta_{123} = PP \times PS \times PH,\ \beta_{124} = PP \times PS \times PM,
$$
$$
\beta_{134} = PP \times PH \times PM,\ \beta_{234} = PS \times PH \times PM
$$

The contour plots of the developed equation for the red-dyed samples are illustrated in Figure 10. It can be seen from (a) that PS has the largest impact on increasing the K/S coefficients and from (b), (c), and (d) it is obvious that adding maleic modified poly(propylene) as a coupling agent, has a synergistic effect both with PS and PH. Figure 11 gives K/S coefficients (measured and calculated) of test samples and related errors of the developed equations for red- (a) and yellow- (b) dyed samples. As can be seen, the maximum errors for red and yellow equations are 16.6% and 25.5%, respectively. Such errors are quite significant and are originating from errors involved in sample preparation, the dyeing process, measuring defects, etc. Nevertheless, the calculated values from the predictive equations are approximately similar to the corresponding experimental measurements which could be considered as an eloquence of the fact that the impact factors of components on enhanced dye-ability either as a single individual additive or in combination with other additives (whether synergistic or antagonistic) are almost accurate. Therefore, one can easily foresee the dyeing behavior of a certain blend, only by considering the amount of each component in that blend.

CONCLUSIONS

The dendritic nano-structured modified poly(propylene) samples were produced via reactive blending of two different dendritic polymers, a maleic anhydride modified poly(propylene) as a coupling agent and fiber grade poly(propylene). The simultaneous surface treatment and grafting of dendritics were expected to give desirable characteristics for the subsequent dyeing process. DSC measurements showed that various dendritic states have different impacts on degree of crystallinity, crystallization temperature and crystallite size which are attributed to their

structures and chemical properties and also to the expected grafting reactions. These findings were followed and confirmed by morphological studies in which domain sizes and their dispersion were determined quantitatively. SEM images demonstrated that smaller sized and much more evenly distributed dendritic domains are obtained when maleic anhydride modified poly(propylene) were used as a coupling agent. A reduction in melt viscosity was observed for both grafted and non-grafted samples which were attributed to the unique behavior of dendritic polymers compared with conventional linear macromolecular entities. This behavior was considered to be attractive since the lowering of melt viscosity would automatically mean less consumption of energy in addition to elimination of processing defects in the subsequent spinning processes. Finally the dyeing properties of the blends were examined by a disperse dyeing process. The modified blends showed a significant increase in dye uptakes compared with their unmodified counterparts. The developed predictive equations for the K/S coefficients gave a harmonized behavior compared with the experimental data. Although the errors were quite meaningful but errors in sample preparation, dyeing processes and the predictive model are expected to be large, anyway.

References

1. Xu, G.; Shi, W.; Hu, P.; Mo, S. Eur Polym J 2005, 41, 1828.
2. Karian, H. G. Handbook of Polypropylene and Polypropylene Composites, 2nd Ed.; Marcel Dekker Inc.: Michigan, 2003.
3. Burkinshaw, S. M.; Froehling, P. E.; Mignanelli, M. Dyes Pigm 2002, 53, 229.
4. Tao, G.; Gong, A.; Lu, J.; Sue, H. J.; Bergbreiter, D. E. Macromolecules 2001, 34, 7672.
5. Ujhelyiova, A.; Bolhova, E.; Oravkinova, J.; Tino, R.; Marcincin, A. Dyes Pigm 2007, 72, 212.
6. Frechet, J. M. J.; Tomalia, D. A. Dendrimers and Other Dendritic Polymers; Wiley: West Sussex, 2001.
7. Schmaljohann, D.; Poltschke, P.; Hässler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A. Macromolecules 1999, 32, 6333.
8. Burkinshaw, S. M.; Mignanelli, M.; Froehling, P. E.; Bide, M. J. Dyes Pigm 2000, 47, 259.
9. Bhardwaj, R.; Mohanty, A. K. Biomacromolecules 2007, 8, 2476.
10. Diao, J. Z.; Yang, H. F.; Zhang, J. M.; Song, X. H. Iran Polym J 2007, 16, 97.
11. Orr, C. A.; Cernohous, J. J.; Guegan, P.; Hirao, A.; Jeon, H. K.; Macosko, C. W. Polymer 2001, 42, 8171.
12. Liu, N. C.; Baker, W. E. Adv Polym Technol 1992, 11, 249.
13. Wendell, F. S. Experimental Design for Formulation. ASA-SIAM Series on Statistics and Applied Probability; ASA-SIAM: Philadelphia, 2005.
14. Lazic, Z. R. Design of Experiments in Chemical Engineering; Wiley-VCH Verlag GmbH and Co. KGaA: Weinheim, 2004.
15. Hinkelmann, K.; Kempthorne, O. Design and Analysis of Experiments, Vol. 1; Wiley: New Jersey, 2008.
16. Wilkikson, R. W.; Dole, M. J. Polym Sci 1962, 58, 1089.
17. Kirshenbaum, I.; Wilchinsky, W.; Groten, B. J Appl Polym Sci 1964, 8, 2723.
18. Krigbaum, W. R.; Uematsu, I. J Polym Sci Polym Chem 1965, 3, 767.
19. Albertsson, A. C. Long-Term Properties of Polyolefins; Springer-Verlag: Berlin, 2004.
20. Karger-Kocsis, J. Polypropylene: An A-Z Reference; Kluwer Academic Publishers: London, 1999.
21. Rim, P.B.; Runt, J. P. Macromolecules 1983, 16, 762.
22. Nishil, T.; Wang, T. T. Macromolecules 1975, 8, 909.
23. Runt, J.; Rim, R. B.; Howe, S. E. Polym Bull 1984, 11, 517.
24. Uppuluri, S.; Keinath, S. E.; Tomalia, D. A.; Dvornic, P. R. Macromolecules 1998, 31, 4498.
25. Corcione, C. E.; Frigione, M. Polym Test 2009, 28, 830.
26. Mackay, M. E.; Dao, T. T.; Tuteja, A.; Ho, D. L.; Van Horn, B.; Kim, H.; Hawker, C. J. Nature Mater 2003, 2, 762.
27. Bodnar, I.; Silva, A. S.; Kim, Y. H.; Wagner, N. J. J Polym Sci Polym Phys 2000, 38, 874.
28. Hong, Y.; Cooper-White, J. J.; Mackay, M. E. J Rheol 1999, 43, 781.
29. Hawker, C. J.; Farrington, P. J.; Mackay, M. E.; Wooley, K. L.; Frechet, J. M. J. J Am Chem Soc 1995, 117, 4409.
30. Andrady, A. L.; Nunez, C. M.; Chiou, B. S.; Khan, S. A. Polym Eng Sci 2002, 42, 2065.
31. Anderson, B. J.; Zukoski, C. F. Macromolecules 2008, 41, 9326.
32. Wunder, S. L.; Ramachandran, S.; Gochanour, C. R.; Weinberg, M. Macromolecules 1986, 19, 1696.
33. Hsieh, T. T.; Tiu, C.; Simon, G. P. Polymer 2001, 42, 1931.
34. Hempenius, M. A.; Zoetelief, W. F.; Gauthier, M.; Moller, M. Macromolecules 1998, 31, 2299.
35. Van Ruymbeke, E.; Kapnistos, M.; Vlassopoulos, D.; Huang, T.; Knauss, D. M. Macromolecules 2007, 40, 1713.
36. Van Ruymbeke, E.; Bailly, C.; Keunings, R.; Vlassopoulos, D. Macromolecules 2006, 39, 6248.
37. Stribeck, N.; Ganjaee, M.; Zeinolebadi, A.; Moradian, S.VIII International Conference on X-Ray Investigations of Polymer Structure XIPS, 8–10 December, 2010, Wroclaw, Poland.