Interaction of dendronized polymeric nanocomposites with isomeric cyclohexanediols

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ABSTRACT: Dendronized poly(diethylaminoethyl methacrylamide) (PEAM) was studied in blends containing isomeric cyclic dialcohols. Monomers and polymers were characterized by spectroscopic measurements. The phase behaviors of blends of PEAM with 1,2-, 1,3- and 1,4-cyclohexanediols (1,2-CHD, 1,3-CHD and 1,4-CHD, respectively) were established. Transparent films of the blends exhibited a single glass-transition temperature (T_g). Thermogravimetric analysis (TGA) revealed the temperature at which the polymer releases the small molecules. UV-vis spectra of 1,3-CHD and 1,4-CHD derivatives showed an isosbestic point that indicated the association of the alcohols. FT-IR measurements showed shifts in several absorption bands. The results were analyzed in terms of the side-chain structure and the interactions involved. AFM measurements revealed differences between the polymer and the blends. Compatibilization of blends of PEAM/CHDs occurred via the formation of hydrogen bonds, although hydrophobic interactions could not be disregarded. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42267.

INTRODUCTION

Dendronized polymers are materials composed of a dendritic structure with different conformational arrangements. This chemical structure imparts the macromolecules with special properties, making their behavior interesting from different perspectives. These branched polymers should be able to entrap and receive small guest molecules and can therefore be used as matrices for the delivery of drugs, catalysts, and dyes and for compatibilization of small molecules, etc., via host–guest interactions.[1–6] The literature contains several reports in which these compounds are used for the aforementioned purposes[7–18] and as drug delivery,[12–20] thermal response,[15–23] and optoelectronic materials.[15,16]

Low-molecular-weight molecules are often used as carriers and to prepare new compounds, such as pharmaceutical compounds, dyes, and catalysts.[1–8] High-molecular-weight macromolecules are used in industry. The most significant difference between small and large molecules is that the macromolecules do not have a specific shape and therefore lack predictable properties, unlike small molecules.[1–8] For instance, the diameter of polymers can be changed by altering their physical environment. Investigations of intermediate-sized nanoscale molecules with specific shapes and functionalities and with well-defined molecular weights are interesting. These molecules can be nonlinear oligomeric units called dendrimers. Such systems can be considered a special type of polymer blend, where the interactions between the polymer and the small molecules determine the general behavior of the mixture and the rate of release of the small molecules.[24,25] These special types of mixtures are interesting because they can be used as a good model for investigating the mechanism of the delivery of small molecules, thereby allowing researchers to take advantage of the type of interactions involved in the blending process.[26,27]

Polymer blends are of current interest because, depending upon the blending process, novel materials with new and enhanced
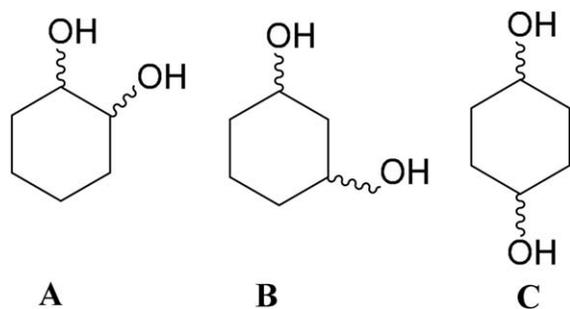
Scheme 1. Chemical structures of (A) 1,2-CHD, 96% mixture of *cis* and *trans*; (B) 1,3-CHD, 98% mixture of *cis* and *trans*; and (C) 1,4-CHD, 99% mixture of *cis* and *trans*.

properties can be obtained.[28–33] The behavior of molecule–polymer blends differs substantially from that of polymer blends. These new types of blends can be analyzed using the same experimental techniques used for polymer–polymer blends, i.e., DSC, TGA, FT-IR, AFM, and UV-vis.

The aim of this work was to study blends composed of a first-generation dendronized poly(diethylaminoethyl methacrylamide) (PEAM) and cyclohexanediols. The small molecules were 1,2- (A), 1,3- (B), and 1,4-cyclohexanediols (C) (CHDs) (see Scheme 1), which allowed us to investigate the effect of the small molecules functionalization on the release mechanism.

EXPERIMENTAL

Synthesis of Monomers and Polymers

All reagents and solvents were purchased from Sigma-Aldrich. The monomer (EAM) was synthesized by the reaction of methacryloyl chloride with N,N-diethylethylenediamine in the presence of triethylamine in dried THF; the reaction mixture was stirred for 72 h at room temperature, as previously reported.[24,25]

The monomer EAM was polymerized using α,α'-azobisisobutyronitrile (AIBN) (0.5% wt) as the initiator under an atmosphere of previously dried N_2. Polymerization was carried out in bulk at 65°C for 48 h. The polymer was purified by reprecipitation from petroleum ether in $CHCl_3$ solution before being vacuum dried, as previously reported[24,25] (Scheme 2).
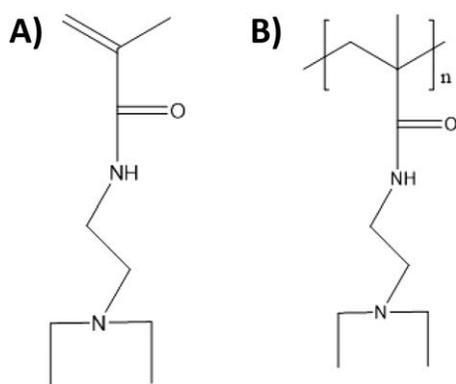
Scheme 2. Scheme of molecular structures of (A) the EAM monomer and (B) the first-generation dendrimer.

Blends Preparation

The films were prepared by dissolution casting. The polymers were dissolved in a 2% wt CH_3OH solution for 12 h to complete solubilization. CHDs were dissolved in 2% wt CH_3OH.

The composition 1,2-CHD 20% wt (80% wt PEAM and 20% wt diol) was prepared by mixing 1.6 g of PEAM and 0.4 g of 1,2-CHD solution on a Teflon support with continuous stirring for 24 h. The blends were then dried under vacuum at 25°C to a constant weight.

The CHDs used for the blends shown in Scheme 1 were purchased from Aldrich Chemical Company, Inc. The isomeric purities provided by the supplier were as follows: 96% mixture of *cis* and *trans* for 1,2-CHD, 98% mixture of *cis* and *trans* for 1,3-CHD, and 99% mixture of *cis* and *trans* for 1,4-CHD.

Spectroscopic Characterization

The blends and pure compounds were characterized by UV-visible and FT-IR spectrophotometry.

UV-vis measurements of the pure compounds and blends were recorded on an Agilent Technologies Cary 60 UV-vis spectrophotometer. The solutions were prepared in methanol at different weight percentages of CHDs. For absorbance of the composition 1,2-CHD 20% (80% wt PEAM and 20% wt diol) was recorded between 320 and 200 nm.

The FT-IR measurements of blends were performed using pellets. Two milligrams of film blends were prepared by the dissolution casting method using 80 mg of KBr.

Molecular Characterization

The molecular characterization of the first generation of the PEAM dendrimer was confirmed by proton nuclear magnetic resonance (^{1}H-NMR) and FT-IR. ^{1}H-NMR spectrometry was performed on a Bruker Avance-400 spectrometer at 400 MHz; the samples were dissolved in $CDCl_3$, and tetramethylsilane was used as an internal standard for the monomer and the PEAM polymer. FT-IR spectra were recorded on a Bruker Vector 22 spectrophotometer using KBr pellets; the spectra were collected at a resolution of 1 cm^{-1}.[24,25]

Weight-average molecular weight (M_w) and polydispersity (M_w/M_n) values were determined using a Viscotek size exclusion chromatograph equipped with a refractive index detector; the samples were dissolved in $CHCl_3$. The molecular weight distribution was based on a calibration curve constructed using monodisperse poly(styrene) standards.[24,25]

Thermal Analysis

Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851. The scans were performed at temperatures ranging from 25 to 700°C at a heating rate of 10°/min under a nitrogen atmosphere. The sample masses were 5–10 mg, and the samples were placed in 40 μL alumina pans. Data were processed using the STAR^e software version 8.1 from Mettler-Toledo. Thermal transitions of the polymer were studied by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC 821-700 differential scanning calorimeter; the samples were analyzed under a dry nitrogen atmosphere at a heating rate of 10°C/min. The thermal curves of the samples were obtained

Table I. Glass-Transition Temperatures (T_g) of the PEAM/DCH Blends with Different Compositions (wt %) of CHD

	Composition (wt %) CHD								
	0	20	40	50	60	80	100		
T_g (°C)								T_m (°C) experimental	T_m (°C) Aldrich reported
1,2-CHD	90	98	96	94	99	100		64	72.5–75
1,3-CHD	90	51	47	–	–	–		245	246–247
1,4-CHD	90	–	–	–	–	–		98	98–100

using the following heating method: 5 min hold at 300°C, decrease in temperature to −100°C at 10°/min, 2 min hold at −100°C, and increase in temperature to 300°C at 10°/min. The second heating cycle was used for analysis. Data obtained were processed using the STAR^e software version 8.1 from Mettler-Toledo.

Atomic Force Microscopy

AFM images were obtained in tapping mode on a Nanoscope IIIa Multimode® scanning probe microscope from Digital Instruments, Veeco. Commercial Si cantilevers with force constants of 20–80 N/m were used. The samples were prepared by being spin-coated at 2000 rpm for 60 s using a Telstar Instru-

ments model P-6708D spin-coater. Blend solutions (0.1–0.2 wt % in MeOH) were coated onto cleaved glass substrates.

RESULTS AND DISCUSSION

Synthesis of the Monomer and Polymers

Functionalized PEAM was obtained in 65% yield by polymerizing the monomer previously obtained by the reaction between the corresponding amine and methacryloyl chloride. The monomer (EAM) and polymer (PEAM) were characterized by ^{1}H-NMR and FT-IR. Different signals were observed for EAM: ^{1}H-NMR, 6.57 (s, 1H; −NH₂), 5.71 (s, 1H; ═CH₂), 5.30 (s, 1H; ═CH₂), 3.74 (m, $J = 6.0$ Hz, 2H; −CH₂), 3.34 (dd, $J = 11.3$, 5.5
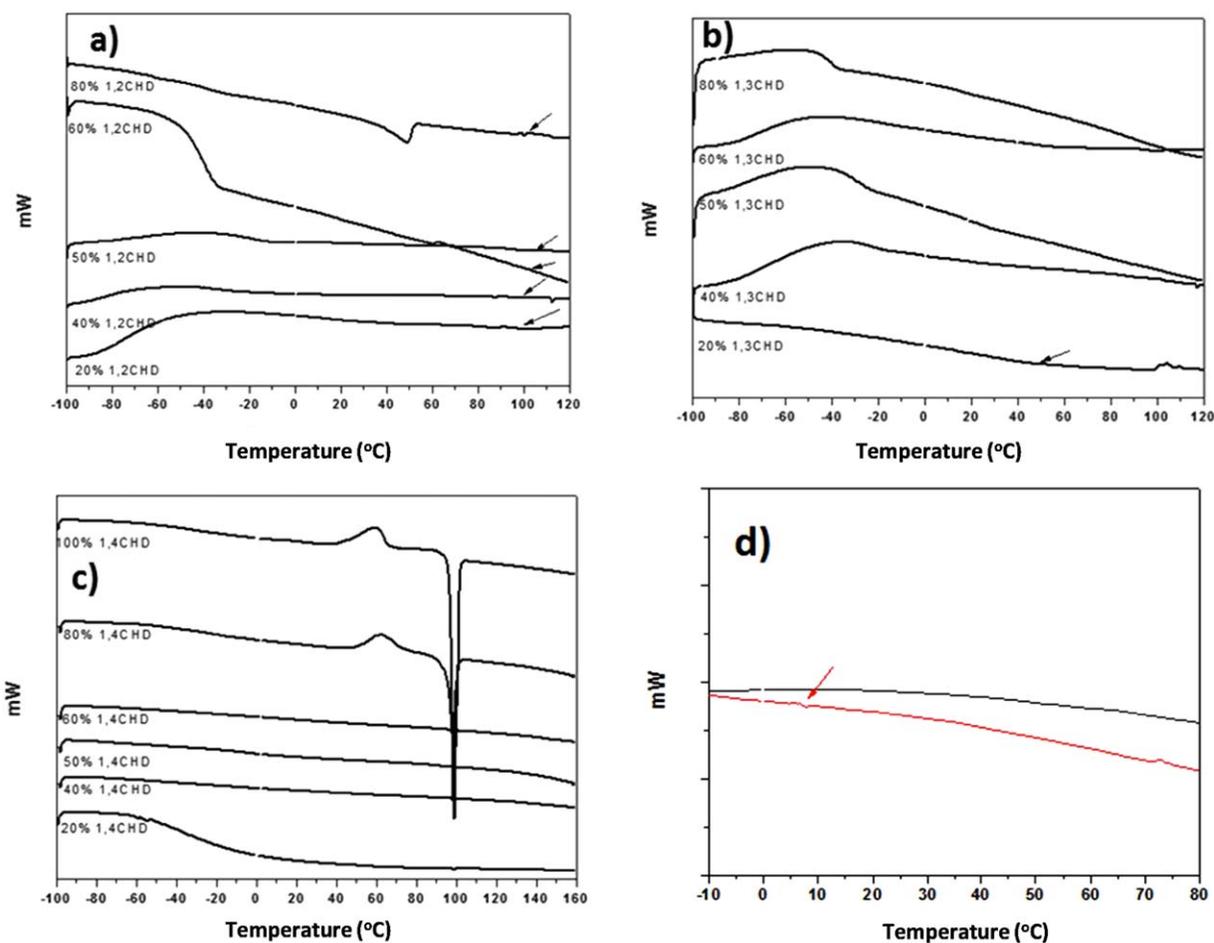

Figure 1. DSC curves of (A) PEAM/1,2-CHD, (B) PEAM/1,3-CHD, (C) PEAM/1,4-CHD, and (D) quenched PEAM/1,3-CHD 50% wt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
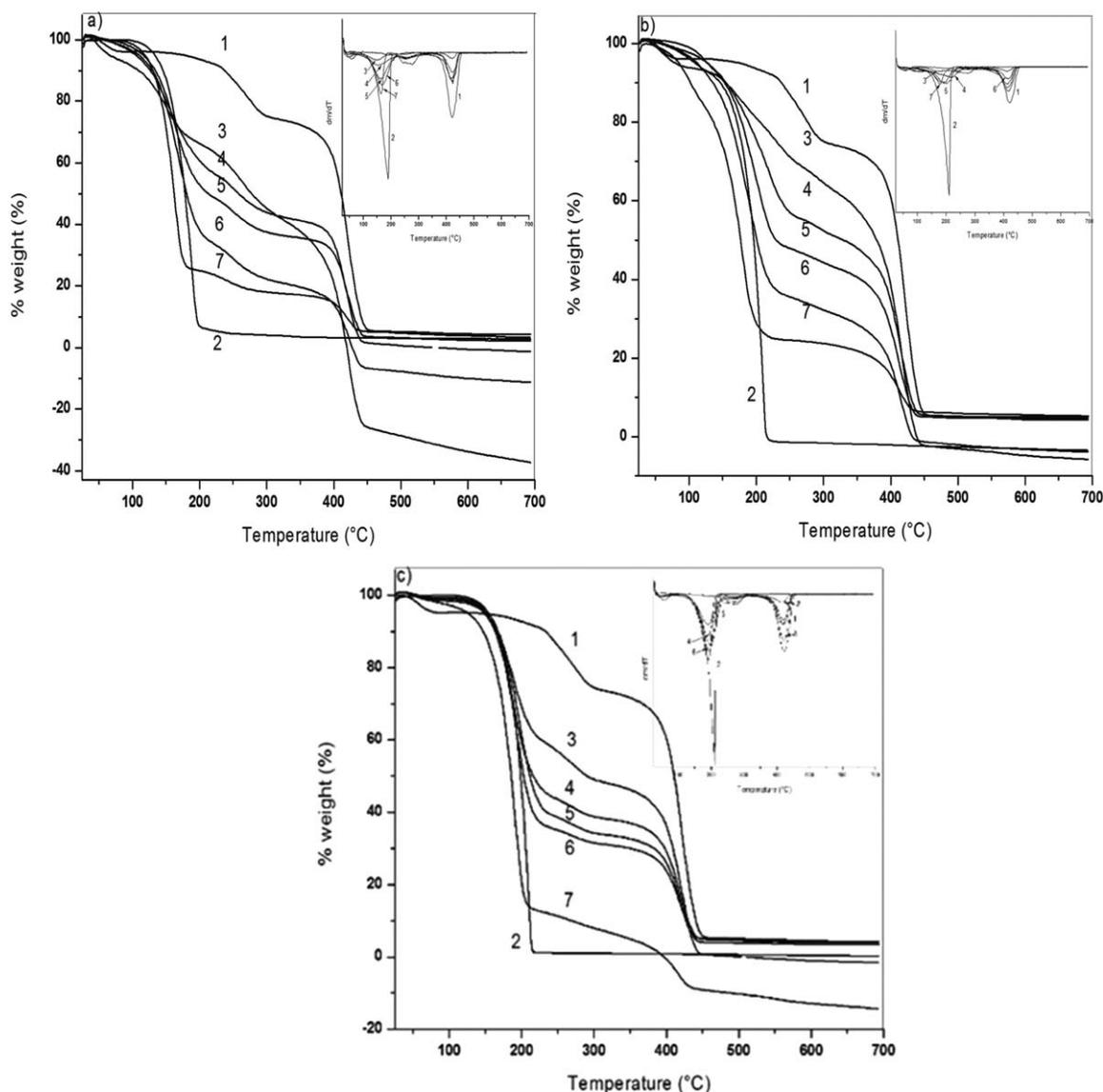
Figure 2. TGA thermograms of (A) PEAM/1,2-CHD: (1) PEAM, (2) 1,2-CHD, (3) 1,2-CHD 20%, (4) 1,2-CHD 40%, (5) 1,2-CHD 50%, (6) 1,2-CHD 60%, and (7) 1,2-CHD 80%; (B) PEAM/1,3-CHD: (1) PEAM, (2) 1,3-CHD, (3) 1,3-CHD 20%, (4) 1,3-CHD 40%, (5) 1,3-CHD 50%, (6) 1,3-CHD 60%, and (7) 1,3-CHD 80%; (C) PEAM/1,4-CHD: (1) PEAM, (2) 1,4-CHD, (3) 1,4-CHD 20%, (4) 1,4-CHD 40%, (5) 1,4-CHD 50%, (6) 1,4-CHD 60%, and (7) 1,4-CHD 80%.

Hz, 2H; CH_2), 2.55 (dt, $J = 14.2$, 6.5 Hz, 6H; —CH_2), 1.98 (m, 3H; —CH_3), 1.01 (s, 6H; —CH_3), FT-IR: 3339 cm^{-1} (—NH), 3089 cm^{-1} (—CH_2=C—), 2973, 2938 cm^{-1} (aliphatic —CH-), 1658 cm^{-1} (—C=O). These signals are consistent with the expected chemical structure. Radical polymerization was carried out using AIBN as an initiator. The vinylic hydrogens observed in the ^{1}H-NMR spectrum of the monomer (at 5.25 and 5.75 ppm) were not observed in the spectrum of the resulting polymer.

The monomer EAM was polymerized using AIBN as the initiator; the polymerization was conducted under an atmosphere of previously dried N_2. Polymerization was carried out in bulk at 65°C for 48 h.[24,25] The polymer was purified by re-precipitation from petroleum ether in $CHCl_3$ solution. The M_w was 52,700

(g/mol), and the PDI was 1,2. Spectroscopic characterization showed different signals for PEAM: ^{1}H-NMR: 7.26 (s, 1H; —NH_2), 3.46 (m, 2H; —CH_2), 1.67 (m, 6H; —CH_3), 1.35 (m, 3H; —CH_3), 0.9 (m, 8H; —CH_2), FT-IR: 3425 cm^{-1} (—NH), 2973 cm^{-1} (—CH_3), 2937 cm^{-1} (—CH_2), 1645 cm^{-1}(—C=O); these results are in agreement with the expected chemical structure of the polymer.[24,25] The molecular structures of the EAM monomer and the PEAM polymer are shown in Scheme 2.

Thermal Analysis

The main criterion for miscibility is the presence of a single glass-transition temperature (T_g) of the material; this T_g should be intermediate between those of the pure components.[27,28] Nevertheless, in the case of polymer/small molecule blends, the melting of the small molecules will no longer be observed in
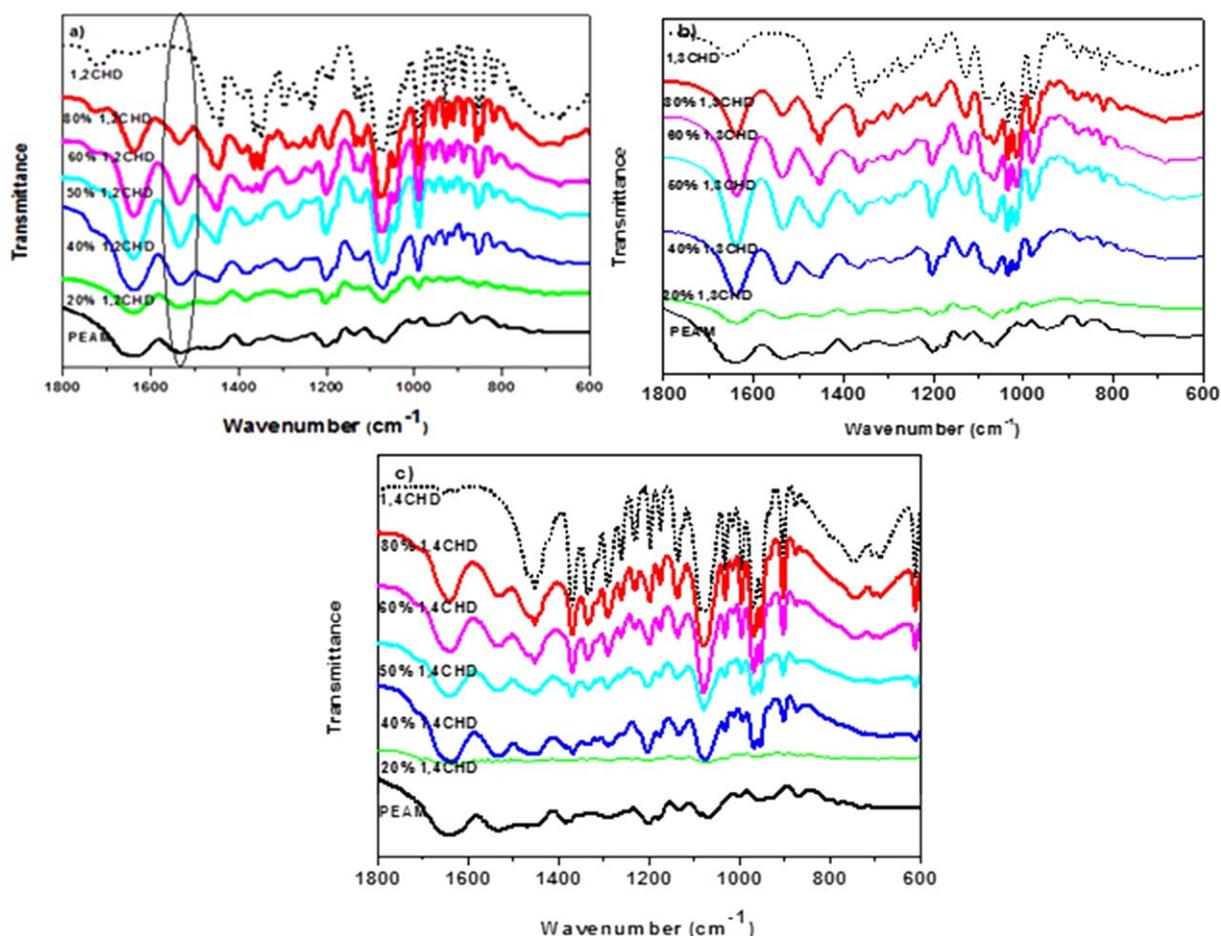
Figure 3. FT-IR spectra of (A) PEAM/1,2-CHD: (1) PEAM, (2) 1,2-CHD, (3) 1,2-CHD 20%, (4) 1,2-CHD 40%, (5) 1,2-CHD 50%, (6) 1,2-CHD 60%, and (7) 1,2-CHD 80%; (B) PEAM/1,3-CHD: (1) PEAM, (2) 1,3-CHD, (3) 1,3-CHD 20%, (4) 1,3-CHD 40%, (5) 1,3-CHD 50%, (6) 1,3-CHD 60%, and (7) 1,3-CHD 80%; (C) PEAM/1,4-CHD: (1) PEAM, (2) 1,4-CHD, (3) 1,4-CHD 20%, (4) 1,4-CHD 40%, (5) 1,4-CHD 50%, (6) 1,4-CHD 60%, and (7) 1,4-CHD 80%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the thermal analysis results, which indicates that the polymer and the small molecules have formed a unique structure. If the blend is immiscible, the T_g and melting-point (T_m) signals of the components should be maintained.

Transparent films were obtained at room temperature, suggesting that no phase separation occurred. The T_g of PEAM was 90°C. The T_g values for PEAM and blends and the T_m values for the CHDs are summarized in Table I; the DSC curves are shown in Figure 1.

Table I shows the T_g values obtained for the blends containing CHDs. Only the blend with 1,2-CHD appeared to be compatible according to these results; nevertheless, this behavior must be verified using complementary experimental techniques. For the blend with 1,3-CHD, a glass transition was observed only when the composition was 20 or 40% wt CHD; the observed T_g values were 51 and 47°C, respectively. Blends with 1,4-CHD did not exhibit a glass transition. These results indicate that the position of the ─OH groups is likely responsible for the degree of compatibility in the new material. As such, interactions between PEAM and the CHDs are favored when ─OH groups

are at the 1,2-positions, which is the position of the substituents on the cyclohexyl group during the blending process. Nevertheless, auto-association of the CHDs is a factor that must be taken into account. In fact, if the CHDs auto-associate, the population of free ─OH groups diminishes and the interaction with PEAM is affected. Therefore, a more detailed analysis of the results should be performed using complementary experimental techniques to clarify this particular result.

The TGA profiles and the first-derivative curves (DTG) for different compositions of PEAM/CHDs blends are shown in Figure 2. All blends exhibit a similar trend, with two stages of decomposition. This result is attributed to the sequential degradation of the polymer molecules. The first step of the degradation is a disruption of the auto-association of the polymer and diols. The second step is the degradation of the polymeric backbone. Therefore, these results suggest that the small molecules could be trapped inside the cavity of the dendronized polymer and then gradually delivered. The point at which 50% of the material was decomposed (TD$^{50\%}$) was approximately 200–250°C. These temperatures provide a qualitative measure of the
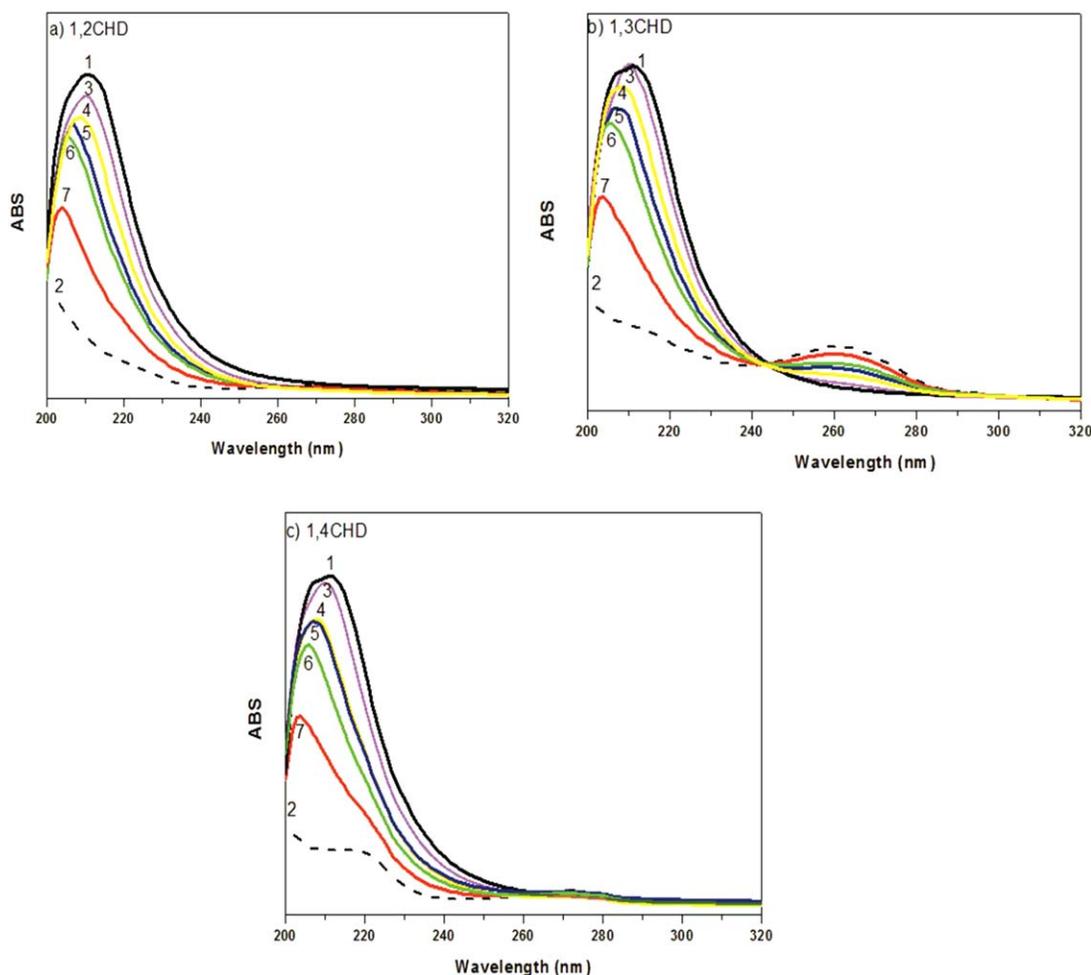
Figure 4. Absorption spectra of (A) PEAM/1,2-CHD: (1) PEAM, (2) 1,2-CHD, (3) 1,2-CHD 20%, (4) 1,2-CHD 40%, (5) 1,2-CHD 50%, (6) 1,2-CHD 60%, and (7) 1,2-CHD 80%; (B) PEAM/1,3-CHD: (1) PEAM, (2) 1,3-CHD, (3) 1,3-CHD 20%, (4) 1,3-CHD 40%, (5) 1,3-CHD 50%, (6) 1,3-CHD 60%, and (7) 1,3-CHD 80%; (C) PEAM/1,4-CHD: (1) PEAM, (2) 1,4-CHD, (3) 1,4-CHD 20%, (4) 1,4-CHD 40%, (5) 1,4-CHD 50%, (6) 1,4-CHD 60%, and (7) 1,4-CHD 80%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

strength of the interaction between the polymer and the small molecules. Notably, however, the T_ms of the small molecules in the blend were not detected in the TGA/DTG profiles, irrespective of the composition, which suggests that an important interaction occurred between the polymer and the small molecules; thus, the PEAM and CHDs were assumed to be miscible. This result differs from the DSC measurements in that the three CHDs behave similarly.

FT-IR Analysis

FT-IR analysis complements the thermal analysis results, providing insight into the interactions involved in different polymer mixtures. Specific interactions between components can be readily observed through band displacements, intensity changes, broadening of the signals, etc.[27–30] In the spectrum of pure PEAM, the absorptions at 1640 cm^{-1} and 1536 cm^{-1} correspond to the amide I band (stretching C=O) and the amide-II bending band (—NH), respectively; both are frequently used to detect displacements in bands related to amides.[32]

Coleman et al.[33,34] analyzed amide/ether interactions, where the presence of C=O and —NH groups led to the formation of

intramolecular hydrogen bonds. Chains are associated and only terminal functional groups of chains are available for specific intermolecular interactions. In this work, FT-IR absorptions of pure components and blends show some displacements, which are evident in Figure 3.

In the case of PEAM/1,2-CHD blends, the band displacements differ. The amide I and II bands are displaced 3 cm^{-1} toward lower wavenumbers in the case of the 80% and 60% CHD blends. The amide II band exhibits increased intensity and definition in the spectra of the 40%-60%-80% CHD/PEAM blends. Notably, the intensity of the amide II band at 1540 cm^{-1} is weak in the spectrum of the pure polymer, but it increases with increasing composition of CHDs [Figure 3(a)], which is indicative of interactions between the functional groups of the polymer and the diols.

Most alcohols exhibit absorption bands in the 1420–1000 cm^{-1} region. These bands are sensitive to hydrogen bonding. The band at 1076 cm^{-1} is attributed to —C—OH stretching. This band shows a displacement of 8 cm^{-1} toward lower wavenumbers. These changes indicate that the polar groups of PEAM can

interact strongly with CHDs through hydrogen bonds or at least through ion-dipole interactions. Consequently, the dendronized polymer matrix can be assumed to trap small molecules.

In the cases of PEAM/1,3-CHD and PEAM/1,4-CHD, no significant displacements of the amide I and II bands are observed. In addition, no change is observed in the band associated with the alcohol groups.

According to these observations, the most important changes in the FT-IR spectra correspond to the blend containing 1,2-CHD, which is consistent with the DSC results but not with the TGA results. Similarly, agreement with the TGA observations is observed for blends containing PEAM with 1,3- and 1,4-diols in that weak interactions appear to be present. Therefore, the interactions involved in these systems strongly depend on the position of the —OH group in the cyclohexyl ring, the composition of the blend, the conformation of the polymer, and the trapping capacity of the dendritic molecule toward the small molecule. These results provide further evidence that important and selective interactions occur in these systems.

UV-Vis Spectroscopy
UV-vis is a powerful tool for detecting interactions among two or more components in a mixture. Any displacements or diminution of the bands corresponding to the constituents of the blend provide information about the interaction of the molecules involved in the system.[26,27,35–38] Figure 4 shows a compilation of the absorption profiles for PEAM/CHD blends with different compositions. A blue shift of the signals was observed in all cases. A shift in the absorption maxima for the pure CHDs relative to the maximum for pure PEAM would indicate the occurrence of important interactions between the components of the blends. This effect cannot be considered a composition effect because the wavelengths of the maxima are shifted, whereas the intensities are similar to those of the pure components. According to the absorption spectra, the maxima shift almost 7 nm, which is attributed to strong interactions between PEAM and the CHDs. These shifts of the absorption maxima could be due to hydrogen bond formation, which is expected because of the strong interacting capacity of the alcohols. The largest difference in the position of the absorbance band was always observed for larger CHD compositions. This result is explained by taking into account that, as the amount of CHDs increases, the number of —OH groups available to interact increases. The shift in the absorbance among the three alcohols with PEAM as a function of composition may arise because, irrespective of the position of the —OH substitution in the cyclohexyl ring, the exposure of the —OH groups is similar. Nonetheless, the analysis of the UV-vis spectra of the CHDs shown in Figure 4 allows a more exhaustive interpretation of the data. The UV-vis spectra of 1,3-CHD and 1,4-CHD exhibit an isosbestic point at 240 and 260 nm, respectively. The existence of an isosbestic point is attributed to the presence of auto-associated species such as dimers, trimers, tetramers, etc. Therefore, the amount of free —OH groups is lower, which explains why the T_g values in these isomers cannot be detected by DSC; i.e., fewer free —OH groups are available to interact with PEAM. In contrast, no isosbestic point was detected in the
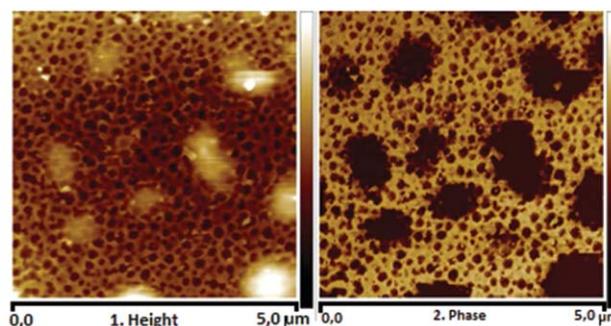

Figure 5. Topographical (left) and phase images (right) of PEAM films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

investigated wavelength range in the case of 1,2-CHD. Auto-association in 1,2-CHD is difficult, and the amount of free —OH groups depends only on the blend composition. A strong interaction between the blend components is concluded to be present; however, this interaction is conditioned by the specific interactions between the CHDs and the polymer. Notably, the hydrophobic interactions between the polymer and the cyclic ring cannot be disregarded.

Another complementary experimental result that confirms the suggested interpretation of the blend behavior is that blends containing 1,3-CHD or 1,4-CHD become quenched when heated to the T_g of PEAM [Figure 2(D)]. The thermograms show that the T_g of the blend can be detected, confirming the presence of associated diols. The quenching process of the blend results in frozen free diols, which, in turn, results in more free —OH groups being available to interact with PEAM. These results therefore confirm that PEAM and CHDs are compatible.

Atomic Force Microscopy Analysis
AFM was used to analyze the morphologies of the PEAM and blends, as another complementary technique for determining the compatibility between the components,[35,36] and to gain further insight into the interactions involved in the blending process.

Figures 5 and 6 show both topographical (left) and phase (right) AFM images of pure PEAM and the PEAM/CHD blends, respectively. The image of PEAM shows different zones and imperfections, which may result from the segregation induced by the interactions among the chains of the polymer, as was demonstrated by thermal and infrared analysis.

The PEAM/CHD blend shown in Figure 6 exhibits a flat, featureless surface. The image differs substantially from that of pure PEAM. Adhesion with the substrate was apparently improved, resulting in a regular thin film. This change in adhesion and surface roughness could be due to interactions among polymers, resulting in a smooth surface, unlike that of pure PEAM. Hard zones corresponding to the presence of diols, which appear as bright points, were also observed. These AFM images suggest that an important interaction occurred between the components of the blend; however, some irregularities were
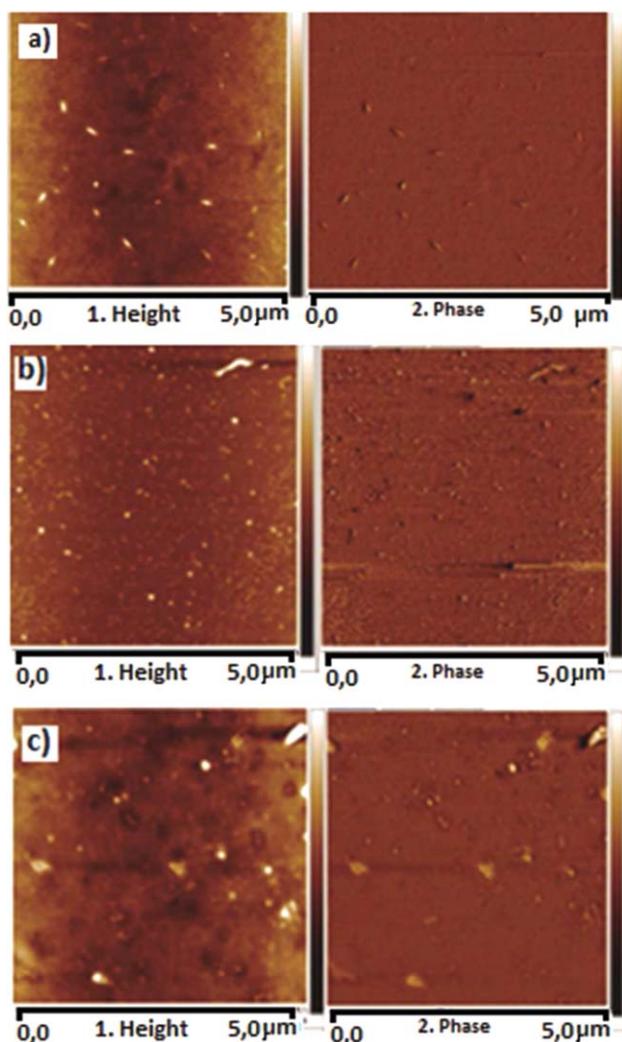
Figure 6. Topographical (left) and phase images (right) of films of (a) PEAM/1,2-CHD,(b) PEAM/1,3-CHD 50/50, and (c) PEAM/1,4-CHD 50/50 (wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also observed. These results are in good agreement with the previously discussed FT-IR results.

CONCLUSIONS

Blends of PEAM with small molecules were characterized using different experimental techniques to analyze their compatibility behavior.

The DSC results showed a single T_g value for the PEAM/1,2-CHD blends; however, in the case of PEAM/1,3-CHD and PEAM/1,4-CHD blends, the T_g values were difficult to detect. Nevertheless, important shifts in the FT-IR and UV-vis absorption bands implied that strong interactions could be responsible of the phase behavior of the blends. The FT-IR and UV-vis spectra suggest that hydrogen-bonding interactions could be the driving force of miscibility. The presence of an isosbestic point in the blends of 1,3-CHD and 1,4-CHD could be responsible for the inability to detect glass transitions. The thermograms of quenched samples of the blends containing 1,3-CHD and 1,4-

CHD confirmed that interactions occurred between PEAM and the CHDs and these interactions are strong, similar to hydrogen bonds. However, the AFM images suggested that the pure polymer auto-associated to some degree; furthermore, the blends with CHD irregularities, because of the association of the components, gave rise to defects in the images. These results also suggested that strong interactions between the polymeric components are responsible for the compatibilization process. However, hydrophobic interactions cannot be disregarded.

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