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Compatibilization of polystyrene/poly(dimethyl siloxane) solutions with star polymers containing a γ-cyclodextrin core and polystyrene arms

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ABSTRACT

Solutions of polystyrene and poly(dimethyl siloxane) in chloroform are compatibilized by the addition of a small amount of a star polymer consisting of a γ-cyclodextrin core and polystyrene arms. Compatibilization is visually observed when turbid PDMS/PS emulsions become clear upon addition of the CD-star molecule. The mechanism of compatibilization involves threading of the CD-core by PDMS and solubilization of the resulting "slip-ring graft copolymer" *via* the PS star arms. This process breaks up the undissolved PDMS domains into smaller, more stable micelles. Evidence for threading of the CD-core by PDMS is found using ROESY 2D-NMR. Intrinsic viscosity measurements for the compatibilized solutions show behavior similar to conventional graft copolymers which form micelles in a selective solvent. Dynamic light scattering measurements suggest that the micelle size is approximately 20 nm. The effects of varying the PDMS molecular weight, PDMS concentration and CD-star concentration are studied.

1. Introduction

Solutions of incompatible polymers, such as polystyrene (PS) and poly(dimethyl siloxane) (PDMS) commonly exhibit bilayer phase segregation [1], or if rapidly mixed at high concentrations, an unstable turbid emulsion. However, incompatible blends can be encouraged to mix by the addition of a compatibilizing component that is designed to stabilize the mixture by bridging the interface between phases [2]. Block copolymers made up of PS and PDMS (PS-*b*-PDMS) have been used in this fashion to physically bridge phase domains in PS/PDMS blends [3,4]. Typically, when block copolymers are added to a solution for compatibilization, one of the blocks is soluble and the other is not, and they take on a "surfactant-like" quality. Abbas et al. [5]. observed that block copolymers of PS-*b*-PDMS in selective solvents will self-organize into micelles which may assume the shape of vesicles, cylinders or spheres, depending on solvent quality.

Cyclodextrins (CDs) are cyclic oligosaccharides containing 6, 7 or 8 glucose units, which correspond to α-, β- and γ-CD, respectively. These molecules have a truncated cone-like structure and a hollow central cavity with a diameter that increases with the number of glucose units. It is well-documented that these CDs have the ability to entrap and retain a wide variety of polymers and small molecules in their hydrophobic cavities, thus forming an inclusion complex [6,7]. This property can be exploited to create a new class of compatibilizers for polymer blends: star polymers which consist of a CD-core and polymeric arms. The arms (polymer A) provide compatibility and molecular dispersion of the CD-star in a matrix of polymer A, while the CD-core is capable of complexing and entrapping a polymer guest (polymer B). The CD-star polymer effectively "handcuffs" and disperses polymer B in polymer A, creating a compatibilized blend. The advantage of this type of compatibilizer is that many different polymers are capable of threading the CD-core, which means that the same CD-star molecule could be used to compatibilize several different A/B polymer blends in which polymer B is varied. Furthermore, many studies have shown that the diameter of the CD cavity restricts inclusion complex formation to polymers that can fit into the cavity. Selection of α-, β-, or γ-CD as the core of the star polymer also allows the compatibilizer to be tailored for selective threading of the desired polymers.

In this paper, a CD-star polymer having a γ-cyclodextrin core and 12 PS arms is synthesized and mixed as a compatibilizer into a solution of PS, PDMS and chloroform. PS dissolves in chloroform, whereas PDMS does not. The core of γ-CD has a cavity diameter of 9.5 Å [8], and has been established to thread several polymers including PDMS [9–11], which has a cross-sectional diameter of 7.99 Å [12]. However, the γ-CD cavity is not large enough to thread

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atactic PS [13], which conveniently prevents PS molecules from complexing with the CD-star polymer. The threading of PDMS into the CD-core is the interaction which compatibilizes PDMS in the solution, while the PS arms on the CD-star enhance the solubility in chloroform. Solid films that are spun-cast from these compatibilized solutions exhibit nanoscale dispersion of PDMS into PS, thus confirming the compatibilizing potential of CD-star molecules. The morphology and properties of these solid PS/PDMS films will be reported in a separate publication. This paper describes the behavior of the precursor PS/PDMS/chloroform solutions compatibilized with a CD-star molecule.

In solution, it is expected that several CD-stars will thread onto each PDMS chain, creating a "slip-ring graft copolymer" which consists of a backbone of PDMS and slip-ring grafts provided by the PS arms on the CD-star. The number of CD-stars threaded onto the backbone will be dictated by the equilibrium conditions established by the concentrations of CD-star, PDMS and PS in the chloroform solvent. Chloroform is a selective solvent, good for PS but poor for PDMS, thus a rich environment for micelle formation is created. Fig. 1 illustrates our working model for this system. Compatibilization of PDMS in PS/chloroform solution is thought to involve the following steps: (1) PDMS is introduced into the PS/CD-star solution, and initially forms insoluble PDMS domains and a PS/PDMS interface to which oligomeric CD-stars will migrate; (2) concentration of the CD-star at the interface helps to initiate threading of PDMS; (3) threading of PDMS into the CD-star takes place which breaks up the PDMS domains and (4) micelle [14] formation occurs stabilizing the PDMS in solution.

Support for this model comes from a few important previous findings. First, it has been established that for a compatibilizer to be successful it must be capable of migrating to the interface between phases and dissolve in both, which creates a thermodynamic environment that is more likely to form micelles [2]. Helfand and Tagami [15,16] employed self-consistent-field theory to demonstrate that oligomers tend to concentrate at an interface in order to lower the interfacial energy. This increase in oligomeric concentration at the interface has been found to apply to both polymer melts and concentrated polymer solutions [17,18]. Furthermore, Helfand and Tagami, and Kajiyama et al. [19]. showed that chain ends are more likely to be found at the phase interface [20], which will result in an increased opportunity for the CD-stars to thread onto the PDMS. Finally, as pointed out previously, it is well established that graft copolymers will form micelles in a selective solvent. With the combined effects of CD-stars migrating to the interface, as well as a higher concentration of PDMS chain ends found at the interface, an environment conducive to PDMS threading into CD-stars is established. The PDMS used in this work has fully methylated end groups which are small enough to thread into the CD-star molecule. The incompatible polymers PS and PDMS will be effectively compatibilized by the physical tying of these two species together. The CD-star arms can then interact with the PS solution to stabilize the PDMS chain by extending into the solution, thereby forming a micellar structure.

In this paper we show that turbid immiscible solutions of PS and PDMS in chloroform become clear (compatibilized) when CD-star is added. Compatibilized solutions are characterized by NMR spectroscopy, dilute solution viscometry and dynamic light scattering to validate the model in Fig. 1.

2. Experimental

2.1. Materials

ACS grade chloroform was purchased from Fisher Scientific and was used without further purification. Polystyrene homopolymer was purchased from Aldrich and was found to have a molecular weight of 325,000 g/mol and a polydispersity index (PDI) of 2.95 via gel permeation chromatography (GPC). Both poly(dimethylsiloxane) homopolymers used in this study were purchased from Gelest, Inc., have PDIs between 2 and 3, molecular weights of 62,700 and 308,000 g/mol and are designated as PDMS62 and PDMS308, respectively.

γ-Cyclodextrin was purchased from Cerestar, and randomly methylated γ-cyclodextrin (50% methylated) was purchased from Cyclodextrin Technologies Development Inc. of High Springs, Florida. An oligomeric PS standard with a molecular weight of 2500 g/mol was purchased from the Pressure Chemical Company.

2.2. Synthesis of CD-star polymers

γ-CD has 24 hydroxyl groups which can be modified to form brominated initiator sites from which PS arms can be grown via atom transfer radical polymerization (ATRP). Li and Xiao reported synthesis of similar initiator sites on β-CD [21]. Their method was adopted in this work, as illustrated in Fig. 2a. The quantities of reagents used were 10.00 g (7.71 mmol) of γ-CD that was dried overnight in a vacuum oven at 80 °C, and 15.2 ml (123.4 mmol) of 2-bromoisobutyryl bromide (98%). The latter reagent contains a bromine functional group similar to the initiator used by

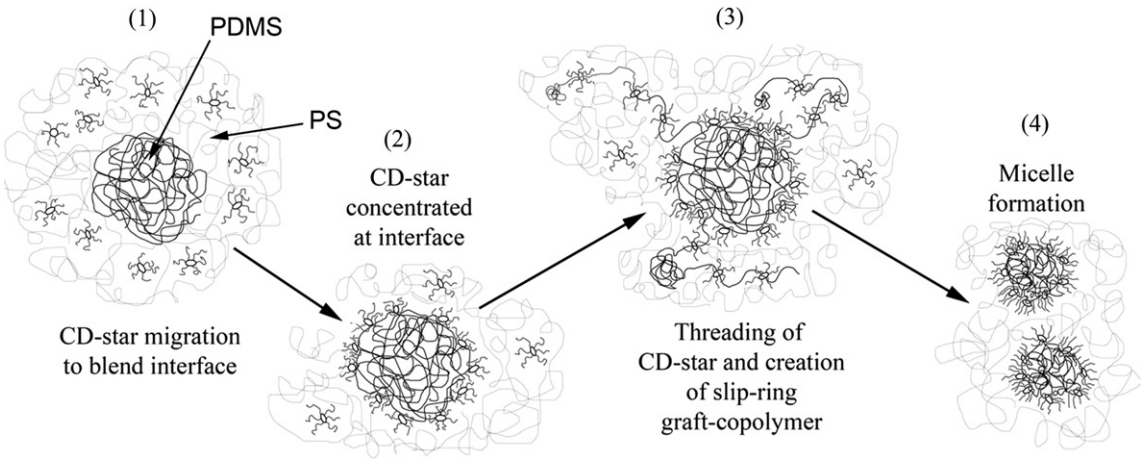

Fig. 1. Model for PS/PDMS solution compatibilization and micelle formation with CD-star molecules.

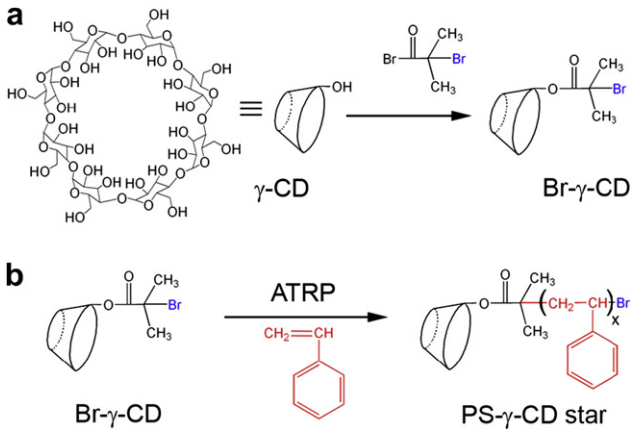

Fig. 2. Synthesis of (a) ATRP initiator and (b) PS-γ-CD-star.

Matyjaszewski et al. [22] in ATRP reactions. The amount of 2-bromoisobutyryl bromide administered targeted 16 of the 24 hydroxyl groups on γ-CD. However, ^{1}H NMR analysis later showed that an average of 12 hydroxyl groups per γ-CD molecule were actually modified with bromine. The physical appearance of the powdered ATRP initiator product (Br-γ-CD) was off-white/light-brown in color and it had a recovered mass of 17.68 g.

2.3. Attachment of PS arms

ATRP was carried out with molar ratios of $[M]_0/[I]_0/[Cu_IBr]_0/[bpy]_0/[Cu_{II}Br_2]_0 = 120/1/1/3/0.05$, where [M] is the styrene monomer, [I] is the number of bromine groups on the Br-γ-CD ATRP initiator, $[Cu_IBr]$ is copper(I) bromide, [bpy] is 2,2′-bipyridine, and $[Cu_{II}Br_2]$ is copper(II) bromide. An illustration of this reaction is shown in Fig. 2b for one of the twelve arms. Br-γ-CD initiator powder was added to a round bottom flask equipped with a Teflon-coated magnetic stir bar. A vacuum of 500 mtorr was pulled on the round bottom flask three times with subsequent nitrogen back filling. After nitrogen purging, 1/3 of the styrene monomer was introduced *via* syringe into the flask. The initiator was allowed to fully dissolve in the styrene monomer while stirring under nitrogen.

A second reaction vessel was prepared in parallel using an oven dried round bottom flask equipped with a Teflon-coated magnetic stir bar. To this flask copper(I) bromide, copper(II) bromide, and bipyridine were added, followed by administering a vacuum of 500 mtorr three times with subsequent back filling of nitrogen. The remaining 2/3 of the styrene monomer was added *via* syringe to the second flask which instantly turned the mixture black in color and formed a suspension. This mixture was placed into an oil bath preheated to 90 °C and was allowed to equilibrate for 10 min while stirring.

The initial styrene/Br-γ-CD solution was added rapidly to the copper/styrene suspension *via* a syringe while continuously stirring under nitrogen. After ATRP was allowed to proceed for a given amount of time (arm length is a function of time), the reaction vessel was removed from the oil bath and the solution was precipitated into a beaker containing a 60/40 mixture of methanol/water (10 times the reaction volume). The solid was allowed to settle and then was collected. Shorter reaction times (45–75 min) produced very short-armed stars (DP ≤ 11) which were soluble in methanol/water, therefore an additional purification step was necessary. Chloroform, which preferentially solvates these short-armed stars, was added. The product was recovered by pipetting the chloroform layer from the two-phase mixture and evaporating the chloroform.

The recovered product was dissolved in chloroform and twice passed through basic alumina in order to remove residual copper. The eluant was then stirred with acid ion-exchange resin (Dowex Marathon, Dow Chemical Co.) for two hours and again passed through basic alumina. The chloroform was evaporated or the solids were recovered by precipitation in methanol, as noted above. The off-white solid was air-dried overnight and then vacuum dried for 24 h at 80 °C and 500 mtorr. All γ-CD-stars readily dissolved in chloroform giving homogeneous solutions.

The chemical structure of the γ-CD-stars was verified with ^{1}H NMR, ^{13}C NMR and FTIR. ^{1}H NMR analysis showed that the 12 modified hydroxyl groups include 8 secondary and 4 primary hydroxyls. Given the positions of these groups on the γ-CD molecule (Fig. 2a), the "top" (smaller diameter end) of the CD truncated cone will have 4 arms and the "bottom" will have 8 arms after polymerization. Thus, it is reasonable to assume that threading of the guest polymer will occur predominantly from the top of the CD cone since fewer arms are present on that side. Star arm DP was also determined using ^{1}H NMR. By controlling the reaction time, five different γ-CD-stars were prepared with arm DPs ranging from 6 to 51. For this work, we chose the γ-CD-star having arms with DP = 6 to promote migration to the micelle interface. This sample has a number average molecular weight of 10,460 g/mol and GPC analysis showed that it was narrowly dispersed with a polydispersity index of 1.12.

2.4. Solution preparation

Solutions of PS and PDMS with and without γ-CD-star (hereafter "CD-star") were prepared at a total solids concentration of 10 g/dl in chloroform. No dependence of the solubility on the order of addition of the components was observed, so all solids were added simultaneously. Rapid stirring was employed using a Teflon-coated magnetic stir bar in an appropriately sized vial (typically 2 dram). The vial was heavily sealed with Teflon tape around the threads to minimize solvent evaporation which was monitored by placing an ink mark on the vial directly on the solvent line. Tables 1, 3 and 4 list the compositions for the various solutions used in this work, where the percentages are based on the total amount of solids. It should be noted that whenever the sample composition changes, PS is removed to keep the total mass of solids constant at 500 mg. The amount of CD-star in the solutions is specified as "wt% CD-core", which excludes the mass of the PS arms. All solutions were turbid immediately after preparation, but became clear after stirring for 2–4 days at 60 °C or stirring at room temperature for 1–3 weeks.

2.5. Nuclear magnetic resonance spectroscopy

^{1}H NMR spectra were collected on a Bruker 500 MHz Spectrometer. The solutions used for these experiments were also prepared at a solids concentration of 10 g/dl.

Table 1
Compositions of solutions in chloroform with varying PDMS content.

PDMS[a] (wt%)	CD-star[b] (mg)	PDMS[c] (mg)	PS (mg)	Total mass (mg)	Mols PDMS repeat units per mol CD-star
0	40.3	0	459.7	500.0	0
1	40.3	5	454.7	500.0	17.5
5	40.3	25	434.7	500.0	87.7
10	40.3	50	409.7	500.0	175
20	40.3	100	359.7	500.0	350

[a] Percentages are based on total solids content. Solution concentration is 10 g solids/dl.
[b] This mass corresponds to 1 wt% CD-core.
[c] Either PDMS62 or PDMS308.

2.6. Intrinsic viscosity

Dilute solution viscosities were measured with a Cannon Ubbelohde viscometer (#25), specifically designed for low-viscosity solutions. For these experiments, the maximum solution concentration was adjusted to 1 g/dl to ensure that the dissolved homopolymers were well below their overlap concentration, c^*. It was determined that the minimum value of c^* for these solutions is about 3 g/dl. Additionally, all solutions were prepared just before introduction into the viscometer and were filtered through a 1 μm Teflon syringe filter to remove any particulates. Once introduced into the viscometer, the solutions were equilibrated and maintained at 25 °C in a water bath. Reduced and inherent viscosities were measured at concentrations of 1.0, 0.833, 0.625, 0.428 and 0.231 g/dl. Intrinsic viscosity, $[\eta]$, was then obtained *via* separate extrapolation of these quantities to zero concentration using the Huggins and Kraemer relationships [23].

2.7. Dynamic light scattering

The same solutions used in the intrinsic viscosity measurements were subjected to dynamic light scattering analysis. These experiments were performed with a Brookhaven 90-Plus nanoparticle size analyzer, which has sizing capabilities ranging from 1 nm to 6 μm. All experiments were performed at 25 °C and a wavelength of 660 nm with a detector angle of 90°. Solutions were filtered through a 1 μm Teflon syringe filter to remove any particulates before introduction into the sample cuvette. At least 10 separate measurements were made for each solution.

3. Results and discussion

3.1. Solution observations

The compatibilizing effect of adding CD-star to solutions of PS and PDMS in chloroform can be seen in Fig. 3. The compositions of

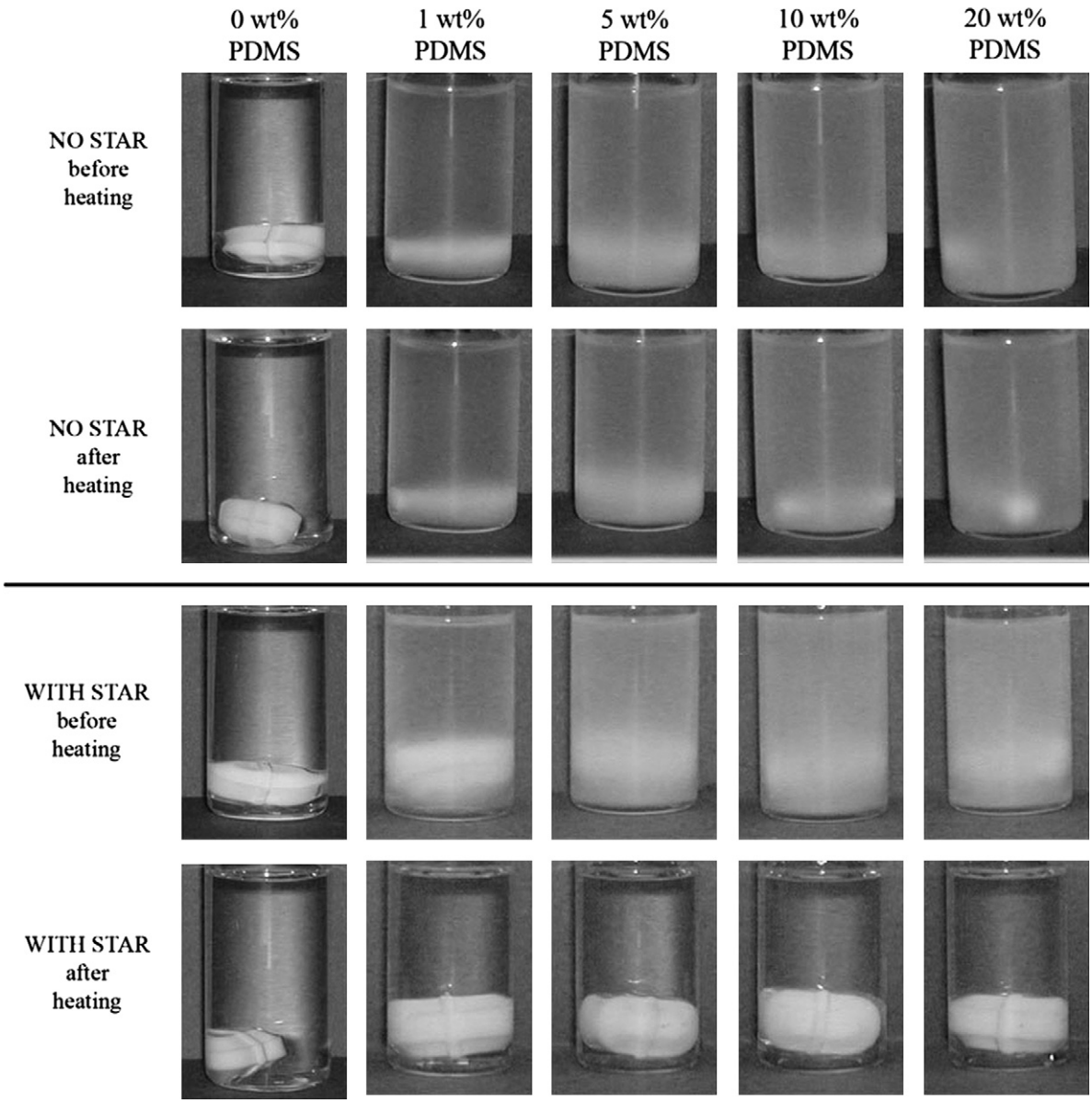

Fig. 3. Solutions of PS and PDMS in chloroform with and without CD-star before and after stirring at 60 °C for 1–3 days. The white magnetic stir bar on the bottom of the vials can be used to gauge solution clarity.

the solutions containing CD-star are listed in Table 1. The as-prepared solutions are turbid, whereas stirring at room temperature for 1–3 weeks or heating at 60 °C for 2–4 days produces clear solutions only when CD-star is present. Solutions without CD-star did not clear under any conditions. In addition to the increase in chain mobility, the reduction in solubilization time with increasing temperature might be partly due to the expansion of the CD cavity at higher temperatures, thus facilitating threading by PDMS. It has been shown by Cameron and Cooper [24] that β-CD has a higher thermal expansion coefficient for an empty cavity than for a guest-filled cavity, and γ-CD is expected to behave similarly.

The time required for the solutions to become completely clear increases with PDMS concentration, but did not depend on PDMS molecular weight. Both PDMS62 and PDMS308 produced clear solutions when CD-star was added. The clearing of these solutions indicates there is a sufficient enthalpic driving force [25,26] at room temperature for threading of the CD-core by PDMS. Solutions containing CD-star remained stable indefinitely. No phase separation was observed over a period of several months. Conversely, solutions without CD-star remained cloudy and eventually separated into two liquid layers. Addition of CD-star to these solutions apparently induces molecular dispersion of the PDMS or reduces the PDMS domain size below the point where scattering of visible light occurs. Due to the extreme chemical incompatibility of PS and PDMS [27], the latter explanation is more likely.

On a molar basis, very little CD-star is needed to compatibilize PDMS and PS. The ratio of PDMS repeat units to CD-star molecules is 350 for the 20 wt% PDMS solution, assuming all of the CD-stars thread onto PDMS chains (see Table 1). This corresponds to 12 CD-star molecules per PDMS chain for PDMS308 and 2.4 CD-star molecules per PDMS chain for PDMS62.

Several experiments were conducted to evaluate separately the effects of the solvent, the PS homopolymer, the type of CD-core and arms of the CD-star molecule on the compatibilization process. To evaluate the type of CD-core, separate solutions were prepared with pure γ-CD, 50% methylated γ-CD and brominated γ-CD in place of the CD-star. To evaluate the effect of the CD-star arms, a PS oligomer with a molecular weight of 2500 g/mol was used in place of the CD-star. Like the CD-star molecule, all of the modified CD materials had on average 12 of their 24 hydroxyls chemically substituted. The concentration of each of these components in the solution was adjusted to be identical to their concentrations in the original CD-star solutions. All of the solutions contained 5 wt% PDMS308. These solutions were all cloudy as-prepared, and none of them cleared after several days of stirring at 60 °C. This indicates that the specific chemical structure and architecture of the CD-star molecule is necessary for it to act as a compatibilizer, and that solubilization is not simply due to the thermodynamics of mixing of the various parts of the CD-star molecule.

In order to test the solvent effect on compatibilization, various solvents were selected that were increasingly good for PDMS. Solutions were prepared that were identical to the 5 wt% PDMS solutions in Table 1 (PDMS308 was used), except that methyl ethyl ketone (MEK), toluene or cyclohexane was substituted for chloroform. These solutions were stirred at 60 °C for 3 days. Results are listed in Table 2, along with polymer-solvent interaction parameters (χ) for these solvents with PS and PDMS. These observations show that the solvent must be selective for PS and poor for PDMS for solubilization to take place. Furthermore, this suggests that if the solvent offers a lower-energy environment for PDMS than the CD-core, then the driving force for threading of PDMS into the CD-core is reduced (as evidenced for toluene and cyclohexane).

A final experiment was performed to test the influence of the PS homopolymer on solubilization. Solutions similar in composition to those in Table 1 were prepared (PDMS308 was used), but without the PS homopolymer. The overall solids concentration of these solutions was adjusted to 10 g/dl by reducing the amount of chloroform. In all cases, the as-prepared solutions were cloudy and remained so after 2 days of stirring at 60 °C. These solutions could be re-solubilized by adding the appropriate amounts of PS and chloroform (to re-establish the compositions in Table 1) and stirring at 60 °C for 2 days. Apparently the presence of PS creates a less favorable solution environment for PDMS, which induces PDMS to thread the CD-stars and form micelles.

3.2. Confirmation of PDMS threading via NMR

Other researchers who have investigated PDMS and γ-CD inclusion compounds have used ^{13}C NMR to confirm inclusion of PDMS into γ-CD [10,28], but due to the very low concentration of CD-core in our solutions this was not possible. Instead, ^{1}H NMR experiments were conducted in order to determine if any localized interactions could be identified that confirm PDMS threading. For these experiments, several solutions were prepared in deuterated chloroform ($CDCl_3$) in which the amount of CD-star was varied while leaving the PDMS308 amount constant at 1 wt%. The compositions of these solutions are shown in Table 3. Stirring at 60 °C for 2 days again produced clear, stable solutions.

Fig. 4 shows the ^{1}H NMR spectra for these solutions. Since the concentration of CD-core is low, it is difficult to recognize the CD-star signals due to the majority of the signal strength belonging to the PS homopolymer. A small peak due to PDMS is seen at 0.2 ppm, whereas no CD-star peaks can be seen from 2.5 to 4.5 ppm. For each sample, an expanded PDMS region is also shown in this figure. Peaks at 7.1 and 6.8 ppm are attributed to the styrene phenyl ring and peaks at 1.9 and 1.5 ppm are due to the PS backbone hydrogens (–CH–) and ($–CH_2–$), respectively. It can be seen in Fig. 4 that the PDMS peak at 0.2 ppm decreases and broadens with increasing CD-core concentration. This might be an indication that threading of the PDMS into the CD-star is occurring. As more threading interactions between PDMS and the CD-core take place, the PDMS segments in the CD cavity are found in a different environment than in the PDMS domains, which is indicated by the broadening of the PDMS peak.

Rotating frame Overhauser Effect Spectroscopy (ROESY) [29] 2D-NMR affords a more sensitive measure of threading between PDMS and the CD-star. Several researchers have used this technique to observe localized guest interactions in CDs. Tellini and coworkers saw proton-proton interactions between the β-CD-core protons and the di-adamantyl acetic acid guest in D_2O, confirming

Table 2
χ values for PS and PDMS in various solvents.

Solvent	χ (PS)	χ (PDMS)	Solution behavior[a]
Chloroform	0.01	0.47	Clear
Methyl ethyl ketone	0.01	0.49	Clear
Toluene	0.01	0.33	Turbid
Cyclohexane	0.14	0.09	Turbid

[a] Refers to solutions containing solvent, PS, PDMS and CD-star. See text.

Table 3
Compositions of solutions in $CDCl_3$ for ^{1}H NMR analysis.

CD-core[a] (wt%)	CD-star (mg)	PDMS308 (mg)	PS (mg)	Total mass (mg)
0.2	8.2	5.0	486.8	500.0
0.6	24.7	5.0	470.5	500.0
1	40.3	5.0	454.7	500.0

[a] Percentages are based on total solids content. Solution concentration is 10 g solids/dl.

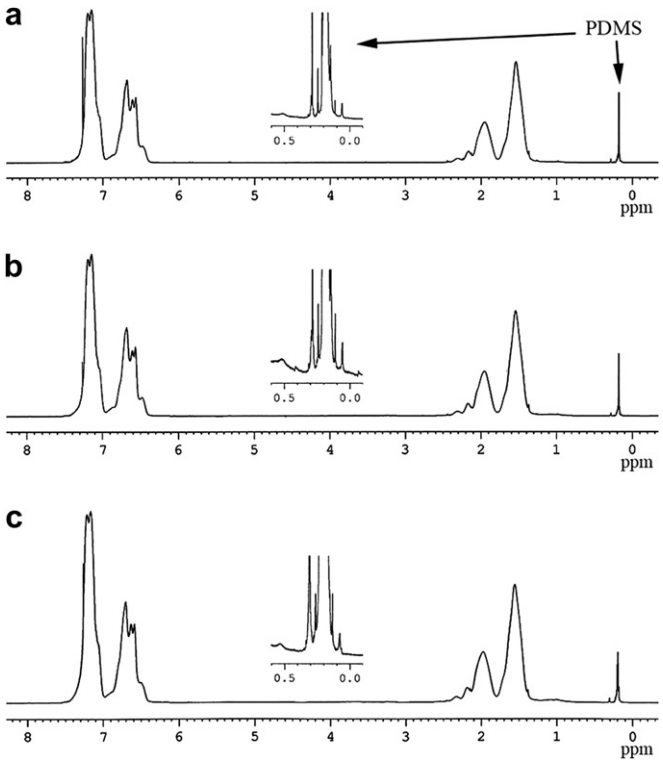

Fig. 4. ^{1}H NMR spectra for PS and PDMS blends containing 1 wt% PDMS308 with (a) 0.2, (b) 0.6 and (c) 1 wt% CD-core.

the inclusion of the guest into the β-CD cavity [30]. Whang et al. saw cross-peaks from CD-core protons on the β-CD with those of the guest cloprostenol, indicating inclusion into the cavity [31]. Furthermore, a novel β-CD-(PEG)-β-CD was complexed with a guest of bisadamantane-PEG-dimer (Ad-PEG), and ROESY was used to determine that the CD-core protons for the β-CD coordinated with Ad-PEG within the cavity [32]. ROESY has also been successfully used with γ-CD/flavonol kaempferol inclusion compounds [33], in which the H-3 and H-5 γ-CD protons were seen to interact with the guest molecule. These findings are just a few examples illustrating the use of ROESY 2D-NMR to correlate interactions in CD inclusion complexes.

The same sample solution used in Fig. 4c was analyzed with ROESY 2D-NMR and results are shown in Fig. 5. Due to the low concentrations of PDMS and CD-star in this sample, the CD-star/PDMS interactions are very weak but appear in the circled region of Fig. 5a. Magnification of this region in Fig. 5b shows that the CD-star proton signals are just discernable above the noise and exhibit cross-peaks with the methyl groups on the PDMS. These cross-peaks confirm that threading of the CD-core by PDMS takes place. Because of the statistical distribution of the arms attached to the γ-CD-core, many environmental effects can influence the CD-core hydrogen responses, which are evidenced as a broad peak between 3.1 and 3.3 ppm in Fig. 5b. This leaves the exact identification of the CD cavity hydrogens responsible for the PDMS guest cross-peaks impossible to determine with certainty.

3.3. Intrinsic viscosity measurements

Two viscosity studies were conducted for solutions of PS/PDMS/CD-star in which (i) the amount of CD-star was held constant and (ii) the amount of PDMS was held constant. Both of these studies showed the same relative trends for compatibilized solutions containing CD-star. Fig. 6 displays intrinsic viscosity values for the first case, showing results for solutions with and without CD-star. Both PDMS62 and PDMS308 were used and compared in these experiments. The samples without CD-star remain uncompatibilized and contain small domains of PDMS dispersed in a PS/chloroform solution. Recall that PS is removed from the solution as PDMS is added in order to maintain a constant solids concentration. Since PDMS exhibits a lower viscosity in chloroform compared to PS (PDMS does not dissolve in chloroform), addition of PDMS to PS/chloroform solutions results in a linear decrease in intrinsic viscosity, which can be regarded as "rule of mixtures" behavior. This type of behavior is observed for samples containing both PDMS62 and PDMS308 (data sets A and B in Fig. 6), with PDMS62 exhibiting the expected lower viscosity at each PDMS concentration.

Data sets C and D in Fig. 6 represent solutions containing CD-star. Data set C corresponds to a solution which was analyzed

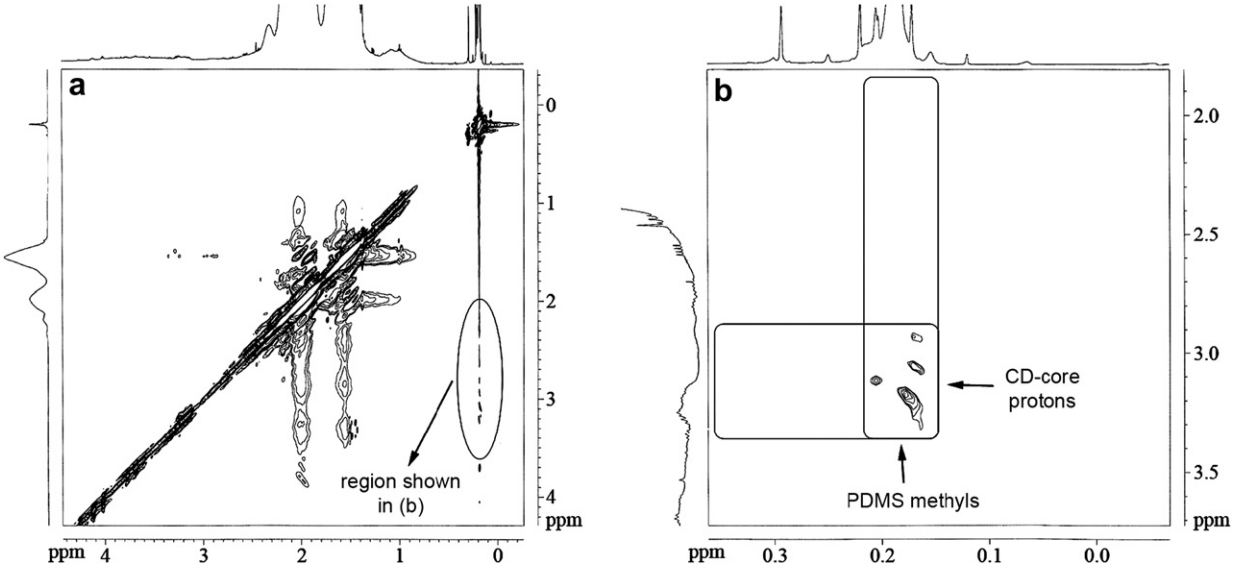

Fig. 5. (a) Partially correlated ROESY 2D-NMR spectra from compatibilized solutions of PS/PDMS/CD-star containing 1 wt% CD-core and 1 wt% PDMS308. (b) Magnified view of the circled region in (a). The full spectrum appears in Fig. 4c.

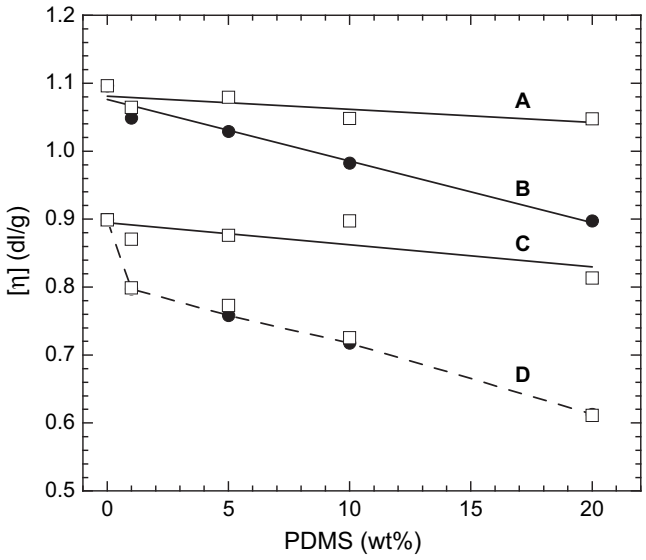

Fig. 6. Intrinsic viscosities for solutions in Table 1 diluted to 1 g/dl containing PDMS62 (filled circles) or PDMS308 (open squares). Data sets A and B do not contain CD-star, while data sets C and D contain CD-star. Data set C corresponds to an uncompatibilized solution analyzed immediately after preparation. Data sets D correspond to compatibilized solutions analyzed after stirring at 60 °C. Lines for data sets A, B and C are linear fits to the data. The dashed line for data sets D is drawn as a guide for the eye.

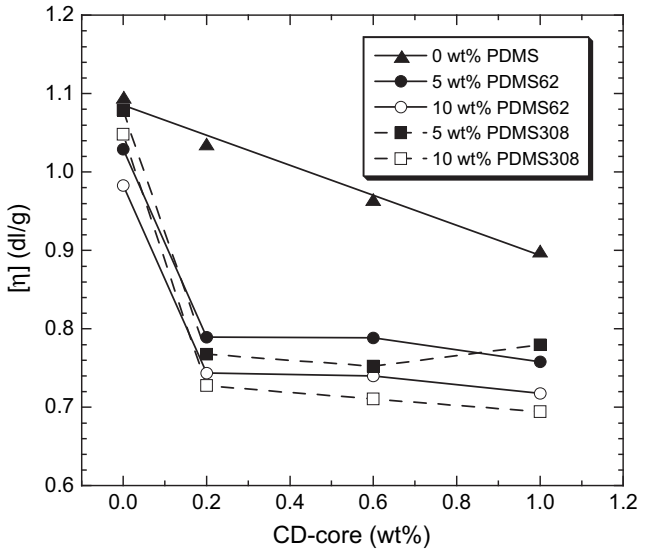

Fig. 7. Intrinsic viscosities for solutions in Table 4 diluted to 1 g/dl and containing PDMS62 (circles) or PDMS308 (squares). All solutions were compatibilized before analysis. The line for the 0 wt% PDMS data set is a linear fit to the data. The other lines are drawn as guides for the eye.

immediately after preparation and was not compatibilized *via* heating, whereas data sets D represent solutions which have been stirred at 60 °C for 3 days and are compatibilized before intrinsic viscosity analysis. The uncompatibilized solution (data set C) contains PDMS domains in a solution of PS and CD-star, and is expected to exhibit "rule of mixtures" behavior as for lines A and B. This is indeed the case, as line C is parallel to line A, both corresponding to solutions containing PDMS308. The viscosity values are lower for data set C due to the diluting effect of adding the low molecular weight CD-star to these solutions and removal of more PS.

The compatibilized solutions (data sets D) show a more significant drop in intrinsic viscosity compared to uncompatibilized solutions of the same composition (data set C). Threading of CD-star by PDMS causes a breakup of the PDMS domains followed by formation of micelles, as shown in Fig. 1. The micelles are smaller than the original PDMS domains, leading to a lower hydrodynamic volume and lower intrinsic viscosity. It is interesting to note that the variation of intrinsic viscosity with PDMS content is identical for both PDMS62 and PDMS308. This suggests that the hydrodynamic volume for the PDMS micelles in these two solutions is similar. This result is further confirmed by dynamic light scattering measurements in the next section.

In the second series of viscosity experiments (Fig. 7), the PDMS content is fixed at 0, 5 or 10 wt% and the CD-star concentration is varied. Compositions for these solutions are provided in Table 4. All solutions containing PDMS and CD-star have been stirred at 60 °C and are compatibilized before analysis. The intrinsic viscosity values for the 0 wt% PDMS solutions exhibit "rule of mixtures" behavior as CD-star is added and PS is removed. Addition of 5 or 10 wt% PDMS to a PS solution (at 0 wt% CD-core) results in a small decrease in intrinsic viscosity. However, a rapid decrease in intrinsic viscosity takes place upon addition of 0.2 wt% CD-core to the PDMS-containing solutions, again illustrating the compatibilizing effect of CD-star. The intrinsic viscosities of the PDMS solutions do not parallel the line for 0 wt% PDMS, showing clearly that the "rule of mixtures" is not followed for these solutions and that some structural reorganization takes place. As discussed above, this corresponds to the breakup of PDMS domains and formation of micelles which are smaller than the PDMS domains. After the initial decrease, the intrinsic viscosity remains fairly constant upon further addition of CD-star. Solutions containing 5% PDMS exhibit slightly larger intrinsic viscosities than 10% PDMS solutions, and the effect of PDMS molecular weight is not significant.

Several researchers have seen this same trend of reduced intrinsic viscosities [34] for block [35] and graft copolymers [36] in selected solvents after micelle formation. For example, it was found that graft copolymers of PS-graft-(4-vinyl-N-ethylpridium bromide) in an aqueous solution formed unimers regardless of concentration and displayed a reduction in intrinsic viscosity [37]. Reverse micelle behavior was seen for PMMA-g-PEO [38] or PS-g-PEO [39] in toluene and these samples exhibited a decrease in viscosity once micelles were formed. Graft copolymers of PS-g-PMMA in THF, a selective solvent for PS, had intrinsic viscosities that were lower than single chains in a good solvent for both blocks [40]. It is apparent that graft copolymers in selected solvents

Table 4
Compositions of solutions in chloroform with varying CD-star content.

PDMS[a] (wt%)	CD-star (mg)	PDMS[b] (mg)	PS (mg)	Total mass (mg)
0	0	0	500.0	500.0
0	8.2	0	491.8	500.0
0	24.7	0	475.5	500.0
0	40.3	0	459.7	500.0
5	0	25	475	500.0
5	8.2	25	466.8	500.0
5	24.7	25	450.3	500.0
5	40.3	25	434.7	500.0
10	0	50	450.0	500.0
10	8.2	50	441.8	500.0
10	24.7	50	425.3	500.0
10	40.3	50	409.7	500.0

[a] Percentages are based on total solids content. Solution concentration is 10 g solids/dl.
[b] Either PDMS62 or PDMS308.

show the same type of decreased viscosity trends that we see in our solutions, suggesting micelle formation is occurring.

3.4. Dynamic light scattering of compatibilized solutions

Dynamic light scattering (DLS) measures the diffusion coefficient of the dissolved or dispersed species in a solvent. If a spherical shape is assumed for the diffusing particle, its radius can be calculated from the Stokes–Einstein relationship [41]. For polydisperse samples, an average or effective radius is obtained, which in this work is multiplied by two and reported as an effective diameter, d_{eff}. For comparison with the DLS results, an estimate of the expected mean diameter (d) for the homopolymers used in these solutions was obtained using Equation (1), which assumes a random coil conformation for the dissolved polymer.

$$d = 2\left(\frac{MC_n l^2}{6M_b}\right)^{1/2} \quad (1)$$

Here l is the backbone bond length, C_n is the characteristic ratio, M_b is the molecular weight of the repeat unit per backbone bond and M is the polymer molecular weight. Equation (1) yielded d values of 18.1, 8.0 and 17.7 nm for PS, PDMS62 and PDMS308, respectively.

DLS measurements for pure PS in chloroform yielded a d_{eff} of 19.1 nm, in good agreement with the value calculated from Equation (1). However, DLS produced anomalous results for the PDMS homopolymers. Their limited solubility in chloroform gave d_{eff} values on the order of micrometers with large standard errors pointing to agglomeration in the solution. In addition, sample solutions containing only PS and PDMS showed large swings in the d_{eff} data, from tens of nanometers to micrometers and no consistent trends with PDMS content. For these reasons, the DLS data from these solutions are not presented.

Reliable DLS measurements were obtained for two sample sets: (i) compatibilized blends containing CD-star 2 h after diluting to 1 g/dl (from 10 g/dl as-prepared), and (ii) the same solutions as in (i) but aged for 2 days at room temperature after diluting to 1 g/dl. Aggressive stirring was implemented for the "2-day" solutions just before DLS analysis to re-homogenize the solutions. The 2-h samples remained homogeneous, therefore aggressive stirring was not used. Turbidity was not observed for either of these solutions at 1 g/dl. The compositions of sample set (i) are identical to the solutions subjected to intrinisic viscosity analysis in Fig. 6, data sets D.

Fig. 8 shows the d_{eff} values for these solutions as a function of PDMS content, where (a) displays the results 2 h after diluting to 1 g/dl, and (b) displays the results after aging the solutions for 2 days. The d_{eff} values in Fig. 8a range from 19 to 23 nm and are in good agreement with the values calculated for pure PS and PDMS308 using Equation (1). A slight increase in d_{eff} with PDMS content is indicated, and the values for PDMS308 are slightly higher than those for PDMS62.

The d_{eff} value obtained from DLS is an average of the sizes of all dissolved or dispersed species in the solvent. In these compatibilized solutions, contributions to d_{eff} come from the dissolved PS homopolymer and the micelles containing PDMS and CD-star. The fact that the d_{eff} values are relatively constant and hover around the expected value for individual PS or PDMS308 molecules suggests that the micelle size is on the order of the size of an individual PS or PDMS molecule. Otherwise, larger increases in d_{eff} with PDMS content would be expected, especially at 20 wt% PDMS. Furthermore, this suggests that the micelles formed from PDMS62 probably contain several PDMS chains. The insensitivity of d_{eff} to PDMS molecular weight is consistent with the nearly identical intrinsic viscosity values noted for PDMS62 and PDMS308 in Fig. 6, data sets D. However, the decrease in intrinsic viscosity with PDMS content for these data sets implies a decrease in hydrodynamic volume, which is not consistent with the lack of significant variation of d_{eff} with PDMS content noted in Fig. 8a. This latter result is not completely understood at present. A contributing factor could be the presence of shearing forces in viscosity measurements which may disrupt the micellar structure [42], whereas the solution is not subjected to shear in DLS measurements.

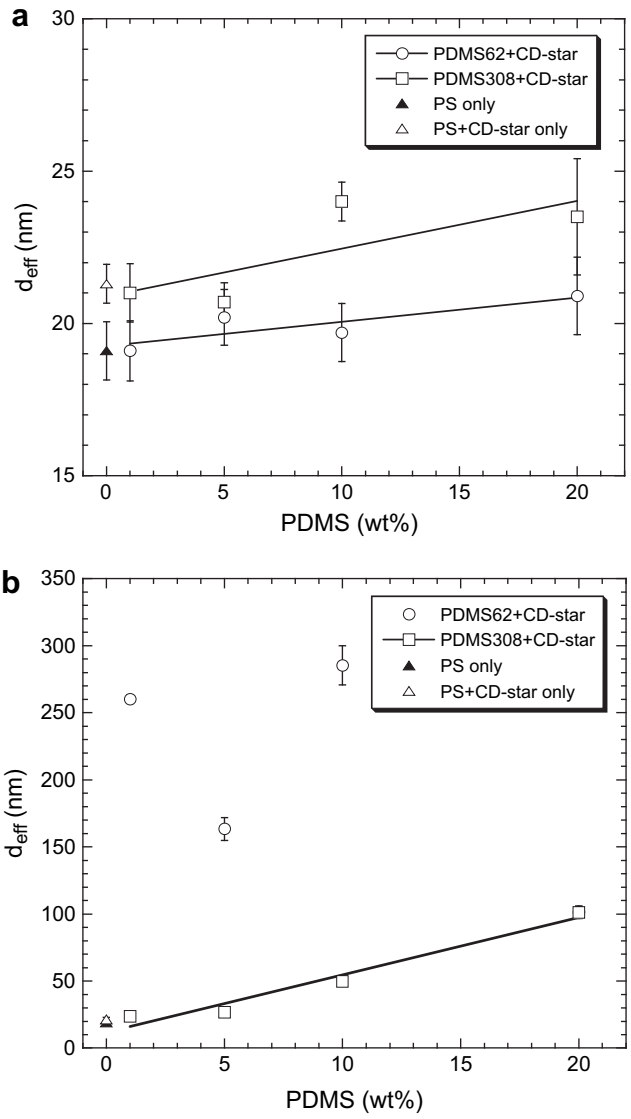

Fig. 8. Effective diameters obtained from DLS for compatibilized solutions (a) 2 h and (b) 2 days after diluting from 10 to 1 g/dl. The line is a linear fit to the PDMS308 data set. Solution compositions before dilution for samples containing CD-star are given in Table 1. In Fig. 8b, error bars are smaller than the data points when they are not shown, and data points for PDMS62 and PDMS308 overlap at 20 wt% PDMS.

A dramatic increase in d_{eff} is noted upon dilution of the compatibilized solutions from 10 to 1 g/dl, then aging for 2 days as shown in Fig. 8b. This indicates that these solutions are not stable at the lower concentration. This is in contrast to the observed stability of the 10 g/dl solutions shown in Fig. 3, which remained clear for several months. Lowering the concentration will upset the equilibrium partitioning of CD-star molecules between the PDMS micelles and the solvent, probably leading to de-threading of the PDMS from the CD-stars. As a result, more of the PDMS chains

become exposed, giving rise to re-agglomeration of PDMS into separate phase domains and larger d_{eff} values. The larger d_{eff} values for PDMS62 in Fig. 8b suggest that more de-threading and re-agglomeration occurs for PDMS62 than for PDMS308. This would be expected since de-threading of CD-star from a shorter molecule should be easier compared to de-threading from a longer molecule. These results may also indicate that the critical micelle concentration for this system occurs between 1 and 10 g/dl.

4. Conclusions

Compatibilization of PS and PDMS in chloroform is achieved by addition of a small amount of a star polymer containing a γ-CD-core and PS arms. Compatibilization is visually observed when turbid, as-prepared solutions become clear upon heating or extended stirring at room temperature. At a solids concentration of 10 g/dl, these solutions remain clear over several months. The mechanism of compatibilization involves threading of the CD-core by PDMS and solubilization of the resulting "slip-ring graft copolymer" *via* the PS star arms. This process breaks up the undissolved PDMS domains into smaller, more stable micelles. Evidence for threading of the CD-core by PDMS is found using ROESY 2D-NMR. Compatibilization requires a solvent which is good for PS and poor for PDMS.

Characterization of the compatibilized solutions by dilute solution viscosity and DLS shows that they behave similarly to graft copolymers in selective solvents which are known to form micelles. As with graft copolymers, micelle formation in the CD-star solutions is accompanied by a reduction in intrinsic viscosity. The size of the micelles is not affected by CD-star content or PDMS molecular weight within the ranges studied here. DLS measurements show that dilution of the solutions from 10 to 1 g/dl induces de-threading and agglomeration of PDMS, suggesting that the critical micelle concentration for this system lies between 1 and 10 g/dl.

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