Sum Frequency Vibrational Spectroscopy of the Comb Copolymer Cetyl Dimethicone Copolyol

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The sum frequency (SF) vibrational spectrum in the C−H stretching region of a comb copolymer, cetyl dimethicone copolyol (CDC), consisting of a poly(dimethylsiloxane) backbone and grafted poly(ethylene oxide) (PEO) and cetyl side chains has been recorded after deposition on a gold-coated substrate. Resonant assignment of the SF spectrum of CDC has been achieved by examining the spectra of several structural analogues of the polymer. Since sum frequency generation is dependent upon both infrared and Raman activity, assignment of the SF spectrum of CDC was aided by recording complementary infrared and Raman spectra. Sum frequency resonances attributable to the methyl groups of the polymer backbone and the cetyl side chains of the polymer were observed, implying conformational order of these moieties. Further, it was concluded from the phase of the cetyl resonances that the grafted alkyl chains were oriented away from the polymer/air interface. Conversely, the PEO side chains of CDC were found to be SF inactive.
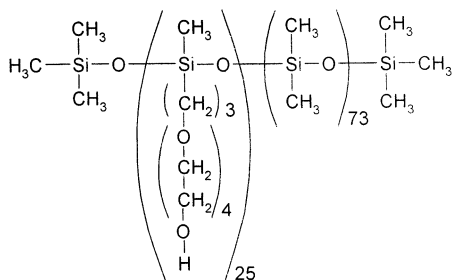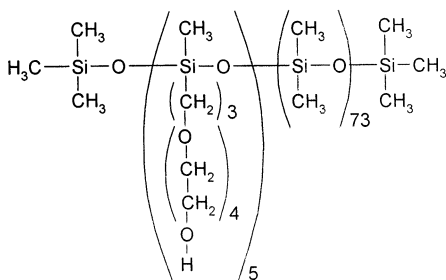
Introduction

Polymer adsorption at interfaces is employed in a diverse array of industrial and biomedical processes to advantageously modify surface properties. Many factors contribute to the surface excess, orientation, and conformation of adsorbed polymeric species. One important factor is the number and nature of the polymer end segments.[1] This dependence arises due to the interplay between maximizing the enthalpy of adsorption and limiting the loss of conformational entropy upon adsorption. For simple linear polymers of high molecular weight the effect of end segments is typically small since the two end groups comprise only a minor fragment of the polymer. By introducing chain branching, however, the number of chain ends can be significantly increased with consequent modification of the surface behavior of the polymer. Comb copolymers (also referred to as graft copolymers) represent one means of achieving an increased number of chain ends. These polymers consist of a long backbone with one or more chemically different side chains grafted onto it at regular intervals. Comb copolymers with long side chains provide an opportunity to tailor surface properties for numerous applications in, for example, adhesion and biocompatibility.[2]

Recently, the nonlinear optical technique of sum frequency vibrational spectroscopy (SFS) has emerged as an important tool in the study of polymeric surfaces.[3,4] SFS is an interfacially specific probe of molecular orientation and conformational order. The surface specificity of SFS has resulted in its successful application to the characterization of homopolymers such as polyethylene, polypropylene,[5] poly(vinyl alcohol),[6] and polyimide.[7] In contrast, few SF studies have been reported on adsorbed comb copolymers. Oh-e et al.[8] have probed the surface orientation and conformation of alkyl side chains of polyimides, discussing the effects of side chain length and mechanical rubbing of the surface on the SF spectra. Gautam and Dhinojwala[2] used SFS to determine the orientation and degree of order of the octadecyl side chains of poly(vinyl octadecylcarbamate-*co*-vinyl acetate) at the polymer/air interface. In both of the above cases a single type of side chain was investigated by SFS; further, no evidence of SF activity of the polymer backbone was reported.

In the present study SFS in the C−H stretching region (2800−3000 cm^{-1}) has been used to investigate the orientation and conformational order at the polymer/air interface of a comb copolymer, cetyl dimethicone copolyol (CDC), employed in the oral care industry.[9] CDC consists of a poly(dimethylsiloxane) (PDMS) backbone, with pendent cetyl and poly(ethylene oxide) (PEO) side chains, as shown in Figure 1. The three components of CDC (cetyl and PEO chains and PDMS) each contain methylene and/or methyl groups; consequently, the SF spectra may potentially contain contributions from all three moieties. Alkyl chains in particular are typically strongly SF active, a fact which has been widely exploited in the study of the surface activity of surfactant species[3,10,11] and, as mentioned above, has recently been extended to the investigation of the alkyl chains of comb copolymers.[8] In addition, the backbone of the CDC polymer, PDMS, has been shown to be SF active.[12] Specifically, Zhang et al.[12] concluded that the methyl groups of a homopolymer of PDMS were orientated approximately along the surface normal at the polymer/air interface. Extension of this work to a comb copolymer consisting of PDMS end groups grafted onto a hydrophilic polyurethane backbone revealed that the PDMS groups dominated the air/polymer interface.[12] Finally, SFS has been successfully applied to PEO and PEO-containing copoly-

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SF Vibrational Spectroscopy of the Copolymer CDC

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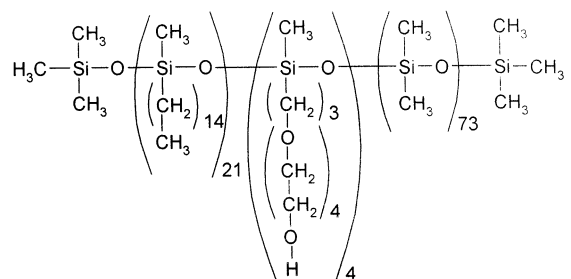
Cetyl Dimethicone Copolyol (CDC)

Dimethicone Copolyol 25 (DC25)

Dimethicone Copolyol 5 (DC5)
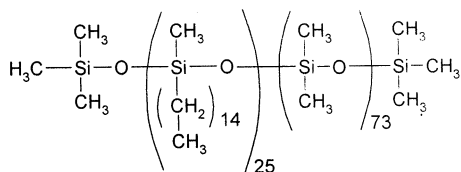
Cetyl Dimethicone (CED)

Figure 1. Molecular structures of CDC, DC25, DC5, and CED.

mers. For example, Dreesen et al.[13] studied thin films of a homopolymer of PEO and observed resonances attributed to stretching modes of the methylene groups neighboring oxygen atoms. Further, Zolk et al.[14] employed SFS to investigate alkanethiol self-assembled monolayers terminated by ethylene oxide (EO) groups, concluding that the EO oligomer exists in several energetically similar conformations. It is evident from the above discussion that SF spectra of CDC may potentially contain a convolution of multiple resonant contributions and that careful assignment and interpretation is necessary to obtain meaningful information.

The SF spectra of CDC films, formed by solvent casting onto gold substrates, were recorded at the polymer/air interface. The assignment of these spectra was achieved by comparison to simplified structural analogues of CDC, i.e., with one or the other type of side chain (or both) omitted. The assigned vibrational spectrum was confirmed via complementary Raman and infrared (IR) spectroscopies. The latter were also used to determine the relative contributions of infrared and Raman transition moments to the CDC SF spectra.

Experimental Section

The Cambridge nanosecond SF spectrometer has been described elsewhere.[15,16] Briefly, a fixed-frequency visible laser pulse ($\lambda = 532$ nm) and a variable-frequency IR pulse are overlapped both spatially and temporally on a surface. The high-energy electric field established induces a nonlinear response of interfacial species, resulting in the emission of a pulse of light at the sum of the frequencies of the two input beams ($\sim$461 nm for spectra in the 2800−3000 cm^{-1} region). The SF emission is detected by a photomultiplier tube, the output of which is recorded by a digital oscilloscope interfaced to a computer. Recording the SF intensity as a function of the IR frequency produces a vibrational spectrum of the interfacial species. Spectral modeling is performed via normalization by the nonresonant background signal of the gold substrate and fitting Lorentzian resonance line profiles using a Levenberg−Marquardt least-squares fitting routine.[15]

Polymer films for SF investigation were cast onto approximately 150 nm thick gold layers thermally evaporated onto silicon wafer supports. A thin layer of chromium ($\sim$10 nm in thickness) was evaporated onto the silicon wafer substrate prior to the gold coating to improve adhesion. The substrates were stored in methanol and subjected to a UV-ozone cleaning procedure prior to use, following the procedure of Ron et al.[17] Typical polymer samples were cast from 0.1 wt % solutions in chloroform (HPLC grade, Aldrich) using a drop volume of approximately 10 μL. The solvent was allowed to evaporate in air. Annealing the samples overnight at 80 °C had no discernible effect on the SF spectra recorded. The relative intensities of the observed SF resonances were independent of the amount of polymer deposited, in accordance with the predicted SF inactivity of isotropic bulk media and activity of surface species. In common with other workers,[18,19] spectral analysis was performed under the assumption that the dominant SF signal arose from the polymer/air interface rather than the buried polymer/gold interface. The assumption was validated through the observation of significant spectral changes when the polymer films were immersed in water, thereby perturbing the exposed polymer surface structure.

Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer in the transmission mode. Polymer solutions were prepared at a concentration of approximately 0.4 wt % in research grade carbon tetrachloride and introduced to a variable-path-length flow-through cell with CaF$_2$ windows via a peristaltic pump. Typically 64 spectra were co-added. Raman spectra of neat polymer films on glass microscope slides were collected using a Renishaw Raman imaging microscope System 1000. The excitation source was an SDL-XC30 diode laser from SDL Inc. operating at a wavelength of 785 nm and a power of 35 mW (at the sample position). The spot size was approximately 5 mm in diameter, achieved using a 50/0.75 Leica N Plan objective. A typical scan time of 3 min was employed. To facilitate a comparison between Raman spectra of neat polymer films and IR spectra of solvated polymers, IR transmission spectra of neat polymer films on CaF$_2$ substrates were recorded to quantify solvent effects. The wavenumbers of the resulting IR bands were typically within 1 cm^{-1} of those of the corresponding solution spectra, with comparable relative band intensities. It is concluded therefore that solvent effects are minimal and may be ignored for the purposes of comparison.

Overlapping bands in both infrared and Raman spectra were deconvoluted using the GRAMS/386 software package with the number and initial positions of contributing resonances selected on the basis of literature IR and Raman spectra of PEO,[20]
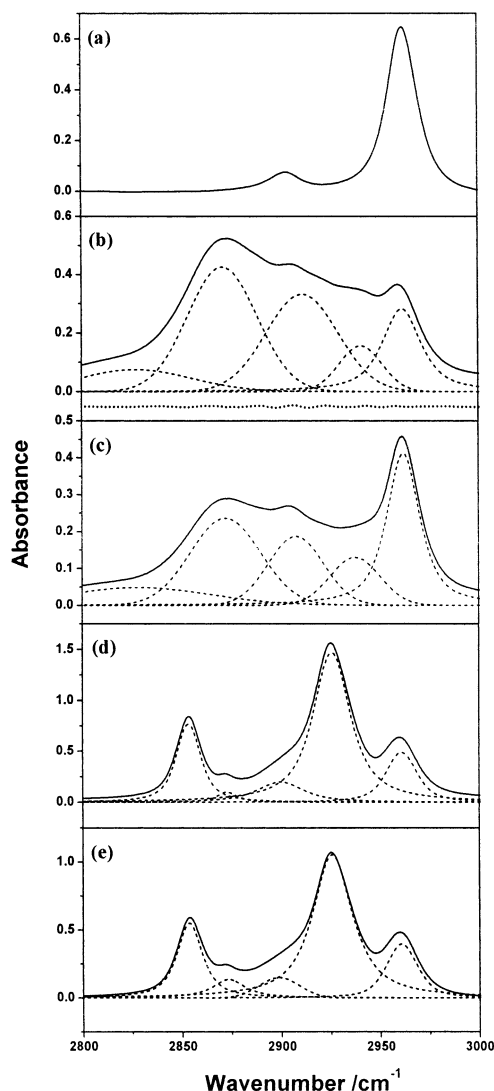
Figure 2. Transmission infrared spectra of (a) PDMS, (b) DC25, (c) DC5, (d) CED, and (e) CDC recorded in a ~0.4 wt % CCl$_4$ solution: spectral data, —; deconvoluted peaks, ---. (b) shows a typical residual of the fit, ···.

PDMS,[12,21] and *n*-alkane chains.[22,23] Peak positions, intensities, widths, and Gaussian or Lorenzian contributions were subsequently allowed to vary with the spectral fit optimized by least-squares fitting. Care was taken to ensure that the deconvoluted peak positions were internally consistent throughout related spectra and concurred with the literature values. The residual intensities achieved by this methodology (the difference between the experimental and simulated data) were typically very small (as may be seen for the representative infrared spectrum of Figure 2b and the Raman spectrum of Figure 3b), indicative of good agreement. The CDC polymer and its structural analogues employed in this study were supplied by Procter & Gamble Technical Centers Ltd., U.K. The structure of each analogue, together with that of CDC, is given in Figure 1. The copolymers were custom synthesized by randomly grafting a known average number of side chains onto the PDMS backbone. Poly(ethylene oxide) was obtained from Aldrich. All polymers were used as received.

Results

Infrared Spectra. The wavelengths of maximum absorption of the bands observed in the infrared spectra of all five polymer analogues (Figure 2) are listed in the second column of Table

TABLE 1: Observed C−H Band Frequencies (cm^{-1}) and Infrared, Raman, and SFS Assignments of CDC, PDMS, DC25, DC5, and CED[a]

polymer	IR	Raman	SFS	mode assignment
CDC	2854	2848	2855	cetyl d$^+$
		2856		cetyl d$^+$ FR
		2873		r$^+$ cetyl/PEO d
			2877	r$^+$ cetyl
		2878		d$^-$/r$^+$ cetyl (PEO d)
	2898			cetyl d+ FR
		2903		r$^+$ PDMS (cetyl d$^+$ FR)
			2908	r$^+$ PDMS
	2925			cetyl d$^-$
		2931	2933	cetyl r$^+$/d$^+$ FR
	2960	2963	2968	r$^-$ cetyl/PDMS
PDMS	2903	2904	2908	r$^+$
	2962	2965	2963	r$^-$
DC25	2828	2811		PEO d
	2871	2873	2869	PEO d
	2911			PEO d
		2904		PDMS r$^+$ (PEO d)
			2908	PDMS r$^+$
	2941	2939		PEO d
	2962	2963	2969	PDMS r$^-$
DC5	2828	2821		PEO d
	2872	2876		PEO d
	2907			PEO d
		2904		PDMS r$^+$ (PEO d)
			2908	PDMS r$^+$
	2936			PEO d
	2962	2964	2967	PDMS r$^-$
CED	2853	2848	2857	cetyl d$^+$
		2857		cetyl d$^+$ FR
	2873		2878	r$^+$ cetyl
		2880		d$^-$ cetyl (r$^+$ cetyl)
	2899			cetyl d$^+$ FR
		2903		r$^+$ PDMS (d$^+$ cetyl FR)
			2907	r$^+$ PDMS
	2926			cetyl d$^-$
		2930	2928	cetyl r$^+$/d$^+$ FR
	2961	2963	2967	r$^-$ PDMS/cetyl

[a] FR denotes "Fermi resonance".

1. Corresponding assignments are described in the text below and are summarized in the fifth column of Table 1. The IR spectrum of PDMS (the CDC backbone) is given in Figure 2a. A strong band is evident at 2962 cm^{-1} with a second weaker band present at 2903 cm^{-1}, in agreement with literature reports.[12,24] In accordance with Zhang et al.,[12] these bands are assigned to the methyl asymmetric (r$^-$) and symmetric (r$^+$) stretching modes, respectively. It is noted that a Fermi resonance of the r$^+$ mode (commonly present in IR spectra of alkyl chains at approximately 2930 cm^{-1} [23]) is not observed. We attribute this to the fact that the r$^+$ band is shifted to higher frequency by approximately 30 cm^{-1} in comparison to that typically observed by the presence of the adjacent silicon atom. Overlap with the overtone of the methyl asymmetric bending mode is therefore significantly reduced, and consequently, a Fermi resonance is not observed.

The infrared spectrum of the CDC structural analogue consisting of a PDMS backbone and 25 grafted PEO side chains (subsequently referred to as DC25 and represented schematically in Figure 1) is given in Figure 2b. It is evident that the IR spectrum of DC25 differs dramatically from that of PDMS, Figure 2a. The most intense band of the spectrum occurs at 2871 cm^{-1}, with deconvolution revealing the presence of additional weaker bands at 2828, 2911, and 2941 cm^{-1}. Comparison with the infrared spectrum of PDMS (Figure 2a) allows the assignment of the highest frequency band at 2962 cm^{-1} to the r$^-$ stretching mode of the PDMS backbone. The r$^+$

mode of PDMS (2903 cm^{-1}) may be expected to make a small contribution to the spectrum although no such band is observed. This finding is attributed to the absorbance of this mode being approximately one-tenth that of the r$^-$ mode (Figure 2a). Consequently, the PDMS r$^+$ mode is masked in the DC25 spectrum by the relatively strong additional bands evident in Figure 2b. An infrared spectrum of a PEO homopolymer (Supporting Information Figure 1) indicates that the four remaining bands obtained by deconvolution of Figure 2b are associated with methylene modes of the PEO side chains. The exact assignment of the PEO bands (to d$^+$ or d$^-$ modes) is unresolved in the literature and is therefore not given here.

The infrared spectrum of the CDC structural analogue containing a PDMS backbone and five grafted PEO side chains (DC5, Figure 2c) displays band positions comparable to and an overall profile similar to those of the spectrum of DC25 (Figure 2b). A significant decrease in the intensities of the bands at approximately 2828, 2871, 2911, and 2941 cm^{-1} is observed, supporting the assignment of these bands to methylene modes of the PEO side chains. It is noted that an increase in the intensity of the PEO mode at approximately 2907 cm^{-1} relative to that at 2872 cm^{-1} is observed in Figure 2c. This may result from a change in conformation of the PEO side chains when fewer are present in the polymer structure, a proposal supported by the fact that the intensities of C−H stretching modes are known to be sensitive to the chain conformation.[23,25] Alternatively, the relative increase in the intensity of the peak at 2907 cm^{-1} may be due to a proportionally larger contribution from the PDMS r$^+$ mode at 2903 cm^{-1} (Figure 2a) in relation to the PEO band contribution. Supporting evidence is found in the fact that the r$^-$ mode of the PDMS backbone at 2962 cm^{-1} becomes relatively more prominent in the spectrum. Further, the apparent shift in wavenumber observed for the 2907 cm^{-1} feature (from 2911 to 2907 cm^{-1}) may be attributable to the increased influence of the PDMS r$^+$ mode, which occurs at a slightly lower wavenumber (2903 cm^{-1}).

Figure 2d is the infrared spectrum of the CDC structural analogue containing 25 cetyl side chains grafted onto a PDMS backbone (shown in Figure 1, subsequently referred to as CED). The spectrum is dominated by a strong band at 2926 cm^{-1}, with weaker bands occurring at 2853 and 2961 cm^{-1} and shoulders at 2873 and 2899 cm^{-1}. In accordance with the assignment of the spectra of PDMS, DC25, and DC5, the band at 2961 cm^{-1} is attributed to the r$^-$ mode of PDMS. It is noted however that the asymmetric stretching mode of a methyl group terminating an alkyl chain typically also occurs at approximately 2960 cm^{-1}.[23] The 2961 cm^{-1} band in Figure 2d is therefore assigned to a combination of the r$^-$ modes of PDMS and the cetyl side chains. The remaining bands in the spectrum closely resemble those of linear hydrocarbon chains in terms of both their relative intensities and wavenumbers.[23] Consequently, the 2853 cm^{-1} feature is assigned to the d$^+$ mode of the cetyl side chains, the intense band at 2926 cm^{-1} arises from the corresponding d$^-$ mode, and the 2873 cm^{-1} band is attributed to the r$^+$ mode of the terminal cetyl chain methyl groups. In common with spectrum 2d, a shoulder on the low wavenumber side of the strong d$^-$ mode is often observed in infrared spectra of hydrocarbon chains and is assigned to a Fermi resonance of the d$^+$ mode. Alternatively the shoulder observed in the IR spectrum of CED (2899 cm^{-1}) may be due to the r$^+$ mode of PDMS, which occurs at a similar position (2903 cm^{-1}). However, the relative intensities of the PDMS r$^+$ and r$^-$ modes indicate that the r$^+$ stretching mode of the backbone would most likely be too weak to contribute significantly to the infrared

spectrum of Figure 2d. Consequently, the shoulder at 2899 cm^{-1} is tentatively assigned to the d$^+$ Fermi resonance of the cetyl side chains.

With reference to the full spectral assignment of each of the structural analogues of CDC above, an assignment of the bands observed in the IR spectrum of CDC itself (Figure 2e) may be made. First, it is noted that the spectrum of CDC is comparable to the spectrum of the CED structural analogue (Figure 2d) in terms of the bands present and their relative intensities. It is therefore concluded that the vibrational modes of the grafted cetyl chains dominate the infrared spectrum of CDC in the C−H stretching region. The strongest feature (at 2925 cm^{-1}) is consequently assigned to the d$^-$ mode of the cetyl chains, while that at 2854 cm^{-1} is attributed to the corresponding d$^+$ mode. In common with the assignment of CED, the 2960 cm^{-1} mode is attributed to a combination of r$^-$ modes arising from the backbone and cetyl side chains of the polymer, while the shoulder on the d$^-$ band (2898 cm^{-1}) is assigned to a Fermi resonance of the d$^+$ mode of the alkyl chains. The r$^+$ mode of the cetyl side chains would be expected to contribute to the shoulder at 2873 cm^{-1} although deconvolution of the spectrum indicates that the intensity of this mode is greater in the CDC infrared spectrum relative to the other cetyl bands. It follows that the strongest band of PEO at 2863 cm^{-1} (Supporting Information Figure 1) contributes to the CDC feature at 2873 cm^{-1}. The apparent absence of contributions from other (weaker) PEO modes is attributed to the dominance of the strong cetyl side chain resonances in the infrared spectrum.

Raman Spectra. The Raman spectra recorded for each of the five structural analogues of CDC are presented in Figure 3. The Raman spectrum of PDMS (Figure 3a) contains (in common with the corresponding infared spectrum, Figure 2a) two bands attributable to the methyl r$^+$ (2904 cm^{-1}) and r$^-$ (2965 cm^{-1}) modes. However, while these bands occur at wavenumbers comparable to those in the IR spectrum, their relative intensities are reversed. The dissimilar relative peak intensities in the Raman and infrared spectra are attributed to differences in the relative strengths of the inherent Raman and infrared transition moments.

The Raman spectrum of the DC25 polymer analogue of CDC is given in Figure 3b. Five bands are observed in the spectrum with maxima occurring at 2811, 2873, 2904, 2939, and 2963 cm^{-1}. Comparison of the DC25 spectrum with that of PDMS (Figure 3a) facilitates the assignment of the bands at 2904 and 2963 cm^{-1} to the r$^+$ and r$^-$ modes, respectively, of the PDMS backbone of the polymer. It is noted however that PEO possesses a band at 2907 cm^{-1} (see Supporting Information Figure 2) attributable to a methylene stretching mode. Consequently, the 2904 cm^{-1} feature of the Raman spectrum of DC25 must be assigned to a combination of an r$^+$ mode of PDMS and a methylene mode of the grafted PEO side chains. The remaining bands observed in the Raman spectrum of the DC25 polymer analogue of CDC which are not attributable to the PDMS backbone (2811, 2873, and 2939 cm^{-1}) arise from the grafted PEO side chains. Indeed, comparison of the deconvoluted components of the Raman spectrum of PEO (Supporting Information Figure 2) with the features of Figure 3b allows assignment of the DC25 modes to methylene stretching modes.

In the same manner as was observed for PDMS, the general profile of the Raman spectrum of DC25 is significantly different from that of the corresponding infrared spectrum (Figure 2b) in terms of relative band intensities. For example, while the methylene stretching mode of PEO was the strongest feature of the infrared spectrum, this band appears only as a weak
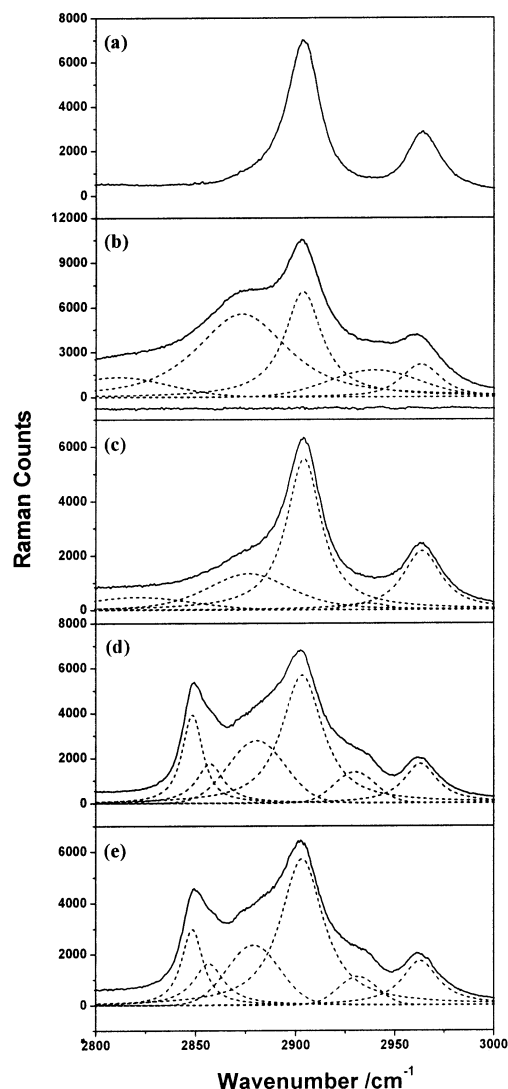
Figure 3. Raman spectra of neat polymer films of (a) PDMS, (b) DC25, (c) DC5, (d) CED, and (e) CDC: spectral data, —; deconvoluted peaks, ---. (b) shows a typical residual of the fit, ⋯.

shoulder on the PDMS r^+ mode of the Raman spectrum. As discussed previously, this observation is attributed to differences in the relative strengths of the infrared and Raman transition moments of each band. The Raman spectrum of the DC5 structural analogue of CDC (containing five grafted PEO side chains on the PDMS backbone) is given in Figure 3c. The same spectral band assignments as for the DC25 polymer analogue may be made, supported by the fact that the relative intensities of the bands assigned to the PEO side chain modes decrease substantially in intensity relative to those of the PDMS backbone.

Figure 3d is the Raman spectrum of the CED structural analogue of CDC (consisting of 25 cetyl side chains on a PDMS backbone). Comparison of the CED Raman spectrum with that of PDMS (Figure 3a) allows the assignment of the 2903 cm^{-1} band to the r^+ mode of PDMS, although a Fermi resonance of the d^+ mode of the cetyl side chains (observed in the infrared spectrum, Figure 2d) may make a minor contribution. Similarly the 2963 cm^{-1} resonance in the CED Raman spectrum may be attributed to a combination of the r^- modes of the PDMS backbone and the cetyl side chains. The PDMS contribution to the r^- feature is however expected to dominate over the cetyl chain contribution since the latter band is typically weak in Raman spectra of hydrocarbons.[22] Assignment of the bands

observed in the Raman spectrum of CED which are not attributable to the PDMS backbone may be made following the detailed assignment given by Snyder et al.[22] The d^+ symmetric stretching mode of the cetyl side chains is observed at 2848 cm^{-1}, with a shoulder attributed to a Fermi resonance of the same mode occurring at 2857 cm^{-1}. The shoulder on the 2903 cm^{-1} band at 2930 cm^{-1} is ascribed to a combination of Fermi resonances of the d^+ and r^+ modes. Finally, the broad feature at 2880 cm^{-1} is attributed to a combination of the d^- mode (shifted by $\sim$40 cm^{-1} from the corresponding IR band) and r^+ mode of the cetyl side chains.

The Raman spectrum of CDC is given in Figure 3e and closely resembles that of the CED structural analogue (Figure 3d), a phenomenon paralleling that observed for the corresponding infrared spectra. The assignment of the CDC spectrum consequently follows directly from that of CED. The bands at 2848 and 2856 cm^{-1} are attributed to the d^+ mode and a Fermi resonance of the d^+ mode, respectively, of the cetyl side chains. The broad shoulder centered at 2878 cm^{-1} is assigned to a combination of the r^+ and d^- modes of the alkyl chains. The intense band at 2903 cm^{-1} is ascribed primarily to the r^+ stretching mode of the PDMS backbone, with a potential minor contribution from a Fermi resonance of the d^+ mode of the cetyl side chains. A combination of r^+ and d^+ Fermi resonance modes gives rise to the small shoulder observed at 2931 cm^{-1}. PDMS and cetyl r^- asymmetric stretching modes both contribute to the 2963 cm^{-1} band, with the PDMS contribution expected to dominate. Detailed scrutiny of the deconvoluted spectra of CED and CDC reveals that there is a decrease in the intensity of the methylene modes of CDC relative to the r^- band, which is attributed to the removal of four cetyl side chains from the structure of the latter. Similarly, there is a relative decrease in the band at 2878 cm^{-1}, suggesting its assignment to a C$-$H stretching mode of the cetyl side chains. However, the decrease in intensity of the 2878 cm^{-1} band is less pronounced than that of the cetyl methylene modes, most probably due to the additional presence of a PEO band at 2876 cm^{-1} (from Figure 3c). Consequently, some contribution of this PEO methylene mode to the CDC band at 2878 cm^{-1} must be assumed.

Sum Frequency Vibrational Spectra. The sum frequency spectra of CDC and its structural analogues are presented in Figure 4. It should be noted that, unlike their infrared and Raman counterparts, SF spectra recorded on gold substrates may contain resonances with phases ranging from $-90°$ (dips) to $+90°$ (peaks). The actual phase observed for a particular resonance (in the absence of thin film interference effects) is related to the orientation of the molecular species undergoing resonance and hence may potentially provide information on the detailed conformation of the interfacial layer. For the purpose of assignment, however, the phase of an SF resonance is immaterial; solely the central wavenumber (obtained via the spectral modeling procedure outlined in the Experimental Section) is required. The SF spectrum of PDMS (Figure 4a) contains two resonances which may be assigned to the r^+ (2908 cm^{-1}) and r^- (2963 cm^{-1}) stretching modes of the methyl moieties. These assignments are in accordance with the corresponding infrared and Raman spectra of Figures 2a and 3a, respectively, and an earlier SF study of PDMS reported by Zhang et al.[12] It is noted that the phases of the two resonances differ (the r^+ mode appears as a peak, while the r^- mode is a dip), the significance of which is discussed below.

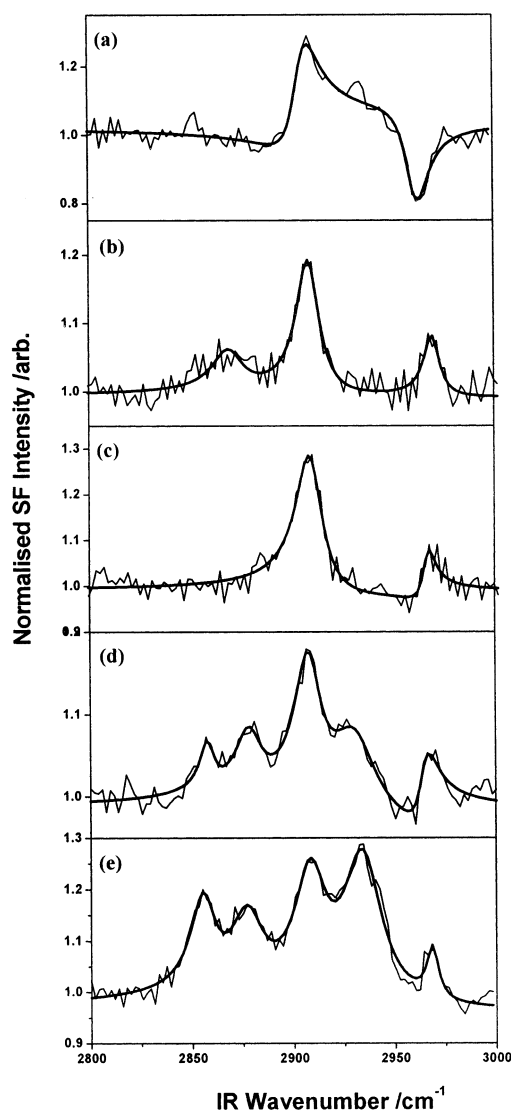The SF spectrum of the DC25 structural analogue of CDC (containing 25 grafted PEO side chains on a PDMS backbone)

Figure 4. Sum frequency spectra (ppp, sum frequency, visible, infrared, beam polarization combination) of polymer films of (a) PDMS, (b) DC25, (c) DC5, (d) CED, and (e) CDC, deposited on gold by solvent casting from chloroform: spectral data, light line; fit, dark line.

is presented in Figure 4b. The two resonances attributed above to the methyl groups of PDMS (Figure 4a) are evident in the SF spectrum of DC25, although it is noted that the phase of the r^- resonance has changed dramatically (the resonance now appears as a peak). In addition to the r^+ and r^- resonances arising from the PDMS backbone, a resonance at 2869 cm^{-1} is observed. This resonance appears prominently in both the infrared and Raman spectra of DC25 (at 2871 and 2873 cm^{-1}, respectively) and is assigned to a methylene stretching mode of the PEO side chains. Specifically, the resonance corresponds to a stretching mode of a methylene group adjacent to an electronegative oxygen,[13] as opposed to a group linking the side chains to the backbone or indeed a group bound to the terminal hydroxyl moiety of the PEO grafts. The SF spectrum of DC5 (Figure 4c) contains PDMS r^+ and r^- resonances comparable to those of DC25, but no PEO d resonance. In contrast, this same PEO feature was observed in both the IR and Raman spectra of DC5, but with reduced intensity due to the decreased number of PEO side chains present in DC5.

Figure 4d presents the SF spectrum of the CED polymer analogue of CDC. In common with the SF spectra of Figures

4a−c, the two resonances observed at 2907 and 2967 cm^{-1} in Figure 4d are attributed to the r^+ and r^- stretching modes, respectively, of the PDMS polymer backbone. It is noted that there may potentially be an additional contribution to the 2967 cm^{-1} resonance arising from the r^- mode of the terminal methyl group of the cetyl side chains of the polymer. Three resonances not attributable to the PDMS backbone are evident in the SF spectrum of the CED polymer. These resonances occur at 2857, 2878, and 2928 cm^{-1} and are attributable (in accordance with the infrared and Raman assignments of Figures 2d and 3d) to d^+, r^+, and a combination of r^+ and d^+ Fermi resonance modes, respectively, of the cetyl side chains of CED. It is noted that the significant wavenumber shift observed for the d^- resonance of the cetyl chains between the infrared and Raman spectra ($\sim$40 cm^{-1}) most likely precludes the SF activity of this mode; consequently, it is not assigned as contributing to the observed 2928 cm^{-1} resonance.

The sum frequency spectrum of CDC is given in Figure 4e. It is evident from comparison of Figure 4d,e that the SF spectra of CDC and its structural analogue CED are similar. The resonant assignment of CDC consequently follows directly from that of CED. Specifically, the resonances at 2855 and 2877 cm^{-1} are attributed to the d^+ and r^+ modes of the cetyl side chains of CDC, respectively, while the resonance at 2933 cm^{-1} is assigned to a combination of Fermi resonance modes of the d^+ and r^+ alkyl chains. The 2968 cm^{-1} resonance is attributed to r^- modes arising from both the PDMS backbone and the cetyl side chains of the polymer. Finally, the resonance observed at 2908 cm^{-1} is assigned as the r^+ mode of PDMS. In contrast to the infrared and Raman spectra, the absence of PEO resonances from the SF spectrum of DC5 would suggest that PEO does not contribute to the CDC SF spectrum, provided that the conformation of the PEO chains is not affected by the cetyl side chains.

Discussion

Following the assignment of the sum frequency spectra of CDC and its structural analogues, interpretation of the spectra of Figure 4 in terms of the orientation and conformation of the polymers in the cast films can now be made. It is therefore pertinent to briefly review the factors affecting the intensity and phase of SF resonances. More detailed discussions are available in the literature.[4] First, for a resonance to demonstrate SF activity, it must be both Raman and infrared active. The intensity of the resultant SF resonance is consequently dependent upon the strength of both the Raman and IR transition moments of the mode. Second, SF activity requires the resonant moiety to exist in a noncentrosymmetric environment, a constraint which has both macroscopic and molecular scale implications. At the macroscopic level isotropic distributions of species (for example, species in bulk solution) are inherently centrosymmetric and consequently SF inactive. The presence of an interface however induces asymmetry in the system and hence SF activity of surface species, provided the adsorbed conformation itself is not isotropic: sum frequency spectroscopy is consequently interfacially specific.

On a molecular level SF spectroscopy may be employed to provide information on the degree of conformational order of interfacial species. Specifically, SFS is commonly used to probe the conformation of interfacial hydrocarbon chains of surfactants.[10] In an *all-trans* hydrocarbon chain the constituent methylene groups lie in a locally centrosymmetric environment and hence are SF inactive. However, the presence of *gauche* defects in surfactant methylene chains breaks the local centrosymmetry, thereby making the resonances SF active. Con-

versely, terminal methyl groups of alkyl chains have no local center of symmetry, and the strength of their sum frequency activity is determined by the degree of ordering of the alkyl chains themselves. The occurrence of a methylene resonance in the absence of a methyl resonance consequently indicates the presence of *gauche* defects in the methylene chain and an isotropic distribution of the methyl groups terminating the alkyl chains, consistent with an interfacial alkyl chain layer of low conformational order. An increase in the strength of methyl resonances in relation to methylene resonances is indicative of a decrease in the extent of methyl group orientational isotropy and indicates a rise in the overall ordering of the hydrocarbon chain. Finally, the observation of solely a methyl resonance indicates that the methylene groups are entirely *trans* in conformation and are therefore SF inactive.

The phase of an SF resonance may potentially provide information regarding the orientation of the resonant species in relation to the interface being probed, provided the substrate itself has nonresonant sum frequency activity. The gold substrate, coupled with the counterpropagating beam geometry employed in this work, leads to the prediction (in the absence of thin film interference effects) that species at the polymer/air interface resonating in a direction away from the interface will generate resonant "peaks", while species resonating toward the substrate will generate resonant "dips" in the SF spectrum.[10] The absolute orientation of individual components of the interfacial species may therefore be determined simply by observing the phase of the relevant resonances in the sum frequency spectrum.

Importantly, the first conclusion which may be drawn from consideration of Figure 4 is that the observation of SF resonances indicates that the polymer films formed from CDC, and each of its structural analogues, contain a degree of interfacial conformational order. Specifically, the presence of r^+ and r^- vibrational modes in the SF spectrum of PDMS (Figure 4a) indicates that the methyl groups of the polymer are ordered in the interfacial region. This finding is consistent with the work of Zhang et al.[12] as discussed in the Introduction. Additional information regarding the orientation of the methyl groups of PDMS may potentially be obtained from the phase of the resonances in the sum frequency spectrum, as described above. Interpretation of Figure 4a is however complex since the two methyl resonances have opposite phases.

Several possible causes have been considered for this observation including a spectral contribution from the polymer/gold interface, interference effects arising due to the thickness of the films, and the existence of methyl groups in two or more distinct orientations. The possibility of significant contributions from the interface between the polymer and the gold substrate to SF spectra has been negated by the observation of major spectral changes upon perturbation of the exposed polymer surface (polymer/air interface) by immersion of the cast films in water. This finding indicates that in fact the polymer/air interface is the dominant site of SF generation and that any contribution from the buried polymer/gold interface is negligible, a conclusion supported by the recent study of Briggman et al.[19] on a related system.

The authors' group has over several years made a detailed investigation (both theoretical and experimental[15,26,27]) of thin film interference effects in sum frequency spectra. For the ppp (sum frequency, visible, infrared) beam polarization combination employed in the present work, constructive interference between the x and z components of the sum frequency electric fields generated at the polymer/air interface and transmitted into the

film, and that generated at the gold surface, results in a dominant interference term with a very slow periodicity (on the order of 3 μm). Negligible effects on measured phases and intensities of the symmetric methyl and methylene resonance over the range of film thicknesses relevant to the current study are expected. Consequently, an interpretation of general polar orientation by analysis of the r^+ and d^+ resonant phases is unaffected by potential interference effects. Conversely, due to sign differences in the second-order susceptibilities between the symmetric and asymmetric modes, destructive interference occurs for the x and z components of the sum frequency electric fields discussed above. Theoretically, a high-frequency interference term with a periodicity on the order of 160 nm (arising from the x and z components of the sum frequency electric fields generated at the polymer/air interface and transmitted into air, and that generated at the gold surface) dominates the spectra for the asymmetric stretching resonances. In practice, however, the imprecise deposition methodology (solvent casting) employed for film formation in the present study is likely to have resulted in polymer films with thicknesses varying sufficiently within each film to produce cancellation of the high-frequency periodicity due to averaging of many different phase signals. Such an occurrence would result in observed resonant phases governed by the very much weaker underlying 3 μm periodicity and consequently little phase variation in the asymmetric resonances of the measured SF spectra. It should be noted that a phase offset is predicted experimentally for the asymmetric resonances such that at near zero film thickness negative phases are expected. A very weak interference effect of long periodicity may consequently complicate interpretation of the phases of the asymmetric methyl and methylene resonances in the present study.

The final potential cause of the dual methyl phase behavior is the existence of methyl groups in two or more distinct orientations. Indeed, conformational ordering of the polymer such that one methyl group is orientated away from the interface along the axis of the surface normal with the second methyl group attached to the same silicon atom oriented below the plane of the surface (toward the bulk polymer) would be predicted to give rise to the observed sum frequency spectrum. Specifically, in the ppp (sum frequency, visible, infrared) beam polarization combination, the methyl group oriented in the axis of the surface normal would be predicted to have a strong r^+ methyl resonance of positive phase and a weak r^- resonance. Conversely, the methyl group oriented below the plane of the surface would be predicted to have negligible r^+ resonance strength but intense r^- resonance activity of negative phase.[28] In the subsequent SF spectra of PDMS modified with grafted side chains of PEO and/or cetyl chains (Figure 4b,e), the r^+ and r^- resonances both appear as peaks. In the absence of appreciable thin film interference effects, this finding suggests that the PDMS backbone at the polymer/air interface has undergone a conformational rearrangement to optimize the interfacial energy of the modified polymer. Confirmation of this hypothesis will not be possible until a full analysis of the PDMS SF spectrum, currently taking place, has been completed. However, PDMS has a high degree of flexibility, and therefore, such a conformational reorganization is entirely feasible.

The presence of a PEO methylene resonance in the SF spectrum of the DC25 structural analogue (Figure 4b) implies that, in addition to the PDMS backbone, the grafted PEO side chains possess a degree of conformational order. In a manner comparable to that discussed above for the SF activity of alkyl chains, an *all-trans* conformation of PEO side chains would be

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expected to demonstrate little or no SF activity due to symmetry considerations. Similarly, completely disordered PEO chains would be predicted to be SF inactive due to isotropy. Consequently, the appearance of a PEO resonance in Figure 4b indicates that while the side chains contain some *gauche* defects, an overall degree of ordering exists. One potential PEO chain conformation which would satisfy these conditions is the energetically favorable helical conformation of the hydrated crystalline phase of PEO.[29] Importantly, it may be deduced from the occurrence of the 2869 cm^{-1} resonance as a peak that the overall orientation of the PEO side chains is away from the substrate (in the absence of appreciable interference effects, as discussed above). It is noted that, upon reducing the number of PEO side chain units from 25 to 5, the PEO resonance is lost from the SF spectrum (Figure 4c). Two possible explanations for this observation are proposed: First, the increased volume available per side chain compared with DC25 may result in a more random conformation of the PEO chains, leading to negligible orientational and conformational order. Second, the reduced number of PEO units may provide insufficient SF intensity for observation (while retaining the same conformational order as in DC25).

The sum frequency spectrum of the CED structural analogue of CDC (consisting of 25 cetyl side chains on a PDMS backbone), Figure 4d, contains strong resonances attributable to the grafted alkyl chains. The phase of the cetyl chain resonances is positive (peaks), indicating that the overall orientation of the chains is away from the substrate. Such an orientation is consistent with the expected behavior of hydrophobic moieties at the polymer/air interface. Further, the observation of both methylene and methyl modes of the cetyl chains implies (as outlined earlier) that the alkyl chains contain a moderate degree of conformational order, that is, a proportion of *gauche* defects which is insufficient to result in an isotropic distribution of the terminal methyl groups.

Finally, the sum frequency spectrum of CDC, Figure 4e, may be interpreted in terms of its orientational and conformational order by reference to the conclusions drawn from the SF spectra of its structural analogues. First, the apparent absence of PEO resonances in the CDC SF spectrum is attributed, as for the DC5 polymer, to either a completely disordered conformation of the PEO chains or to there being an insufficient number of PEO side chains to produce a detectable SF signal. In a manner comparable to that observed in the SF spectrum of the CED structural analogue, strong cetyl chain methyl and methylene stretching modes are observed in Figure 4e. The resonances are observed as peaks, implying that, as for CED, the cetyl chains are oriented into air and away from the substrate. Further, the fact that both the r and d resonances of the cetyl side chains are observed to be strong suggests that the alkyl chains are comparatively well ordered. Comparison of Figure 4d,e shows that significant differences in the relative intensities of the resonances in the CED and CDC spectra exist. The origin of these differences may be conformational differences associated with the presence of PEO side chains in the CDC polymer. However, it is noted that relative spectral intensities were generally found to alter slightly from sample to sample as a result of the imprecise deposition methodology. Consequently, a detailed analysis of the conformation of the cetyl side chains in the related polymers is not feasible. Finally, it should be appreciated that SFS is primarily a probe of molecular level structure and hence does not report on the macroscopic morphology of interfacial layers. No conclusions may therefore be drawn with regard to the three-dimensional structure of the deposited polymer films; for example, the possibility of aggregate formation due to the amphiphilic nature of CDC cannot be excluded.

Conclusions

The sum frequency spectrum of a commercial comb copolymer, CDC, solvent cast onto gold has been assigned by comparison with the spectra of simplified structural analogues. Resonant assignment was aided by the application of complementary infrared and Raman spectroscopies. It was concluded that the PDMS backbone of the polymer orders at the polymer/air interface and that the addition of either PEO or cetyl side chains most likely leads to a conformational rearrangement of the backbone. Further, the grafted cetyl side chains of CDC were found to preferentially orient away from the interface into air and to possess a degree of conformational order. No evidence of conformational ordering of the grafted PEO side chains was found.

Supporting Information Available: IR and Raman spectra of PEO. This material is available free of charge via the Internet at http://pubs.acs.org.

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