# Diacetylene polymerization in self-assembled monolayers: influence of the odd/even nature of the methylene spacer

H. Menzel[a,1], S. Horstmann[a], M.D. Mowery[b], M. Cai[c], C.E. Evans[c,*]

[a]*Universität Hannover, Institut für Makromolekulare Chemie, Am Kleinen Felde 30, 30167 Hannover, Germany*
[b]*Merck and Co., 78-210, P.O. Box 4, West Point, PA 19486, USA*
[c]*Chemistry Department, University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109-1055, USA*

## Abstract

In this study, the interdependence between molecular architecture and photo-polymerization is evaluated for self-assembled monolayers containing diacetylenes. While such assemblies provide added robustness and versatility in molecular design, direct surface-attachment significantly limits the degrees of freedom within the monolayer structure. As a result, the polymer conjugation length as evidenced by the chromatic properties cannot be directly predicted from the extensive literature on Langmuir–Blodgett (LB) films. Indeed, a clear odd/even effect is observed in the polymerization properties of these surface-confined monolayers that is not evident in LB systems. Odd-numbered methylene spacers between the surface and the polymer backbone lead to the longer conjugation length blue form, whereas even-numbered spacers yield the shorter conjugation length red phase. This observation is consistent with simple modeling that indicates a release in localized strain upon polymerization for the odd-numbered spacer architectures. While spacers of both 5 and 9 methylene unit yield similar conversion efficiency to the blue-phase polymer, the kinetic profiles with UV exposure are quite different. The longer conversion times for the shorter spacer are attributed to lower freedom of movement within the monolayer to achieve the spatial alignment required for the topochemical polymerization. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Photo-polymerization; Diacetylene polymerization; Self-assembled monolayers

## 1. Introduction

Characterized extensively as crystals and Langmuir–Blodgett (LB) films [1–14], polydiacetylenes (PDAs) (Fig. 1) are known to exist in several chromatic phases, which appear blue, purple, or red. Although the exact nature of this chromism remains elusive, it is generally attributed to variations in the effective $\pi$-delocalization length along the polymer backbone, which is determined by the length of the polymer chain, the chain conformation, and the local environment of the polymer backbone [5,6,11,12,15]. Throughout this paper, chromatic observations will be discussed in terms of the polymer conjugation length or the effective $\pi$-delocalization length. It is understood, however, that the local environment of the backbone plays an important role in determining the chromatic properties of the polymer. As a result, factors involving chain packing and the proximity of neighboring polymer backbones may also significantly impact the chromatic properties. Both reversible and irreversible chromatic phase transitions, particularly between the blue and red phases, have been observed for multilayer films and single crystals. These colorimetric phase changes have been utilized as a transduction mechanism in sensor applications for PDAs incorporated within LB films [16–18] or liposomes [19,20]. In these sensor designs, the conjugation length of the polymer, conjectured to diminish upon interaction of a target molecule with the diacetylene (DA) bilayer, leads to a color change response.

Recent studies have shown that PDA assemblies can also be prepared as self-assembled monolayers (SAMs) on gold surfaces [21–31]. These SAMs are of particular interest because they are much more stable than LB films due to covalent binding to the substrate [26]. Furthermore, recent advances in gold deposition techniques using nanoparticle technology have extended the applicability of SAMs to more diverse nonplanar substrates [27]. Although covalent linkage to the substrate provides added durability, the

* Corresponding author. Tel.: + 1-734-763-8012; fax: + 1-734-647-4050.

*E-mail addresses:* menzel@mbox.imc.uni-hannover.de (H. Menzel), mark_mowery@merck.com (M.D. Mowery), ceevans@unmich.edu (C.E. Evans).
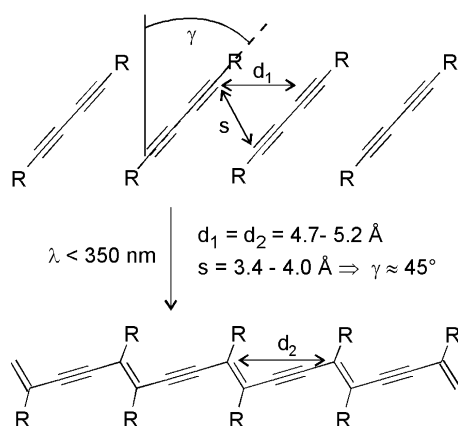
[1] Fax: + 49-511-762-4996.

Fig. 1. Steric requirements for the polymerization of diacetylenes [10,12,14].

increased interaction between the headgroup and the substrate also limits the degrees of freedom within the monolayer. As a result, the interdependence between molecular structure and polymerizability in these surface-attached diacetylene monolayers is expected to vary considerably from previous observations of diacetylene LB films [3,5–9,12].

Generally, self-assembled monolayers that incorporate diacetylene groups have been characterized as alkylthiol monolayers with an internal functional group. However, the overall structural order of these assemblies may differ from simple alkylthiol monolayers due to the presence of an internal molecular scaffolding that orders the monolayer laterally. Indeed, the spatial proximity required for polymerization [10,12,14] (Fig. 1) may be expected to yield significant interactions between neighboring, electron-rich diacetylene units. This close-packed structure of $\pi$-systems has been shown to give rise to lateral association within the monolayer [29] similar to that observed in systems showing hydrogen bonding [32,33], $\pi$-stacking [34,35], or dipole coupling [36]. As a result, the nonpolymerized monolayers apparently form a noncovalent molecular scaffolding by lateral association of adjacent diacetylene groups [29]. Using this approach, monolayer structures may be considered to consist of three distinct regions: the alkyl spacer region between the surface and the diacetylene, the tail region above the diacetylene, and the diacetylene units themselves. Indeed, previous studies of various photopolymerizable diacetylenic disulfides with different tail and spacer groups have shown two regions of spectroscopically discernible crystallinity, attributed to the tails and spacer regions, respectively [25,29].

In order to effectively polymerize the monolayer, the arrangement of the diacetylene groups within the assembly should meet the same strict spatial requirements found in crystals (Fig. 1) [10,12,14]. However, the structural variations within the different regions of the polymethylene chains can influence the properties of the SAMs and the polymerization process. In particular, the spacer has to

accommodate both the arrangement of the diacetylene units in a crystal-like structure (Fig. 1) and the orientational requirements of the Au–S bond. Previously, polymerization was found to be best for longer, odd-numbered alkyl spacers [25,29]. This was attributed to the fact that the longer spacer offers increased degrees of freedom and reduces lattice strain induced by the orientational requirements of the anchor groups at the gold surface and the packing of the diacetylene moieties. However, simple modeling reveals that, along with the overall length of the spacer, the odd or even number of methylene units may also influence the arrangement of the diacetylene units and the consequent polymerizability [31]. In this paper we describe the influence of the spacer chain on the polymerizability in diacetylene-containing self-assembled monolayers. Monolayers are fabricated using various analogs of the structure below

$$CH_3–(CH_2)_n–C{\equiv}C–C{\equiv}C–(CH_2)_m–S$$
$$|$$
$$CH_3–(CH_2)_n–C{\equiv}C–C{\equiv}C–(CH_2)_m–S$$
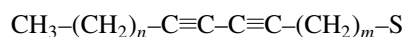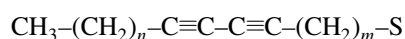
in which the tail length ($n$) is maintained at 15 methylene units and the spacer length ($m$) is varied. In particular, an analog with a shorter, odd-numbered spacer ($m = 5$) is included along with compounds with 4, 6, and 9 methylene unit spacers. Monolayers formed from these compounds are referred to as $n,m$-DA and $n,m$-PDA to refer to the unpolymerized and polymerized assemblies, respectively. In addition, the implications of this odd/even character for controlling the polymer phase properties are investigated for potential applications in sensor design.

## 2. Experimental methods

*Synthesis.* The synthesis of di(tetracosa-5,7-diyn)disulfide (15,4-DA), di(hexacosa-7,9-diyn)disulfide (15,6-DA), and di(nonacosa-10,12-diyn)disulfide (15,9-DA) was performed as described previously [25,28]. Di(pentacosa-6,8-diyn)disulfide (15,5-DA) was synthesized by the same route, which comprises isomerization of 2-heptyn-1-ol [37] using the potassium salt of 1,3-diaminopropane [38,39]. The resulting 6-heptyn-1-ol is coupled with iodinated 1-octadecyne in a Cadiot-Chodkiewicz coupling. The resulting pentacosa-6,8-diyn-1-ol is tosylated and subsequently treated with sodium hydrogen sulfide under sonication. This results in a mixture of the thiol and the symmetrical disulfide, which can be chromatographically purified using silica gel and hexanes/dichloromethane (4:1) as solvent. A white, crystalline material is obtained in all cases, with a single spot observed by TLC (hexanes/dichloromethane 4:1).[2]

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[2] $^1$H-NMR (CDCL$_3$): $\delta$ (ppm) = 2.69 (t;CH$_2$–S–S), 2.35–2.21 (m;C${\equiv}$C–CH$_2$), 1.90–1.26 (m; –CH$_2$–), 0.89 (t; –CH$_3$); FTIR (KBr, cm$^{-1}$): 2918 (CH asymm. stretch), 2948 (CH symm. stretch), 1418 (CH scissor), 718 (CS stretch). Elemental analysis: Calc. C 79.89% H 11.57% S 8.54% Found C 79.35% H 11.67% S 8.62%.
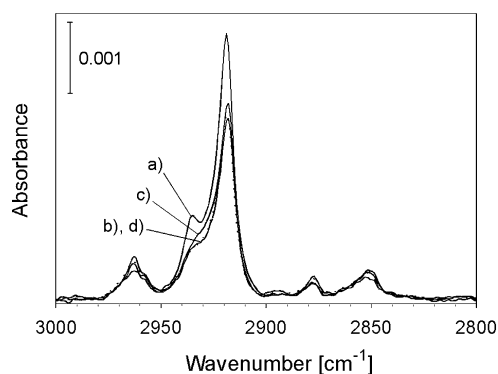
Fig. 2. Grazing-angle Fourier transform infrared spectra in the CH stretching region for diacetylene SAMs with various molecular architectures: (a) 15,9-DA; (b) 15,6-DA; (c) 15,5-DA; and (d) 15,4-Da.

*Monolayer fabrication.* Gold films were deposited on mica using a custom-built UHV thin-film deposition system described previously [29]. Using this fabrication method, atomically flat Au(111) domains of >100 nm are expected [27]. After gold deposition, the substrates were removed, immediately immersed in a 1 mM chloroform solution of the diacetylene disulfide of interest, and allowed to equilibrate at room temperature for 48 hours. Strict light control was maintained during the preparation and storage of the diacetylene solutions and monolayer films. Substrates were then removed and rinsed extensively with chloroform and deionized water (Model UV Plus Milli-Q, Millipore; >18 MΩ), and dried under nitrogen. The resulting diacetylene monolayers were subsequently polymerized under nitrogen with a low intensity UV lamp (Model UVG-11; Ultra-Violet Products Inc.; $\lambda = 250 - 260$ nm) at a distance of 2 cm.

*Fourier-transform infrared spectroscopy.* Grazing-angle FTIR experiments were accomplished using a nitrogen-purged Nicolet 550 Magna IR spectrometer with a liquid nitrogen cooled MCT detector. Spectra were obtained with a Spectra-Tech Inc. specular reflectance accessory using p-polarized light incident on the samples at 85° with respect to normal. All spectra were taken as the average of 1024 scans at a resolution of 2 cm$^{-1}$ and were referenced against a freshly prepared, unmodified gold film.

*Resonance Raman spectroscopy.* Resonance Raman spectra with 633 nm excitation were acquired using a He–Ne laser (Melles Griot), a microscope objective (10×, 0.25 NA), a spectrograph (Holoscope f/1.8; VPT; Kaiser Optical System), and a charge-coupled device (TK1024AB, Photometrics). The incident power of the laser on the sample was 4–5 mW, and the detector was cooled with liquid nitrogen to −110°C. All spectra were integrated for 1 min and calibrated using a neon lamp.

## 3. Results and discussion

The formation of the high conjugation length blue-phase polymer in self-assembled polydiacetylene monolayers on gold surfaces is crucial for potential chemical sensor applications in which the blue-to-red color transition is utilized as a transduction mechanism. In order to design interfacial systems with structural versatility and consistently good polymerization efficiency into the blue phase, it is necessary to evaluate the effect of both spacer length and odd/even character on these diacetylene monolayers. In this paper, the role of the odd/even characteristics of the alkyl spacer in determining the polymer phase behavior is investigated. Previous Langmuir–Blodgett multilayer studies indicate no discernable odd/even effect [8]. However, increased degrees of freedom within the multilayer structure may act to minimize this impact. With direct surface attachment, the degrees of freedom are significantly constrained for the monolayers investigated here.

*Odd/even effects.* In previous studies, the occurrence of blue and red polydiacetylene phases was attributed to strain in the polymer backbone which limits the effective conjugation length in the case of the red form [3,4,6–10,15,16,40,41]. The combination of the diminished degrees of freedom in surface-attached monolayers and orientational differences in the alkyl chains caused by the odd/even character of the spacer may also influence the degree of strain on the polymer backbone. In this way, the odd/even character of the alkyl spacer may play a mediating role in the ability to form blue-phase polymers in surface-attached assemblies. By maintaining the tail length at 15 methylene units and varying the alkyl spacer (4, 5, 6, and 9 methylene units), the relationship between odd/even character, alkyl spacer crystallinity, and polymer phase can be directly evaluated.

Grazing-angle infrared spectra in the methylene stretching region for these unpolymerized diacetylene monolayers are shown in Fig. 2. The methylene stretching peak position for all the architectures is centered at 2919 cm$^{-1}$, indicative of a highly crystalline environment. However, upon closer inspection, a disordered component centered around 2928 cm$^{-1}$ is evident which does not follow the anticipated trends with chain length. In fact, the disordered component is strongest for the odd-spacer length 15,9-DA monolayer, followed by the 15,5-DA assembly. The two, even-spacer length monolayers (15,6-DA and 15,4-DA) have nearly identical spectra, with a very small disordered component. The presence of this disordered component is conjectured to arise from a layered structure in which the alkyl tail appears highly crystalline and the spacer region contains a disordered component [25,29]. The origin of this disordered component in odd-numbered spacers becomes clearer when the alkyl spacer structure is modeled using known structural parameters for self-assembled monolayers and diacetylene compounds. In diacetylene self-assembled monolayers, the polymerization constraints (Fig. 1) require a tilt angle of the diacetylene groups of ~45° with respect to the surface normal [10,12,14]. Constraining this tilt angle of the diacetylene moieties at 45° results in significant
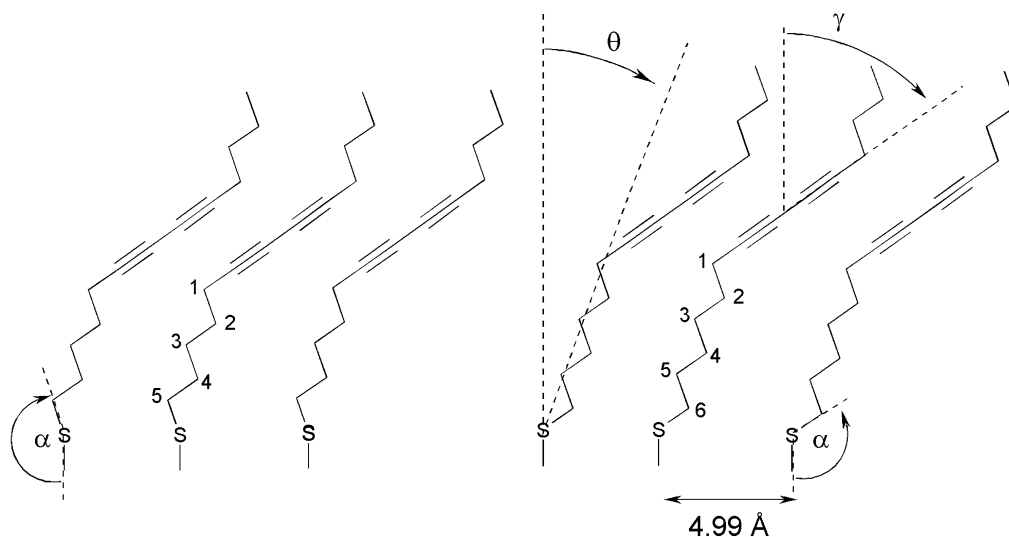
Fig. 3. Schematic representation of the structure of unpolymerized diacetylene monolayers for odd (five methylene units, left) and even (six methylene units, right) numbered spacers.

variations in the gold–sulfur–carbon bond angle for odd- and even-numbered spacers, respectively (Fig. 3). This bond angle should be 109° for an sp³ hybridized sulfur [42]. For odd-numbered spacers, all-trans alkyl chains would result in an angle of nearly 180° (sp hybridization of the sulfur atom) [43]. This anchoring has been deduced from ab initio calculations for alkyl thiol monolayers on gold [43] but, to the best of our knowledge, there is no experimental evidence for such an anchoring configuration. For mono-layers formed from alkyl thiols, it has been demonstrated that end group orientation is dependent on the number of methylene units in the alkyl chain, indicating that the anchoring via an sp³ hybridization is the most stable [44]. Based on the sp³ configuration, some gauche defects must reside within odd-numbered alkyl spacers in order to achieve both a diacetylene tilt angle of 45° and a Au–S–C bond angle of 109°, leading to the disordered component in the infrared spectra (Fig. 2). Conversely, for even-numbered spacers, an all-trans alkyl chain results in a Au–S–C bond angle close to that required for an sp³ hybridized sulfur (109°). As a result, the alkyl chain in even-numbered spacers need contain no gauche defects, and none is observed in the infrared spectra.

The implications of these odd/even effects for the polymerization properties are evaluated using resonance Raman spectroscopy. The resonance enhancement of the Raman signal for the conjugated polymer backbone allows monitoring of the polymerization process without interference from nonresonant transitions. Alkyl-based monolayers and nonpolymerized diacetylenes do not show any signal under the conditions used in this study. Further-more, resonance Raman spectroscopy can be used to discriminate the blue and red polymer phases. Excitation at 633 nm is expected to be in resonance with the blue-phase polymer exclusively, resulting in selective monitoring of the high-conjugation-length polymer phase [8,45–47].

The spectra obtained for the SAMs at 633 nm excitation are shown in Fig. 4. Transitions are assigned to vibrations for double (1459 cm⁻¹) and triple (2088 cm⁻¹) bonds. As expected for a highly conjugated system, these transitions are considerably shifted relative to the transitions antici-pated for the isolated bonds (1620 and 2260 cm⁻¹), respec-tively [46–48]. The transition in the 700 cm⁻¹ region has not been conclusively assigned in the literature, but is conjectured to arise from the in-plane stretching vibrations of the backbone [21,48,49].

Although the unpolymerized monolayers with even-spacers can adopt an acceptable orientation for polymeriza-tion without the presence of gauche bonds, this does not necessarily imply that blue-phase polymer formation is more favorable than for odd-numbered spacers. Indeed, resonance Raman spectra obtained with 633 nm excitation indicate the exact opposite trend (Fig. 4). Only those mono-layers with an odd-numbered spacer (15,9-PDA and 15,5-PDA) form appreciable amounts of the long conjugation length blue-phase polymer. The 15,6-PDA and 15,4-PDA do not form significant amounts of blue-phase polymer, and
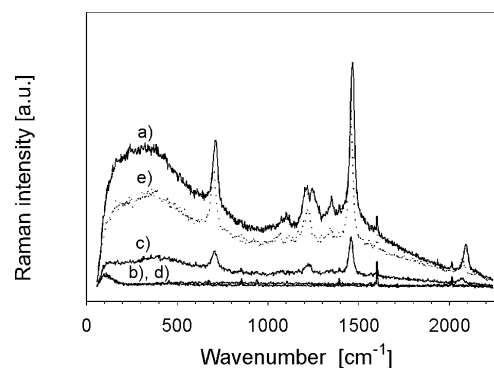


Fig. 4. Resonance Raman spectra after 7 min UV irradiation (a) 15,9-PDA; (b) 15,6-PDA; (c) 15,5-PDA; (d) 15,4-PDA; and after 60 min (e) 15,5-PDA.
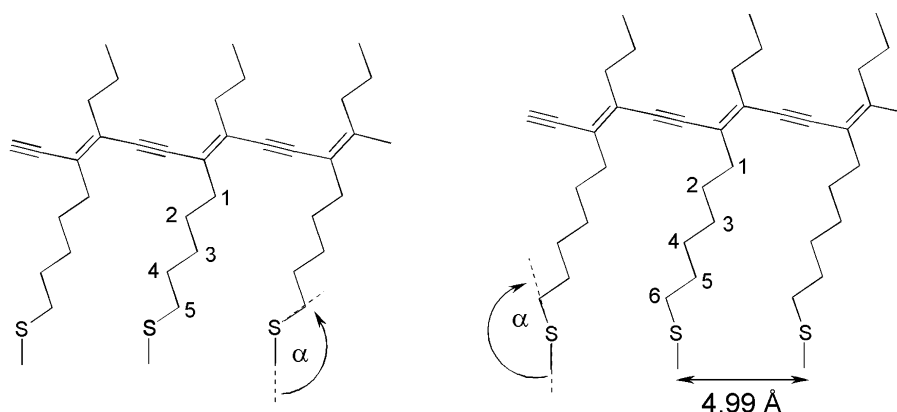
Fig. 5. Schematic representation of the structure of polymerized diacetylene monolayers for odd (five methylene units, left) and even (6 methylene units, right) numbered spacers.

were shown, in the previous dual-wavelength Raman experiments, to form the red-phase polymer, almost exclusively [25]. Again, this dramatic odd/even effect in polymer phase behavior can be explained in terms of the limited degrees of freedom within the alkyl spacer region. Because of the hybridization change from sp to $sp^2$ in the diacetylene moiety upon polymerization, some structural changes have to take place within the spacer region which is bound on one end by the newly formed polymer backbone and on the other by the gold–sulfur bond. Fig. 5 depicts a two-dimensional representation of the structure in a polymerized monolayer, with the polymer backbone constrained at an orientation parallel to the gold surface. As in the case of the unpolymerized monolayers, the major difference between the structures for even- and odd numbered spacers is the difference in the Au–S–C bond angle. In contrast to the unpolymerized monolayers, upon polymerization and the concomitant change in hybridization at the polymer backbone, an odd-numbered spacer now becomes the least strained structure. In polymerized monolayers, the Au–S–C bond angle is close to 109° for an odd-numbered spacer and almost 180° for an even-numbered spacer. As a result, after polymerization, an all-trans alkyl chain and an $sp^3$



Fig. 6. Raman intensity for the double bond vibration at 1459 cm$^{-1}$ for 15,9-PDA and 15,5-PDA as function of UV irradiation time using 633 nm light for excitation (i.e. probing blue-phase polymer).

hybridized sulfur can easily be accommodated for the odd-numbered spacers. However, the even-numbered spacers must have significant gauche defects in the spacer region in order to accommodate the $sp^3$ hybridized sulfur atom and the change in carbon hybridization at the polymer backbone. These gauche defects will likely transfer strain into the polymer backbone, resulting in a predominance of the shorter conjugation length polymer phases for the even-numbered spacers. Although a distinct odd/even effect is observed here, the possibility remains that monolayers with longer, even-numbered spacers may be able to accommodate these gauche defects without inducing strain in the polymer backbone. In fact, some support for this conjecture is evident in the very small amount of blue-phase polymer that is occasionally observed in 15,6-PDA architectures [25].

*Spacer length effects.* The results of polymerization kinetics studies shown in Fig. 6 indicate that approximately equivalent polymerization efficiency into the blue-phase polymer can be achieved for both monolayers with an odd-numbered spacer. Although similar efficiencies are achieved for the 15,9-PDA and 15,5-PDA assemblies, the polymerization kinetics exhibit a marked dependence on the alkyl spacer length (Fig. 6). The 15,9-PDA monolayer has a maximum conversion into the blue-phase polymer at 7 minutes of UV exposure followed by a gradual decrease in the long conjugation length polymer. The decrease was shown in previous dual-frequency studies [40,41] to be due, in part, to a phase transition from blue-to-red polydiacetylene. This phase transition upon extended UV exposure was attributed to localized strain in the polymer backbone induced by the sp to $sp^2$ hybridization change during polymerization (see Fig. 1) [40,41]. In contrast, the 15,5-PDA assembly has a continuous increase in blue-phase polymer up to 60 min of UV irradiation and beyond. The origin of this dramatic difference in polymerization kinetics with spacer length may be associated with the diminished spatial mobility of the shorter spacer in the 15,5-PDA assembly, relative to the 15,9-PDA monolayer. As
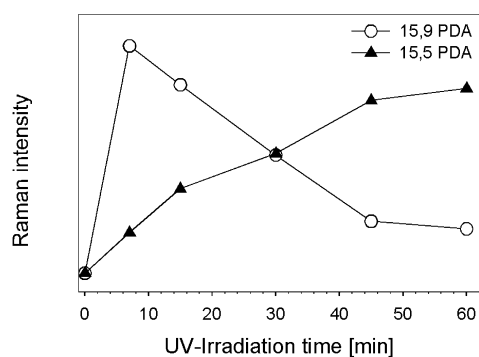
mentioned previously, the sp to sp$^2$ hybridization shift above and below the polymer backbone requires structural changes within the polymethylene chain in the spacer region during polymerization. For monolayers with odd-numbered spacers, significant gauche defects are likely present prior to polymerization. After polymerization and concomitant hybridzation shift, the bonding geometry is accommodated by an all-trans alkyl chain. It is likely that the longer spacer in the 15,9-PDA architecture can more easily accommodate the gauche to all-trans structural changes, leading to faster polymerization kinetics. Alternatively, the anchoring of the polydiacetylene backbone to a surface by a relatively short spacer might have a stabilizing effect on the polymer conformation. Several examples for stabilization of the blue-phase polydiacetylene by limiting the degrees of freedoms already have been described [15,50,51]. Nevertheless, it is significant that approximately equivalent polymerization efficiency into the blue-phase can be achieved for varying architectures. This allows greater versatility in designing interfacial structures that contain large amounts of the long conjugation length polymer for sensor development applications. In the future, these principles can be employed to design polydiacetylene interfacial systems with highly targeted structure and properties.

## 4. Conclusion

In this paper, the effect of the alkyl chain structure in self-assembled monolayers containing photopolymerizable diacetylene groups is investigated. Understanding how the conjugated nature of the polymer backbone is affected by the localized methylene chain structure is crucial for applications utilizing the unique optical and electronic properties of these polymer interfaces. Indeed, the length and the odd/even character of the alkyl chain, which connects the diacetylene units to the gold surface, are shown to significantly impact conversion to the longer conjugation length, blue-phase polymer. A significant odd/even effect was observed for these monolayers, with the long conjugation length blue-phase polymer preferentially formed for monolayers with an odd-spacer length. This dependence is not observed for Langmuir–Blodgett diacetylene monolayers/multilayers and is related to the combined constraints of the surface attachment and the hybridization shift at the polymer backbone. In addition, the polymerization kinetics exhibit a significant dependence on the methylene spacer length, with longer chains resulting in faster polymerization kinetics. By controlling the position of the polymer backbone and polymerization time, a wide range of molecular architectures and chromatic phase properties can be fabricated without large variations in chemical composition. Not only interesting from a fundamental perspective, such monolayer assemblies are central to the design of robust interfaces with well-characterized viscoelastic and optical properties.

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