PAULO FERNANDO RIBEIRO ORTEGA

NOVAS NANOESTRUTURAS DE POLIDIACETILENO: FUNDAMENTOS E APLICAÇÕES

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título de *Magister Scientiae*.

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APROVADA: 2 de julho de 2013.

Ana Clarissa dos Santos Pires

Luciano de Moura Guimarães

Luis Henrique Mendes da Silva
(Orientador)

“Aos meus queridos pais,

dedico este trabalho.”

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LISTA DE SÍMBOLOS E ABREVIAÇÕES

CAPÍTULO 1: Revisão de literatura

B: razão entre as intensidades de absorção em 640 nm em relação a soma das intensidades em 640 e 540 nm;
DA: diacetileno;
FAT: fenilacetamida;
I: Absorbância;
ITC: Titulação Microcalorimétrica Isotérmica;
LB: técnica de Langmuir-Blodgett;
Li-PCDA: sal de lítio de PCDA;
PCDA: ácido 10,12-pentacosadiinóico;
PDA: polidiacetileno;
PEO: poli (óxido de etileno);
PMMA: polimetacrilato de metila;
PVA: Polivinilacetato;
RC: resposta colorimétrica;
RMN: ressonância magnética nuclear;
UV: radiação ultravioleta;
Vis: radiação visível;
λ: comprimento de onda.

CAPÍTULO 2: Synthesis and optical properties of polydiacetylenes in triblock copolymers aqueous solution

A: absorbance;
AEPCDA: N-(2-aminoethyl)pentacosa-10,12-diynamide;
cmc: critic micelar concentration;
CR: colorimetric response;
DA: diacetylene;
EO: ethylene oxide;
ITC: Isothermal titration calorimetry;

M_n: molar mass;

NEO: number of ethylene oxide segments;

NPO: number of propylene oxide segments;

PB: ratio between the absorption intensities at 640 nm and sum of the intensities at 640 and 540 nm;

PCDA: 10,12-pentacosadiynoic acid;

PDA: polydiacetylene;

PO: propylene oxide;

PVDF: Polyvinylidene difluoride;

TCDA: 10,12-tricosadiynoic acid;

T_{tr}: chromatic transition temperature;

UV: ultraviolet radiation;

Vis: visible radiation;

ε: molar absorptivity;

ΔH: enthalpy change;

$\Delta H_{ap\text{-}int}$: apparent enthalpy change of interaction;

ΔH_{obs}: observed molar enthalpy change.

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RESUMO

ORTEGA, Paulo Fernando Ribeiro, M.Sc., Universidade Federal de Viçosa, julho de 2013. **Novas Nanoestruturas de Polidiacetileno: Fundamentos e Aplicações**. Orientador: Luis Henrique Mendes da Silva. Coorientadora: Maria do Carmo Hespanhol da Silva.

Este trabalho apresenta a proposta de síntese e avaliação de novas nanoblendas de polidiacetilenos constituídos por monômeros de ácido 10,12-pentacosadiinóico (PCDA) e ácido 10,12-tricosadiinóico (TCDA) auto-organizados em meio anfifílico formado por soluções aquosas de copolímeros tribloco. As transições eletrônicas das nanoblendas foram estudadas em diferentes temperaturas e na presença de diferentes concentrações de NaOH e Na_2CO_3, examinando os seguintes parâmetros: resposta colorimétrica (RC) e variação de entalpia aparente de interação (ΔH_{ap-int}). Os resultados mostraram ser possível modular a faixa de transição cromática das nanoblendas, induzida pela temperatura, utilizando copolímeros de diferentes estruturas e concentrações na etapa de síntese. Além disso, as RC das nanoblendas, sintetizadas em altas concentrações de L64, apresentaram-se mais sensíveis a presença dos eletrólitos em relação às nanoblendas, sintetizadas em baixas concentrações do copolímero, e às vesículas de polidiacetileno convencionais. Através da técnica de microcalorimetria de titulação isotérmica, a variação de entalpia associada com os processos de interação entre as nanoestruturas de PCDA ou TCDA e os eletrólitos foi também determinada. O valores exotérmicos de ΔH_{ap-int}, obtidos na titulação com as vesículas, foram associados à desprotonação dos grupos carboxílicos da superfície da bicamada, e os valores endotérmicos de ΔH_{ap-int}, nas curvas de titulação com as nanoblendas, evidenciam que o efeito sinérgico entre as mudanças conformacionais da macromolécula e das cadeias de diacetileno adsorvidas desempenham papel fundamental.

ABSTRACT

ORTEGA, Paulo Fernando Ribeiro, M.Sc., Universidade Federal de Viçosa, July, 2013. **New Polydiacetylene Nanostructures: Fundamentals and Applications**. Adviser: Luis Henrique Mendes da Silva. Co-Adviser: Maria do Carmo Hespanhol da Silva.

This work presents the proposal of synthesis and evaluation of new nanoblends of polidiacetilenos made of 10,12-pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) monomers self-assembled in a amphiphilic mid formed by aqueous solutions of triblock copolymers . The electronic transitions of nanoblends were studied at different temperatures and in the presence of different concentrations of NaOH and Na_2CO_3, examining the following parameters: colorimetric response (CR) and apparent enthalpy change of interaction (ΔH_{ap-int}). The results proved possible to adapt the chromatic transition range of the nanoblends, induced by temperature, using copolymers with different structures and with different concentrations in the synthesis step. In addition, the CR of the nanoblends, synthesized in high concentrations of L64, were more sensitive to the presence of electrolytes in relation to the nanoblends synthesized at low concentrations of the copolymer and the conventional polydiacetylene vesicles. Through the isothermal titration microcalorimetry technique, the enthalpy change associated with the processes of interaction between the PCDA or TCDA nanostructures and the electrolytes were also determined. The exothermic values of ΔH_{ap-int}, obtained by titration with vesicles, was associated with deprotonation of the carboxylic groups of the surface of the bilayer, and the endothermic values of ΔH_{ap-int}, in the titration curves with nanoblends, demonstrate that the synergistic effect between the conformational changes of the macromolecule and the diacetylene chains adsorbed play a key role.

CAPÍTULO 1
Revisão de literatura

1. Introdução

O desenvolvimento de novos materiais que objetivem aplicações tecnológicas e que sejam de baixo custo e de simples construção tem sido alvo de grande pesquisa pela comunidade científica de forma geral. Materiais, como os polidiacetilenos, que apresentam sensível mudança em suas propriedades físico-químicas, na presença de baixas concentrações de substâncias estratégicas, têm sido extensivamente estudados devido a sua natureza complexa e ao seu potencial para diferentes aplicações[1].

Os PDAs são polímeros que possuem características estruturais, eletrônicas e óticas únicas, e sofrem uma mudança de cor e uma indução de fluorescência de forma abrupta, sob a ação térmica, mecânica, química e biológica[2]. Apesar do PDA ter sido preparado pela primeira vez por Wegner[3] em 1969, apenas em 1993 que Charych[4] e colaboradores exploraram seu potencial como sensor utilizando um filme de PDA em monocamada ligada a ácido siálico para o reconhecimento específico do vírus Influenza. Desde então, as pesquisas acadêmicas no desenvolvimento desses materiais inteligentes contendo PDAs aumentaram exponencialmente na tentativa de criar novos sensores químicos, biológicos e materiais específicos para aplicação em eletrônica[1,5].

Devido ao elevado número de fatores que influenciam na transição crômica dos PDAs, também há esforços dos pesquisadores tanto na elucidação do mecanismo de transição, ainda não totalmente entendido, quanto no processo de síntese e estruturação dessas surpreendentes moléculas que despertam a atenção das mais diversas áreas da ciência. Além disso, um fator limitante para a utilização dos PDAs como sensores colorimétricos consiste na limitada faixa de intensidade da perturbação que causa a transição cromática. Dessa forma é um desafio científico estender essa faixa ou modulá-la de forma conveniente para a utilização adequada destes materiais como sensores a fim de atender os mais diversos setores tecnológicos.

Portanto, neste trabalho uma nova metodologia de auto-estruturação de moléculas de PDA em meio anfifílico formado por solução aquosa de copolímeros tribloco é mostrada. Esse novo ambiente, no qual os diacetilenos se agregam, facilita não só o processo de auto-organização e polimerização dos monômeros, mas também modifica a barreira energética rotacional da estrutura conjugada dos PDAs, permitindo o controle de sua faixa de transição cromática.

2. Polidiacetilenos: Estrutura e Transição Eletrônica

Os PDAs são polímeros, com ligações duplas e triplas alternadas, formados a partir de monômeros de diacetileno (DA) em uma reação de adição 1,4 induzida por radiação ultravioleta[6], como mostrado na Figura 1.

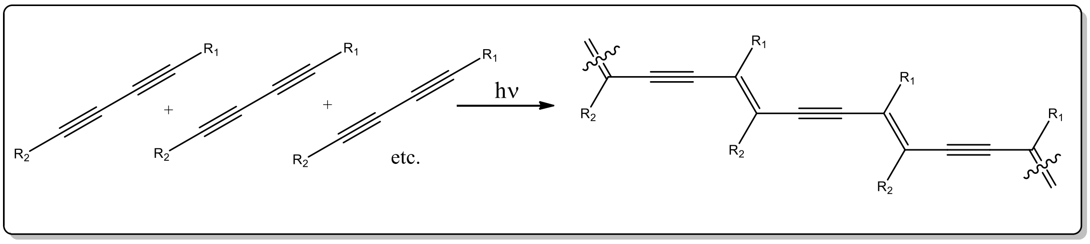

Figura 1. Polimerização dos monômeros de Diacetileno por reação de adição 1,4.

Os grupos R na Figura 1 conferem as características anfifílicas destas moléculas, onde R_1 geralmente contém um grupamento polar e R_2 uma cadeia carbônica saturada. Além disso, os PDAs são formados em estruturas auto-organizadas como filmes monomoleculares[7] ou multicamadas[8], micelas[9], partículas nanoestruturadas[10] ou vesículas[11]. Em qualquer uma destas estruturas o sistema eletrônico π-conjugado confere a estes materiais características especiais como a transição cromática brusca sobre determinados estímulos físico-químicos.

A absorção de radiação por estes materiais ocorre via transição π-π^* na estrutura conjugada do polímero, exibindo um pico de máxima absorção em aproximadamente 640 nm e passando a absorver em 540 nm após o estímulo. Essas pequenas variações dependem da natureza dos grupos R laterais ao esqueleto principal do polímero bem como das diferentes estruturas em que o PDA pode ser formado. A transição cromática também é conhecida na literatura como transição colorimétrica ou transição azul-vermelho e apenas a fase vermelha exibe emissão fluorescente, ao contrário do estado inicial correspondente à fase azul. Isso tem sido justificado por considerações de simetria de orbitais onde os estados excitados de mais baixa energia da fase azul possuem a mesma simetria do estado fundamental (A_g), resultando em uma transição proibida[12,13]. A Figura 2 mostra os espectros de absorção e de intensidade fluorescente típicos dos PDAs antes e após a transição cromática em azul e vermelho, respectivamente.

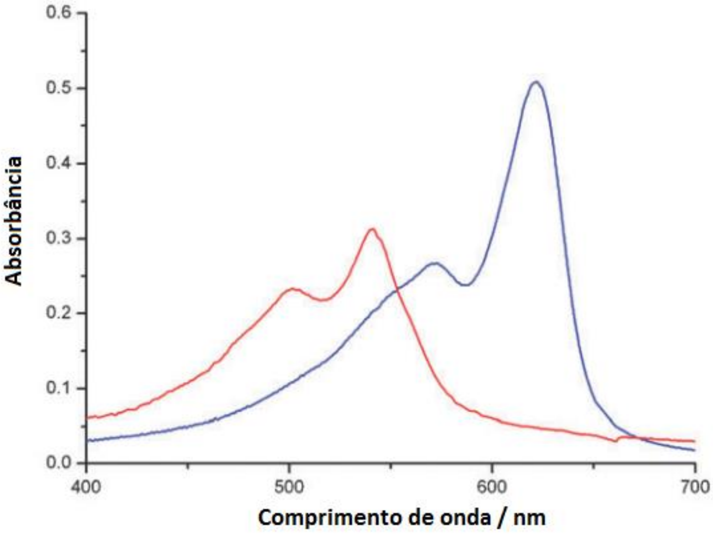

Figura 2. Espectros de absorção UV-Vis típicos dos PDAs.

Os espectros eletrônicos dos PDAs antes do estímulo apresentam uma banda de absorção típica em 640 nm e um ombro vibrônico em 590 nm de tal forma que o material apresenta uma coloração azul (fase azul). Após o estímulo estes sistemas apresentam bandas resultantes de transições eletrônicas em 540 e 490 nm e o material apresenta-se com coloração vermelha (fase vermelha).

Apesar de esforços crescentes objetivando aplicar estes materiais em dispositivos eletrônicos e como sensores para alguns micro-organismos, o mecanismo fundamental envolvido na transição colorimétrica ainda não é totalmente entendido. Uma das propostas sugere que a transição colorimétrica envolve a transformação da estrutura conjugada en-ino para a forma de um butatrieno no qual há três ligações duplas em sequência[2,14]

(Figura 3).

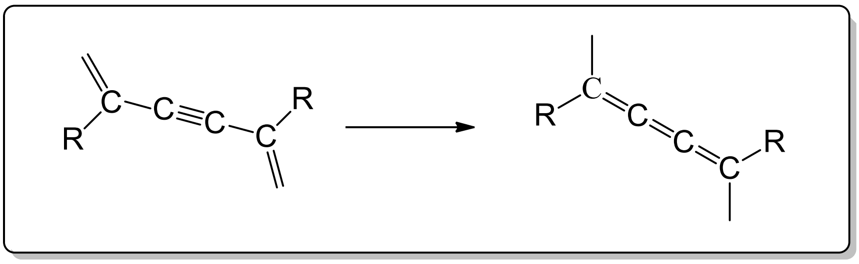

Figura 3. Reestruturação da cadeia conjugana en-ino para a forma de butatrieno.

Entretanto, estudos espectroscópicos e cálculos quanto-mecânicos mostram que a forma en-ino alternada está presente em ambas as fases[15,16]. A segunda hipótese sugere que a transição colorimétrica é resultado de mudanças conformacionais na estrutura conjugada do polímero que geram uma redução do comprimento da caixa dos elétrons π-conjugados. A fase azul e a fase vermelha teriam suas cadeias principais em uma conformação planar (mais conjugada) e não-planar, respectivamente[17]. Alguns estudos utilizando ressonância magnética nuclear (RMN) e espectroscopia no infra-vermelho suportam este modelo, sendo, portanto, o mais aceito pela comunidade científica atualmente[18,19,20,21]. Além disso, cálculos teóricos afirmam que apenas uma pequena rotação em torno da ligação simples C─C reduz a sobreposição dos orbitais π, alterando o espectro eletrônico[22].

A Figura 4 traz uma representação esquemática da rotação em torno das ligações simples na estrutura central do polímero.

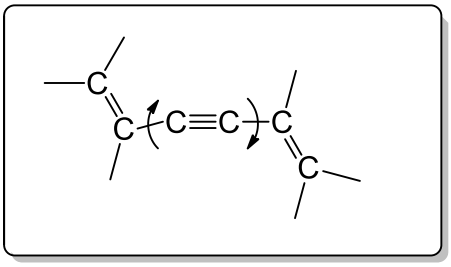

Figura 4. Representação esquemática da rotação em torno das ligações simples na estrutura conjugada dos PDAs.

As diferentes formas na qual as moléculas de PDA são organizadas também reflete em seu mecanismo de transição, além de possibilitar diferentes aplicações para cada caso. Os PDAs podem formar arranjos supramoleculares em uma, duas ou até mesmo em três dimensões, devido a facilidade com que os diacetilenos são estruturados e modificados. É possível também, através de reações químicas simples, modificar a cadeia hidrocarbônica e inserir grupos funcionais específicos nos DAs, alterando as interações intermoleculares e, consequentemente, modificando a barreira energética rotacional do polímero que é uma função da diferença de energia dos estados conformacionais das fases azul e vermelha[1].

Na maioria dos artigos e revisões da literatura, os PDAs sofrem uma transição cromática irreversível que é um fator limitante no desenvolvimento de alguns tipos de sensores colorimétricos. Nesse contexto, Chen e Yoon[23] (2011) modificaram monômeros do ácido 10,12-pentacosadiinóico (PCDA) incorporando um grupo fenilacetamida (FAT) na cabeça polar do ácido carboxílico. A partir dos monômeros de FAT-PCDA, vesículas de polidiacetileno foram preparadas apresentando termocromismo reversível na faixa de temperatura entre 30 e 70 ºC. Os autores atribuíram a causa dessa reversibilidade às ligações de hidrogênio e às interações de empacotamento π entre as cabeças adjacentes dos FAT-PCDA.

Balakrishnan e colaboradores[24] (2010) também investigaram o termocromismo reversível de estruturas baseadas em monômeros de PCDA. Os autores formaram filmes a partir de soluções de álcool polivinílico na presença do sal de lítio de PCDA (Li-PCDA) e de lipossomas de PCDA em placas de Petri secas após 5 dias. Foi observado o termocromismo reversível até 140 ºC apenas nos filmes formados com Li-PCDA, como pode visto na Figura 5.

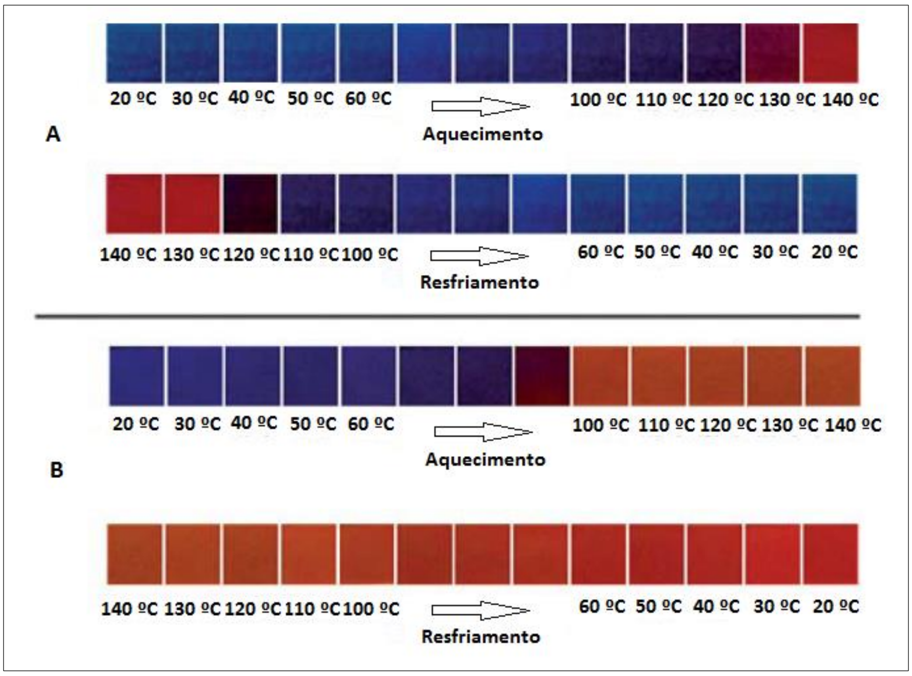

Figura 5. Fotografias da solução de Li-PCDA **(a)** e lipossomas de PCDA **(b)** embebidas em filme de PVA em diferentes temperaturas[24].

As diferentes arquiteturas formadas pelos PDAs quando estes são preparados ainda é de difícil controle e elas são formadas na maioria dos casos aleatoriamente[1]. A formação de estruturas unidimensionais é comumente favorecida de tal forma que Russel e colaboradores[25] (2004), estudando a atividade antibacteriana desses nanomateriais, verificaram que sais de monômeros de diacetileno anfifílicos contendo um grupamento amina em sua cabeça formam tubos finos bem definidos em solventes orgânicos.

Outro método utilizado para a formação de PDAs unidimensionais foi feito através do processo de eletrofiação[26]. Nesta técnica uma solução de polímero é ejetada a partir da superfície de uma solução estoque quando uma diferença de potencial é aplicada a um capilar condutor ligado ao reservatório da solução. As fibras poliméricas são formadas em um jato direcionado por forças eletrostáticas e coletadas em uma tela. No caso da formação de fios contendo os PDAs, inicialmente os monômeros DA estão distribuídos aleatoriamente em solvente orgânico contendo o polímero suporte (PEO, PMMA, PVA, etc.). Após a eletrofiação, o solvente é evaporado e a polimerização ocorre via irradiação UV sobre a tela coletora, formando, por fim, PDAs inseridos em fibras poliméricas e arranjados em uma única dimensão. Essas fibras apresentam diferentes respostas colorimétricas quando expostas em solventes orgânicos e foram aplicadas com um sensor para a identificação da qualidade da gasolina[27].

A Figura 6 ilustra o método de obtenção das fibras de polímero contendo os PDAs com diâmetro de alguns nanômetros até micrômetros.

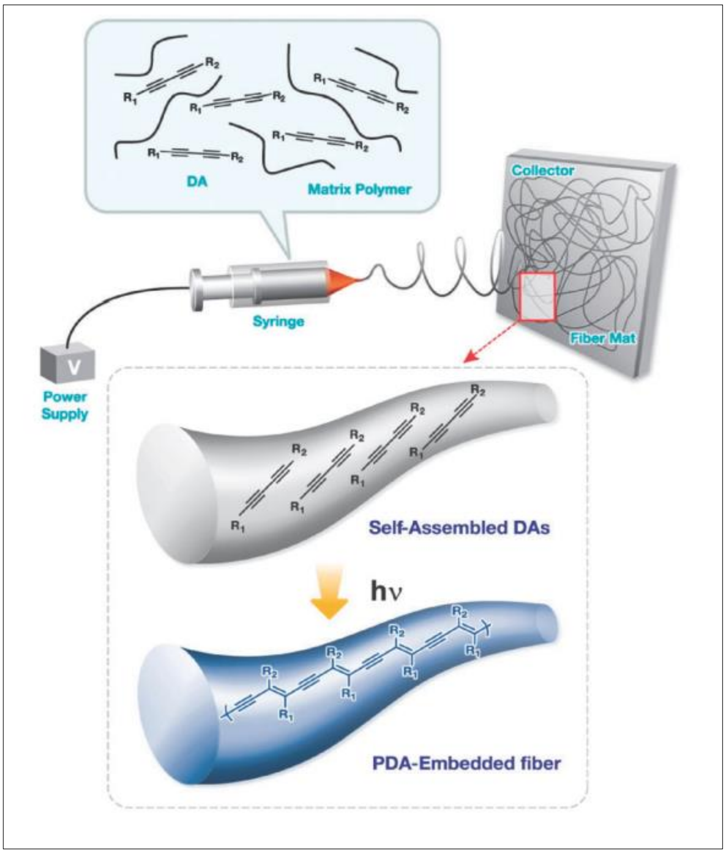

Figura 6. Representação esquemática da formação de nanofibras de PDA-polímero através de eletrofiação[26,27].

A formação de estruturas bidimensionais também tem sido explorada na literatura devido a sua possibilidade de revestir superfícies para tecnologia de imagem[28]. A deposição de monocamadas através da técnica de Langmuir-Blodgett (LB) tem sido muito utilizada na construção de filmes em duas dimensões e com alto grau de orientação e organização estrutural. Essa técnica permite a deposição em nível molecular de monocamadas com diferentes arquiteturas, formando filmes ultrafinos que podem, em princípio, ser utilizados na fabricação de dispositivos de eletrônica molecular[29].

Já os PDAs estruturados em três dimensões incluem os cristais de PDA[30], micelas[9] e vesículas[6,31], e possuem a vantagem de ter uma maior área superficial e maior número de sítios de interação, quando comparados com estruturas uni e bidimensionais. Essas características fazem com que as estruturas tridimensionais sejam as mais indicadas na aplicação de sensoriamento de moléculas ou íons com relevância tecnológica e ambiental.

As vesículas são as formas tridimensionais dos PDAs mais encontradas na literatura e se assemelham, até certo grau, à organização de uma membrana celular. Assim como as membranas biológicas, as vesículas podem reconhecer seletivamente algumas moléculas estratégicas em sua interface, se os monômeros apresentarem sítios de ligação específicos, assim como as “proteínas antena” na superfície da célula.

Essas estruturas geralmente são encontradas na forma de membranas esféricas com características essencialmente fluídicas que englobam em seu interior uma fase aquosa ou orgânica. No caso das vesículas de PDA, a sua construção é feita em meio aquoso e os monômeros diacetilênicos devem ser organizados e orientados favoravelmente para que se consiga a posterior reação de adição 1,4.

Na formação das vesículas de PDA, os DAs são hidratados e individualizados em uma etapa de sonicação. Em seguida, este sistema é acondicionado a 4 ºC por um tempo superior a oito horas, necessário para a auto-organização dos monômeros na forma de bicamada. A temperatura mais baixa também é necessária para que os monômeros alinhados estejam preferencialmente na conformação trans, de forma que após a fotopolimerização o PDA esteja na conformação planar.

A Figura 7 ilustra a arquitetura dos monômeros de PCDA auto-organizados e a formação da fase azul após a ligação 1,4 de monômeros adjacentes.

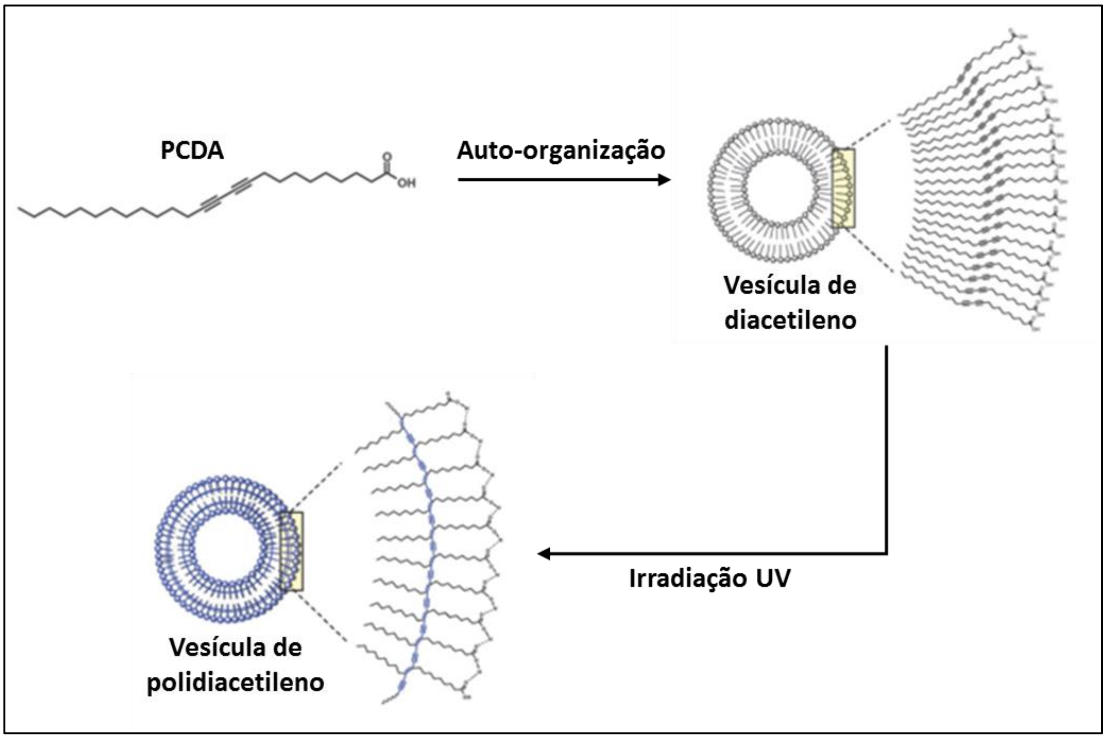

Figura 7. Esquema representando a auto-organização dos monômeros de PCDA e a formação de vesículas de PDA após a irradiação UV.

3. Aplicações dos Polidiacetilenos como sensores colorimétricos

As mudanças em suas propriedades óticas e eletrônica têm motivado os pesquisadores a utilizarem os PDAs como sensores de natureza diversa. Vários estudos na literatura avaliaram a transição cromática dos PDAs induzida por bactérias[32], biomoléculas[33,34], solventes orgânicos[8,35], temperatura[36], pH[37], surfactantes[38], íons[39], dentre outros. A resposta colorimétrica (RC) é um parâmetro proposto por Charych (1993) capaz de informar de forma quantitativa a extensão da transição de cor após um determinado estímulo, além de ser útil como propriedade analítica do sensor[4].

A Figura 8 ilustra os espectros de absorção de vesículas formadas a partir do PCDA antes e após a adição de quantidades crescentes de solução de NaOH. Nota-se que o máximo de absorção em ~ 640 nm diminui sua absorbância, enquanto a fraca absorção em ~ 540 nm aumenta sua intensidade com o aumento do pH do meio.

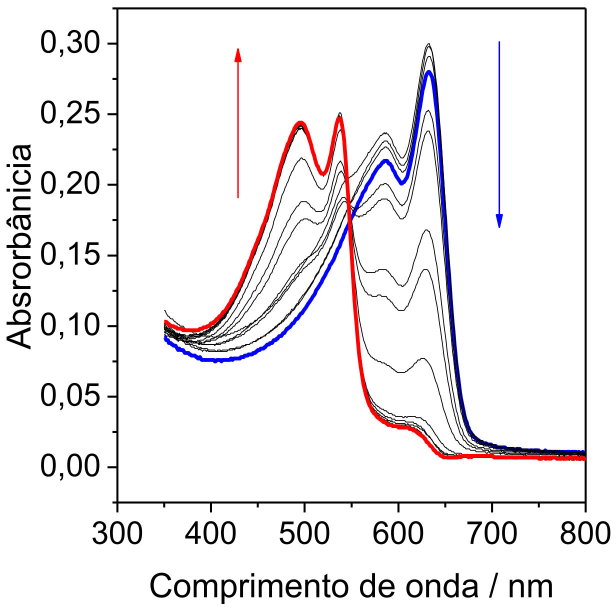

Figura 8. Espectros de absorção UV-Vis das vesículas de PDA na presença de diferentes concentrações de NaOH.

Para quantificar a resposta colorimétrica dos PDAs, os espectros UV-Vis são analisados antes e após o estímulo. Define-se então, a razão entre a intensidade de absorção no comprimento de onda (λ) de 640 nm em relação a soma das intensidades em 640 e 540 nm que correspondem às fases azul e vermelha, respectivamente.

$$B_0 = I_{640}/(I_{640} + I_{540}) \tag{1}$$

onde B_0 corresponde a razão das intensidades antes do estímulo. I_{640} e I_{540} são as absorbâncias em 640 e 540 nm, respectivamente. Após a adição da solução de NaOH ou de agente perturbador dos PDAs, define-se:

$$B_1 = I_{640}/(I_{640} + I_{540}) \tag{2}$$

onde B_1 corresponde a razão das intensidades após o estímulo.

A RC corresponde então a uma medida da extensão da transição de cor dos PDAs, ou da fração de moléculas de PDA que sofreram a transição azul-vermelho.

A RC é expressa em porcentagem de acordo com a equação 3.

$$RC = \frac{(B_0 - B_1)}{B_0} \times 100\% \qquad (3)$$

Como a RC é uma função da concentração do agente perturbador ou da intensidade do estresse aplicado no sistema, tal como o aumento da temperatura do sistema, as curvas colorimétricas permitem uma melhor visualização e compreensão do fenômeno. A Figura 9 ilustra a RC em função da concentração de NaOH calculada a partir dos espectros da Figura 8.

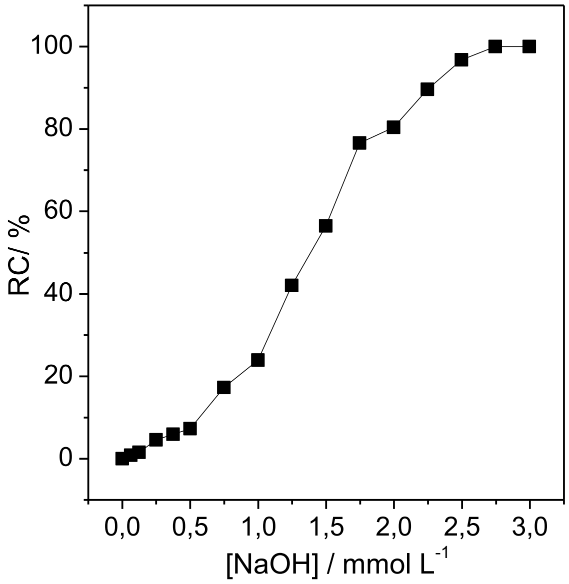

Figura 9. RC das vesículas de PDA em função da [NaOH].

Com a facilidade de construção de materiais baseados nos PDAs e com a simplicidade dos métodos óticos, diversas pesquisas têm sido feitas para utilizar a transição colorimétrica destes polímeros de maneira sensível e seletiva. Uma das formas que tem sido utilizadas em pesquisas recentes consiste na incorporação de receptores moleculares específicos na superfície de vesículas ou em filmes em mono ou multicamadas. Isso pode ser feito modificando apenas uma fração dos monômeros convenientemente ou incorporando moléculas entre os monômeros adjacentes na estrutura do PDA. Dessa forma, quando os ligantes interagirem covalentemente ou por interações fracas com os receptores, uma perturbação no esqueleto conjugado dos PDAs irá resultar em uma transição colorimétrica total ou parcial.

Yoon e colaboradores[40] (2011) prepararam vesículas de PDA a partir de monômeros contendo um grupo imidazólio ligados a grupos azida e alquino. Essas vesículas funcionalizadas foram utilizadas para a detecção de Cu^{2+} em sua superfície através de uma reação click. Os íons Cu^{2+} foram adicionados à suspensão de vesículas na presença de ácido ascórbico sendo reduzidos a Cu^{+}. Essa redução, promovida pelo ácido ascórbico, é catalisada pelos grupos azida e alquino implicando na modificação conformacional da estrutura do polímero conjugado. Os autores obtiveram um sensor específico para íons cobre visto que nenhum outro cátion foi capaz de promover uma resposta colorimétrica superior a 60% em concentrações 50 vezes maior que a da espécie de interesse (Figura 10).

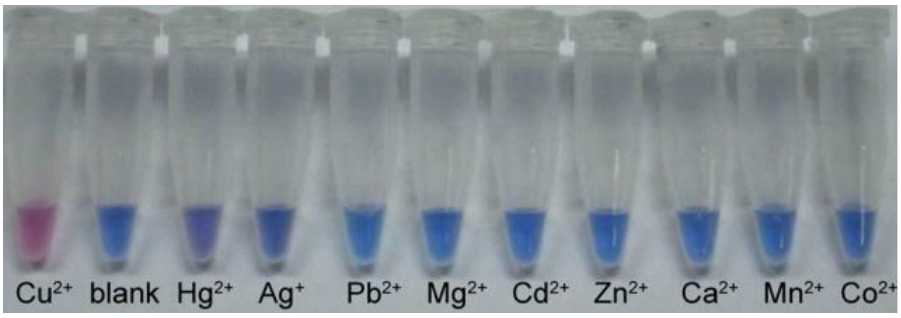

Figura 10. Fotografia das soluções de PDA funcionalizado com grupos azida e alquino na presença de diversos cátions.

Sukwattanasinitt e colaboradores[41] (2011) sintetizaram diferentes ésteres de etileno glicol a partir de monômeros de PCDA e construíram vesículas com misturas destes novos monômeros e PCDA na razão molar de 1:9 para a detecção seletiva de íons Pb^{2+}. O sensor foi capaz de detectar o metal em níveis de partes por milhão e sem RC significativa na presença de vários íons tais como Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{+}, Ni^{2+} e Zn^{2+}. A transição colorimétrica foi atribuída à perturbação das cadeias provocada pela fusão das vesículas induzida pela ligação do Pb^{2+} aos grupos carboxilatos. Essa agregação das vesículas foi proposta pelos autores a partir de imagens obtidas por microscopia de força atômica.

A Figura 11 mostra a representação esquemática do mecanismo proposto pelos autores para a detecção seletiva de íons Pb^{2+}.

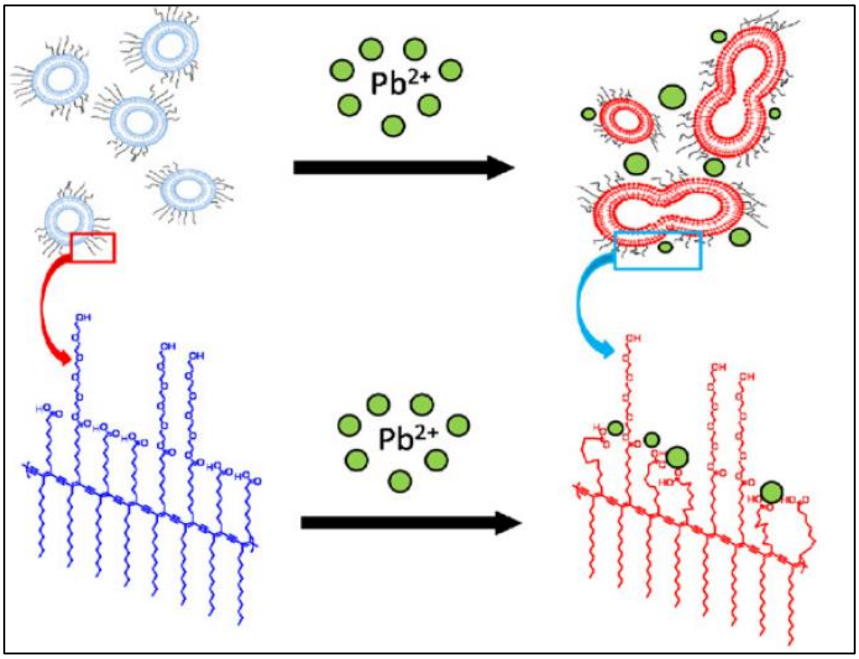

Figura 11. Representação esquemática do mecanismo proposto transição colorimétrica induzida por Pb^{2+} [41].

Outro exemplo importante da aplicação direta dos PDAs foi descrita por Thongmalai e colaboradores[42] (2011). Estes autores utilizaram os PDAs funcionalizados com grupos amino para a detecção colorimétrica de surfactantes aniônicos. A identificação precisa dessas moléculas anfifílicas ainda é um desafio científico e a utilização destes sensores colorimétricos levaria a um método rápido, barato e que permite a detecção visual. Além disso, este não foi o primeiro trabalho a relatar a aplicação dos PDAs como sensores para surfactantes. Porém, neste estudo, os autores afirmam que a cauda dos surfactantes também tem efeito sobre a transição colorimétrica, ao contrário dos trabalhos anteriores, em que a interação dos surfactantes com as cabeças funcionalizadas na superfície das vesículas era a única responsável pela mudança cromática. Dessa forma, apesar dos esforços dos cientistas na obtenção de materiais contendo os PDAs com grande sensibilidade e também na busca de um mecanismo que explique a transição colorimétrica, há pouca informação sobre a natureza das interações intermoleculares envolvidas nesses processos de reconhecimento molecular seletivo.

Pires e colaboradores[43] (2010) mediram pela primeira vez a energia associada às transições colorimétricas induzidas por diferentes solventes orgânicos em vesículas de PCDA e PCDA + colesterol + esfingomielina dispersas em água. Utilizando a Microcalorimetria de Titulação Isotérmica (ITC), os autores investigaram a resposta colorimétrica induzida por diferentes solventes clorados e encontraram um mecanismo de transição diferente para cada um. Tetracloreto de carbono (CCl_4), clorofórmio ($CHCl_3$) e diclorometano (CH_2Cl_2) promoveram uma transição colorimétrica nas vesículas de PCDA de aproximadamente 48, 98 e 52 %, respectivamente. Já nas vesículas contendo colesterol e esfingomielina, as RCs para CCl_4, $CHCl_3$ e CH_2Cl_2 foram de aproximadamente 32, 62 e 42 %, respectivamente. Entretanto, os resultados obtidos por ITC indicaram que apenas o $CHCl_3$ induz uma transição entalpicamente dirigida enquanto os solventes CCl_4 e CH_2Cl_2 o fazem por um mecanismo entropicamente direcionado.

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CAPÍTULO 2

Synthesis and optical properties of polydiacetylenes in triblock copolymers aqueous solution

1. Introduction

Polydiacetylenes (PDAs) are en-yne conjugated polymers formed by the 1,4-addition of diacetylene monomers[1]. For this reaction of polymerization to occur, the monomers must be properly oriented and excited by UV radiation with the occurrence of the polymerization in several self-assembly forms such as monolayer[2], multilayer[3], nanostructured particles[4], micelles[5] and vesicles[6].

The PDAs exhibit interesting optical properties as evidenced in their ability to color change from blue to red, under various stimuli such as temperature[7], pH[8] and in the presence of various species as surfactants[9-11], ions[10,11], organic solvents[12,13], biomolecules[14,15], including virus[16] and bacteria[17]. However, the mechanism involved in this process are not yet fully understood, due to different behaviors observed of the materials when exposed to various environmental perturbations[18]. Nevertheless, a large number of articles have explored the chromatic properties of PDAs to the development of smart sensors[19]. However, there is a particular difficulty for developing and implementing this material as sensors due to the limited range of response for chromatic transition of the PDA. For a complete blue-red transition, the stimulus applied is restricted at a specific and very small range intensity. For example, the vesicles prepared with 10,12-pentacosadiynoic acid monomers (PCDA) undergo an gradual colorimetric transition with increasing of the temperature. However, only at 55 ºC the absorption spectrum and the appearance of the material is abruptly changed, and the PDA molecules are completely converted from blue to red only at ~68 ºC[20]. The original packing state of the monomers is indeed the main factor responsible for the transition range of PDAs and the modification or replacement of the monomers is a laborious alternative to select the desired transition range. Therefore, the possibility to modulate and extend the range of the colorimetric transition of PDA molecules, without modifying the diacetylene structure, is of great scientific and technological importance. One possible approach to modulate the PDA chromatic range is making the auto-organization process to occur into geometric controlled template.

The $(EO)_n$-$(P)_m$-$(EO)_n$ (EO = ethylene oxide, PO = propylene oxide) block copolymers, commercially known as Pluronics, or Synperonics, are amphiphilic molecules capable of self-aggregating in aqueous solution, forming micelles with a hydrophobic core composed mainly by PO segments and hydrophilic shell composed by EO units[21]. The size of aggregates as well as the hydrophobic core depends mainly of molecular weight and the EO/PO ratio of the macromolecule[22]. Thus, the copolymers micelles provide a suitable place for insertion and orientation of diacetylene monomers in the hydrophobic core of the aggregates, which act as special reactors for the polymerization process. Comparing with the PDA vesicles synthesized in water, in the PDA/copolymer blends, the packing state of the monomers is modified.

Therefore, we synthesize the PDAs composed by 10,12-pentacosadiynoic acid or 10,12-tricosadiynoic acid in amphiphilic environments formed by copolymers of different hydrophobicity/hydrophilicity balance, molecular weight and concentration. The chromatic transition of nanoblends was evaluated by the temperature changes and by addition of sodium hydroxide and sodium carbonate in the system. The optic properties of the nanoblends were ever compared with blue-red transition of the classic vesicle. Apparent molar enthalpy of interaction was determined by microcalorimetric technique in order to contribute to elucidating the molecular mechanism associated with the chromatic transition.

2. Material and methods

2.1. Materials

10,12-pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) were purchased from Sigma-Aldrich (U.S.A.). Sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were obtained from Vetec (Brazil). The block copolymers L35, L64, F68, P123 and F127 was purchased from Sigma-Aldrich (U.S.A.). All chemicals were used without further purification.

Milli-QII water (Millipore, USA) water was used for the preparation of all solutions.

2.2. Vesicle preparation

PCDA or TCDA monomers were dissolved in $CHCl_3$, which was then removed by a stream of N_2 gas. Deionized water was added to make the total lipid concentration 1 mM. The resulting systems was sonicated for 10 minutes to obtain a clear solution, wich was immediately filtered using a 0.45 μm PVDF filter (Milipore). The suspensions were then stored at 4 ºC overnight to induce crystallization of lipid membranes. Polymerization was carried out under irradiation at 254 nm wavelength for 5 min and resulted in blue vesicles.

2.3. Nanoblends preparation

PCDA or TCDA monomers were dissolved in copolymer aqueous solution made with different structures and concentrations without any previous step, such that the total lipid concentration is 1 mM. The resulting systems were sonicated for 10 minutes to obtain a clear solution, wich was immediately filtered using a 0.45 μm PVDF filter (Milipore). The suspensions were then stored at 4 ºC overnight and the polymerization was carried out under irradiation at 254 nm wavelength for 5 min, resulting in blue nanoblends.

2.4. Quantifying the colorimetric response (CR)

The temperature effect on PDA vesicles and nanoblends was analyzed by addition of 0.7 μL of sample, diluted by factor of 1:10, into quartz cell spectrophotometer. The heating was promoted by Peltier system (Shimadzu TCC-240A) coupled to the UV-Vis spectrophotometer (Shimadzu UV-2550), with temperature control of 15.0 to 70.0 ºC. The spectra were obtained between 350 and 900 nm after thermal equilibrium. The chromogenic effect promoted by Na_2CO_3 and NaOH solutions was evaluated by addition of aliquots ranging from 25 to 1200 μL in 500 μL of PDA suspension and completing with solvent until 2000 μL. The spectra were obtained from 0.7 μL this mixture between 350 and 900 nm, at 25.0 ºC. To quantify the extent of blue-to-red color transitions, the CR (%) was calculated using the following equation:

$$CR\ (\%) = \left[\frac{PB_0 - PB_1}{PB_0}\right] \times 100 \tag{1}$$

where PB = $A_{blue}/(A_{blue}+A_{red})$. A is the blue (~650 nm) and red (~540 nm) absorbance obtained by UV-vis spectroscopy. The terms blue and red are related to material appearance. PB_0 is the control, blue-ratio of PDA pure at 15 ºC, while PB_1 is the value of sample exposed to different temperature. PB_0 and PB_1 also represent the absorbances before and after the salt solution exposition, respectively.

2.5. Isothermal Titration Calorimetry experiments

The energetic analyses of systems containing PCDA or TCDA vesicles and nanoblends with NaOH or Na_2CO_3 were performed on an isothermal titration microcalorimeter model CSC-4200 (Calorimeter Science Corporation), controlled by ITCRun software. The whole calorimetric procedure was chemically and electrically calibrated to the heat of protonation of (tris(hydroxymethyl)aminomethane) and the joule effect, as recommended.

The titrations were carried out by step-by-step injections (5 μL) of each one of concentrated salt solutions into a 1.75 mL reaction cell containing PCDA or TCDA suspension in the same concentration of the CR experiments. The injections of electrolytes solution were performed by a gastight Hamilton syringe (250 μL) and controlled by an instrument, with time interval of 20 minutes between each injection. The solutions were titrated in the sample cell with stirring at 300 rpm using a helix stirrer, and measurements were conducted at a constant temperature of 25.000 ± 0.001 °C. The reference cell was filled with water, initially placed in the reaction cell. Raw data were obtained as a plot of power (μW) against time (minutes). These raw data were then integrated to obtain ΔH values associated with each injection. ΔH_{obs} parameters were calculated by dividing ΔH per electrolyte amount of substance of each injection. All experiments were realized in triplicate[23,24].

3. Results and discussion

3.1. Synthesis and evaluation of the thermochromism of vesicles and nanoblends

Figure 1 shows the UV-Vis electronic spectra of the PCDA vesicles (a) and the PCDA/L64 nanoblends (b) for both red and blue forms. The PCDA/L64 nanoblends were synthesized with the same concentration of diacetylene monomer, present in the vesicles, and the concentration of L64 used was 1.0 % (w/w).

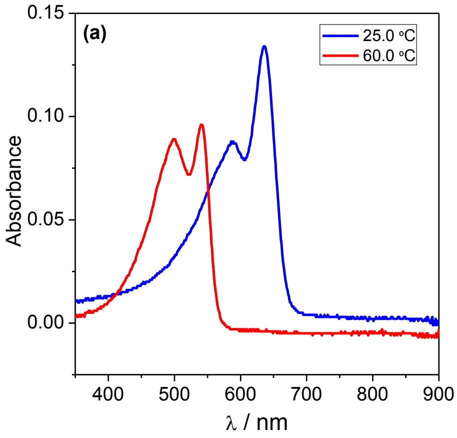

Figure 1. Absorption spectra of PCDA vesicles solution at 25 and 60 ºC **(a)** and absorption spectra of PCDA/L64 nanoblends solution at 25 and 60 ºC **(b)**.

The spectra of the vesicles and PCDA nanoblends are very similar. The absorption of radiation occurs in the same range of wavelengths and there is no significant change in the spectral form including maximum, minimum, and isosbestic point. At 25.0 ºC, both spectra show an absorption band at 640 nm and vibronic shoulder at 590 nm in the blue phase. After the stimulus, the solutions revealed electronic bands at 540 and 490 nm, respectively. The only difference between PCDAs formed into vesicles and nanoblends is shown in the absorption intensities. The molar absorptivity of the nanoblends PCDA/L64 and PCDA vesicles, both in blue phases, correspond to ε = (4.0999 ± 0.0454) and (1.3554 ± 0.07537) cm^{-1} $mmol^{-1}$ L, respectively. This shows that the amphiphilic environment, generated by copolymers, favors the formation of a larger number of resonant species shaped by its hydrophobic core.

The effect of the concentration of L64 in the synthesis of polymeric PCDA nanoblends was also evaluated. Figure 2 shows the spectra of the PCDA nanostructures formed in different concentrations of L64 (0.10, 1.00, 2.00 and 8.00 % (w/w)) and at the same PCDA monomeric concentration.

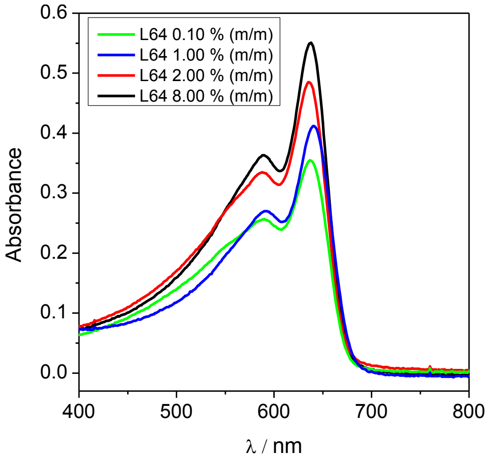

Figure 2. Absorption spectra of PCDA/L64 nanoblends solution made at different copolymer concentrations, at 15.0 ºC.

These spectra refer to blue form of the solutions containing the nanoblends after polymerization. Increasing the copolymer concentration, the absorption intensity increases. This result corroborates with the last ones, showing that copolymers optimize the polymerization of the PCDA monomers, creating an environment more suitable for the process of PCDA self-organization. The higher concentrations of L64 increases the number of copolymer aggregates facilitating the polymerization of PDAs. A possible mechanism for that process is: below the critical micelle concentration (cmc) of the copolymer, the PCDA structures are formed containing traped L64 monomers. Above the cmc of L64 equal to 2.55 % (m/m)[21], the copolymers make up aggregate structures with a hydrophobic core capable of solubilizing and guiding the DA monomers conveniently to carry out the 1,4-addition. Moreover, the polymerization was not observed after irradiation in solutions containing pure L64 or in higher concentrations of copolymer, suggesting that at higher concentrations of copolymer, the DA monomers do not tend to form tridimensional organizations, since the monomers are individually adsorbed in different tamplates, getting far enough for the non-occurrence of the 1,4-addition.

The amphiphilic environment, formed by copolymer in an aqueous solution, affect not only the synthesis of PCDA nanoblends but the chromatic transition range is also changed. Figure 3 shows the electronic absorption spectra of PCDA vesicles (a) and PCDA/L64 nanoblends (b) at different temperatures. In these experiments, the concentration of L64 for the formation of the nanoblend was 1,0 % (w/w). The PCDA structures were diluted in a solvent containing equal concentrations of copolymer used in the synthesis and the temperature difference defined between each spectrum corresponds to 5 ºC. The CR was calculated from these spectra for both PCDA vesicle (c) and PCDA nanoblend (d). The CR represents quantitatively the percentage of molecules that underwent blue-to-red transition after the stimulus.

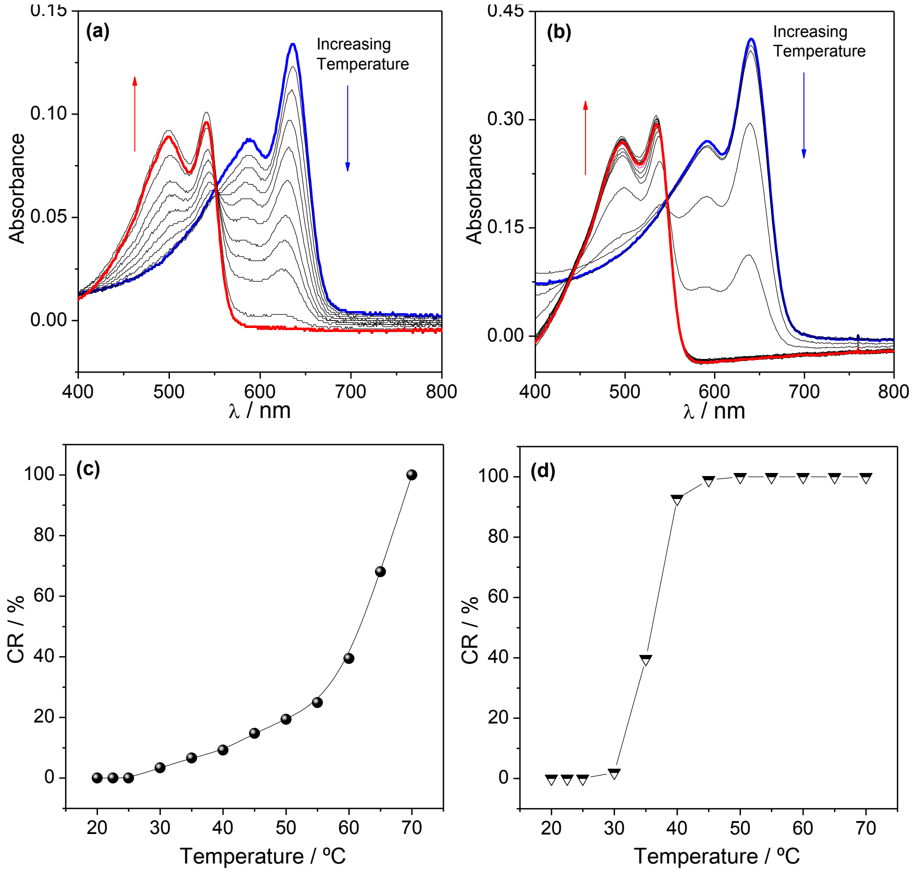

Figure 3. Absorption spectra of PCDA vesicles **(a)** and PCDA/L64 nanoblends solution **(b)** at different temperatures. CR curves as a function of the temperature of PCDA vesicles solution **(c)** and PCDA/L64 nanoblends solution **(d)**.

The temperature increase induces a color transition in both the PCDA vesicles and PCDA/copolymer nanoblends, but at different temperature ranges. The PCDA vesicles are predominantly in the blue form up to approximately 45 ºC, with a gradual increase in red species not exceeding 20% (Figure 3 (a) and 3 (c)). Above 55 ºC, an abrupt change in the spectra occurs indicating the existence of a cooperative process. The temperature change causes a complete conversion (100%) of PCDAs vesicles to red form at 70 ºC. However the PCDA nanoblends are predominantly blue to a temperature below 30 ºC and, from this, these species also suffer an abrupt transition, with full electronic conversion at 50 º C (Figure 3 (b) and 3 (d)).

On the basis of our results, the PCDA/L64 nanoblends has a maximum temperature of transition reduced by 20 ºC, when compared to PCDA vesicles. This indicates that the polydiacetylene macromolecules arranged in amphiphilic reactors make different intermolecular interactions in comparison with vesicular form.

The most accepted model for scientific community suggests that the chromatic transition is a result of rotation about the C-C bond in the conjugated structure of the polymer. This reduces the planarity of the backbone, causing dramatic changes in the π-orbital overlap. Therefore, to occur this process is necessary to disturb the system with energy greater than rotational barrier of the C-C bond. Accordingly, these conformational changes lead to alternations in electronic states and the characteristic optical absorption that can be easily monitored by UV-Vis spectrophotometry[25-29].

PCDA polymer arranged in the nanoblends can form PCDA-PCDA and PCDA-H_2O interactions, as well as in vesicles, but also PCDA-L64 interactions. These last ones compete with the interactions between adjacent PCDA monomers, leading to a greater distance between them and which, consequently, weakens the van der Waals interactions between their carbon chains. As a result, the energy required to break the PCDA-PCDA interactions, overcome the rotational barrier around the C-C bond in the backbone and, therefore, promote the chromatic transition in the nanoblends is less than in the vesicles.

The CRs were also obtained for nanoblends formed in different concentrations of L64. As mentioned above, the nanoblends synthesized in higher concentrations of L64 form resonant structures that generate identical spectra and differ only in intensity of absorption. Interestingly, the chromatic range induced by temperature change is affect by copolymer concentrations. Figure 4 (a) shows the RCs obtained for the PCDA/L64 nanoblends, at different copolymer concentration, versus temperature. Each of these graphs were conveniently adjusted using the Origin software and the temperature where the transition corresponds to 50% of the maximum value of CR was defined as the chromatic transition temperature (T_{tr}).Figure 4 (b) shows the T_{tr} values as a function of the copolymer concentration in the nanoblends. This parameter is useful because it promotes a better view of the chromatic transition interval in terms of a midpoint. The results indicated as 0.00 % (m/m) of L64 refer to PCDA vesicle.

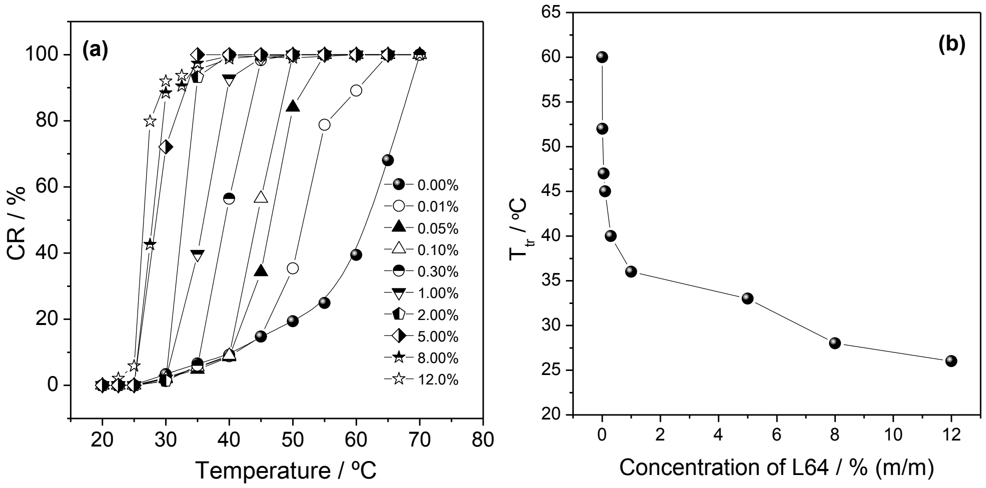

Figure 4. CR curves as a function of the temperature of nanoblends formed in different concentrations of L64 **(a)** and Chromatic Transition Temperature as a function L64 concentration **(b)**.

As can be seen in Figure 4 (a), the temperature in which begins to rise sharply in the CR values are becoming smaller with increasing the concentration of L64. At higher concentrations of this copolymer, the temperature ranges that the chromatic transition occurs are near room temperature. In the Figure 4 (b), the L64 concentration effect becomes clearer. The nanoblends formed by 0.01 % (w/w) of L64 have smaller T_{tr} in relation to vesicles around 8 ºC. A more abrupt decrease in the T_{tr} values is observed up to a concentration of 1.00 % (w/w) of L64 with $\Delta T_{tr} \approx 24$ ºC. However at a concentration of 12.00 % (w/w) of L64, the T_{tr} values decrease in $\Delta T_{tr} \approx 34$ ºC.

These results show that the synthesis of PCDAs in copolymer solutions generate species with chromatic transition bands highly dependent on the concentration of the macromolecule. The temperature range effect on the blue-red transition was highly extended without changing the nature of the diacetylene monomers.

To better understand the cause of these effects of amphiphilic reactors for the synthesis of PCDAs, different triblock copolymers were also used for the construction of polymeric nanoblends at different concentrations. These copolymers are different in terms of the number of ethylene oxide segments (NEO), number of propylene oxide segments (NPO) and the average molar mass (M_m) of the macromolecule. These parameters define their physicochemical properties such as hydrophobicity, hydrophilicity, and interfacial tension. Furthermore, depending on the nominal composition of these copolymers, the critical micelle concentration also changes, as well as the size and shape of the aggregate and hydrophobic core. Thus, various copolymers with different structure permits the construction of PDAs in different environments that will result in chromatic ranges also different, depending on the stimulus applied. The Table 1 shows the nominal composition of the polymers used in this work.

Table 1. Nominal composition of the studied copolymers[22].

Copolymer	NEO	NPO	M_m / (g mol^{-1})
L35	2 X 11	17	1900
L64	2 X 13	31	2900
P123	2 X 19	69	5800
F68	2 X 76	30	8400
F127	2 X 95	64	12000

We evaluate the thermochromism associated the various PCDA/copolymer nanoblends at various concentrations of copolymer. In the synthesis of different nanoblends and obtaining of these spectra was used the same conditions applied for the PCDA/L64 nanoblends at the copolymer concentration of 1.00 % (w/w).

Was also synthesized and evaluated the thermochromism of TCDA/L64 nanoblends copolymer at various concentrations. The PCDA monomers have carbon chain greater than TCDA monomers in two carbon atoms, but both have the same carboxylic acid functional group.

From these spectra were obtained T_{tr} values as a function of copolymer concentration. Figure 5 shows the T_{tr} curves of nanoblends as a function of the concentration of macromolecule.

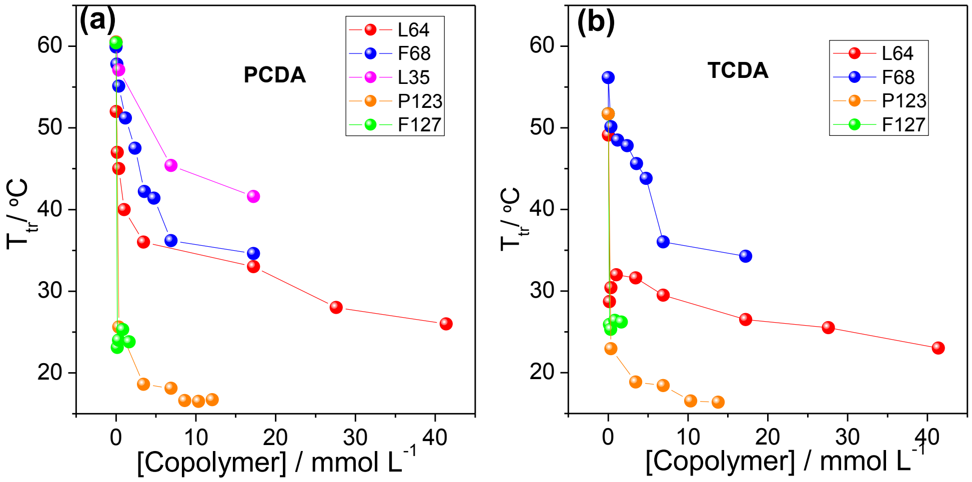

Figure 5. Chromatic Transition Temperature as a function copolymer concentration using PCDA **(a)** and TCDA **(b)** monomers.

All copolymers used at the study, have caused a reduction in the T_{tr} of nanoblends with the increase of its concentration in the systems. Evaluating the different structures of copolymers, the chromatic transition temperature proceeds in the following order: L35 > L64 > F68 > F127 > P123. This sequence matches the order of the number of PO segments of macromolecules. Different numbers of these units in the copolymer structure creates hydrophobic compartments of different sizes in which the diacetylene monomers can be inserted. Into of the nanoregions, a larger number of interactions between monomer and PO segment of the macromolecule occurs causing the weakening of the interaction between diacetylene monomers. In addition, larger hydrophobic cores tend to orient monomers diacetylenes in larger distances, contributing to the decrease of the monomer-monomer interactions. Both processes together, decrease the rotational energy barrier about the C-C bond justifying the reduction in the values of T_{tr} nanoblends.

Comparing the structures formed with different DA monomers, we expected that PCDA/copolymer nanoblends have transition temperatures always higher than TCDA/copolymer nanoblends for the same copolymer. This could be justified by the greater number of van der Waals interactions between the PCDA tail and the hydrophobic region of the copolymer and due to PCDA-PCDA interactions, compared to TCDA, that has a lower carbon chain. However, this trend has been not observed. Therefore, the hydrophobicity is not the only driving force able to influence the chromatic transition of the nanostructures, but also, other secondary parameters such as hydrophilicity and molecular weight of polymers.

Thus, the nanoblends containing copolymers with PDAs embedded have their chromatic transition temperature lowered mainly due to weakening of the interactions DA-DA, what is promoted by the highest number of interactions DA-copolymer formed in the hydrophobic environment of the aggregates.

Controlling this balance of intermolecular interactions, we can control the energy required to promote conformational changes of copolymers that disrupt the planarity of the system en-yne. Therefore, these results show that it is possible to adjust the transition temperature of PDAs chromatic by the choice of amphiphilic molecules with different hydrophobicities, as well as suitable concentrations to obtain the desired transition temperature. These new polymer nanoblends have characteristics that can be exploited not only in the development of irreversible heat sensors for monitoring perishable foods, as well as can be functionalized to become signal transducers even more sensitive.

3.2. Effect of NaOH addition on the PDA nanostructured systems

The PDA vesicles show an irreversible transition from blue-to-red when the pH of the system is increased. This effect has been studied by Hall et al. (2006) by addition of the NaOH solutions and other metal hydroxides in suspensions of TCDA vesicles, with the objective to understand how the acid-base equilibrium affects the chromogenic responses of liposomes[8].

According to these authors, the chromatic transition could be the result of a increased osmotic pressure across the membrane, the electrostatic effect associated with changes to the diffuse layer of counterions and the Coulomb repulsion between ionized groups on the surface of the bilayer. In this case, the Coulomb repulsion between charged heads is the main factor responsible for the disturbance in the PDA backbone, which reduced conjugation lenght and therefore induced blue-red transformations.

Traiphol et al. (2011) evaluated the effect of the head group on the pH-chromism of the PDA vesicles using the 10,12-pentacosadiynoic acid (PCDA) and *N*-(2-aminoethyl)pentacosa-10,12-diynamide (AEPCDA) diacetylene monomers[20]. The addition of hydroxide ions (OH^-) in a suspension of PCDA vesicles leads to breaking of the hydrogen bonds on the surface by transforming the carboxylic acid group to the carboxylate one. With that, the ionic repulsion generated on the surface causes the rearrangement of PDA segments. The behavior of AEPCDA vesicles is very different and opposite to the one observed in the PCDA vesicles. The addition of OH^- does not affect the structure of the lipid membranes, but the addition of the H^+ protonates the surface of the structures causing a full color transition at pH ~ 0.The effect of carbon chain length was also studied by these authors through the transition chromatic of TCDA and PCDA vesicles with the addition of NaOH. To complete chromatic transition, the TCDA vesicles required a smaller number of equivalents of NaOH. As the PCDA has greater length tail in comparison to the TCDA, the stimulus applied to the PCDA vesicles must be higher, because a larger number of interactions between the adjacent tails need to be broken to promote the rearrangement of segments PDA.

In all previous studies, the pH-chromism range was modified using only monomers with different structures. The polymer nanoblends formed by diacetylene monomers and copolymers respond to different pH ranges depending on the packaging of the diacetylene monomers. Figure 6 shows the colorimetric response of PCDA and TCDA vesicles and PCDA/L64 and TCDA/L64 nanoblends, made at a copolymer concentration of 0.05 % (w/w), as a function of the concentration of NaOH in the system at 25 ºC.

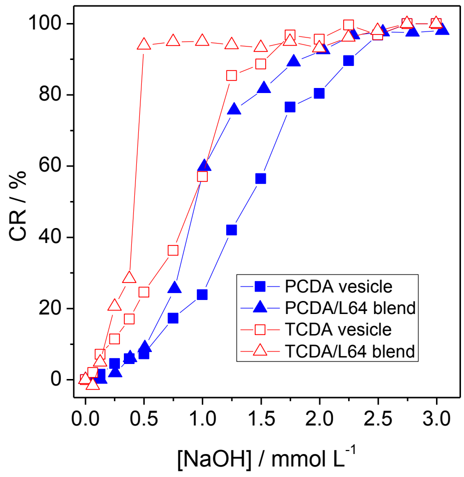

Figure 6. CR as a function NaOH concentration of the PCDA vesicle (■), PCDA/L64 nanoblend (▲), TCDA vesicle (□) and TCDA/L64 nanoblend (Δ), at 25 ºC.

The TCDA vesicles, as already described, are more sensitive to hydroxyl ions than PCDA vesicles, due to differences in the length of the carbon chain of monomers. In the NaOH concentration of 1.0 mM, the RC of PCDA vesicles is smaller than the vesicles TCDA in approximately 23 units. Furthermore, the full electronic transition occurs at concentrations above 2.5 and 2.2 mM to PCDA and TCDA, respectively. Though, the polymer nanoblends are much more sensitive to the basic environment and show a colorimetric transition above 95% at approximately 1.8 and 0.5 mM to PCDA and TCDA, respectively.

This important result shows that the PCDA and TCDA monomers polymerized in the presence of the copolymer weakens the monomer-monomer interactions, corroborating the proposed model for the thermochromism. Furthermore, the electrostatic repulsion of the groups on the surface of the vesicle is the main factor for the color change, because this action disturbs the skeleton of PCDA, being the polymer nanoblends the most sensitive.

The chromatic transition of the nanoblends synthesized at different concentrations of copolymer promoted by OH^- ions were also evaluated. Figure 7 shows RC curves as a function of the concentration of NaOH, for different PCDA/L64 (a) and TCDA/L64 (b) nanoblends.

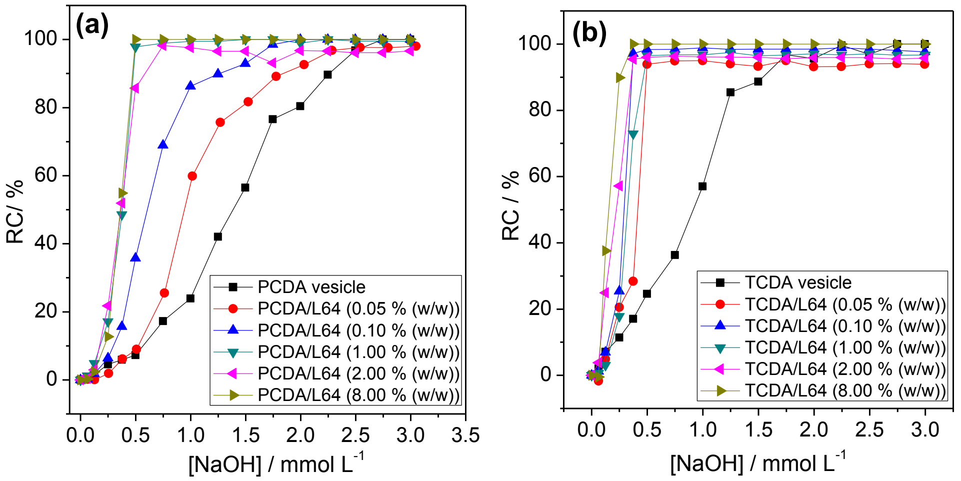

Figure 7. CR as a function NaOH concentration of the PCDA/L64 **(a)** and TCDA/L64 **(b)** nanoblends made in different concentrations of L64, at 25 ºC.

The sensitivity of the nanostructures in relation to the OH^- ion depends on the concentration of copolymer in which the nanostructures are synthetized. The thermochromism associated with the polymer nanoblends has the same trend as the pH-chromism. The nanoblends built in higher concentrations of copolymer are more sensitive to the applied stimulus. As seen, the PCDA vesicles only reach full conversion to the red form in concentrations higher than 2.5 mM. The range between 0.50 and 2.50 mM of NaOH, corresponds to an abrupt transition region of these nanostructures. The agreggates organizes the PCDA monomers, reducing the abrupt transition range with increasing copolymer concentration. At concentrations higher than 1.00 % (w/w) of L64, this region is between 0.12 to 0.50 mM of NaOH. Above 1.00 % (w/w) of L64, no apparent increase in the sensitivity of these blends is verified and the full colorimetric transition occurs at 0.50 and 0.48 mM of NaOH to 1.00 % (w/w) and 8.00 % (w/w) of L64, respectively. Analogous behavior is observed for the TCDA/L64 nanoblends, but at low concentrations of L64, the nanoblends have abrupt transition range and maximum transition colorimetric very similar to the nanoblends made in high concentrations of copolymer. The full colorimetric transition occurs at 0.50 and 0.37 mM of NaOH to 0.05 % (w/w) and 8.00 % (w/w) of L64, respectively.

Isothermal titration calorimetry (ITC) is a sensitive and reproductive technique that gives us valuable information about the processes of interaction between PCDA or TCDA structures and the species that promote the chromatic transition[30]. Thus, the characteristics of the apparent molar enthalpy of interaction curves between PCDA or TCDA vesicles and nanoblends with NaOH (ΔH_{ap-int}) versus [NaOH], provide quantitative energetics informations for verifying the proposed model for the chromatic transition induced by this electrolyte. To determine values of ΔH_{ap-int}, we subtract the dilution curve in solvent from the titration curve of electrolyte in solution containing the nanostructures for each electrolyte concentration. As the amount of ions interacting with the structures of polydiacetylene is unknown, so we cannot calculate the exact molar enthalpy change of this interaction, but only an apparent molar enthalpy change.

Figure 8 shows the enthalpic titration curves obtained from addition of NaOH to PCDA or TCDA solutions, where the apparent molar enthalpy change of interaction for each injection of electrolyte solution is plotted against total electrolyte concentration.

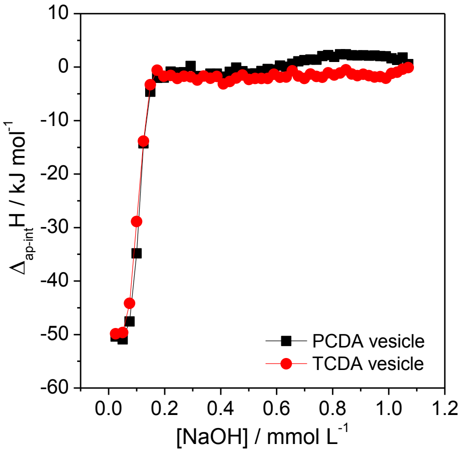

Figure 8. Apparent molar enthalpy change of interaction between (■) PCDA and (●) TCDA vesicles versus NaOH concentration, at 298.15 K.

The curves for both polydiacetylenes shows that up 0.17 mM of the NaOH, the enthalpy change is exothermic, with initial values of -49.8 kJ mol^{-1}. The energy released has become less negative with the increase of NaOH concentration in the system. Above 0.17 mM of NaOH, the process became almost athermal. Based on this behavior, the interaction between the vesicles with ions in solution is enthalpically favorable and the ΔH_{ap-int} values were mainly associated with the deprotonation of the carboxylic groups on the vesicle surface with subsequent neutralization reaction between protons released and hydroxide ions added on the system. This can be justified by the values of the heats of dissociation of carboxylic acid groups (ΔH_{diss}= -0,544 kJ mol^{-1}) and neutralization reaction (ΔH_{neut} = -57,35 kJ mol^{-1}), both exothermic, which are values of the order of ΔH_{ap-int} obtained by ITC[31]. Furthermore, for both vesicles, the abrupt increase in the values of ΔH_{ap-int} shows the occurrence of a cooperative process caused by interactions between the hydroxide ions and the carboxylic groups on the vesicle surface, implying in the possible aggregation of nanostructures caused by formation of hydrogen bonds between the functional groups of adjacent vesicles with partially ionized surface. Therefore, the result of all these molecular processes originates in the disruption of the coplanarity of the en-yne conjugated polymer that leads to the chromatic transition, being the distance amidst adjacent monomers the main factor, caused by the electrostatic repulsion of the charged heads. However, despite the colorimetric transition of the vesicles occur at concentrations above 0.5 mM, the ITC curves over this concentration, reveal that the energy required to overcome the rotational barrier of the backbone conjugated is negligible in comparison with the processes described above. It is also important to emphasize that there is no significant difference between the processes occurring in PCDA and TCDA vesicles. The coincidence in the ΔH_{ap-int} curves shows that the size of the tail of the diacetylene monomers, arranged in vesicles, does not influence in the interaction process of these nanostructures with hydroxide ions, corroborating with the surface model suggested.

Figure 9 shows the ΔH_{ap-int} curves versus [NaOH] obtained from titration of NaOH solutions on PCDA or TCDA nanoblends synthesized in concentration of 1.0 % (w/w) of L64.

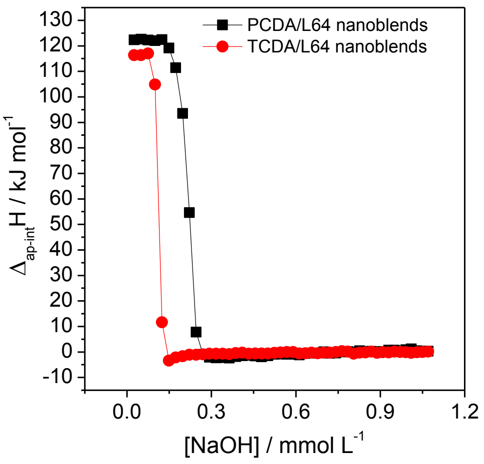

Figure 9. Apparent molar enthalpy change of interaction between (■) PCDA/L64 and (●) TCDA/L64 nanoblends versus NaOH concentration, at 298.15 K.

The ΔH_{ap-int} curves for nanoblends are completely different from the curves obtained for the vesicles. For PCDA/L64 nanoblends, the enthalpy values are endothermic until concentration of ~0.30 mM of NaOH. In the first injections of alkaline solution, until 0.128 mM, the system absorbs an energy of around 122 kJ mol^{-1}. From this concentration, an abrupt decrease in the values of ΔH_{ap-int} shows the occurrence of a cooperative process. In the curves obtained for the TCDA/L64 nanoblends, the profile is similar in relation the nanostructures synthesized with PCDA. Although, different from the behavior observed for the vesicles when they interact with NaOH, the PCDA and TCDA nanoblends differ in terms of magnitude and the concentration range in which thermodynamic processes occur. The first injections of NaOH, the energies are endothermic with values of ~117 kJ mol^{-1} to the concentration of 0.076 mM. After, occurs an abrupt drop in the ΔH_{ap-int} values until ~0.14 mM of NaOH, where the process became almost athermal.

The profiles of the curves obtained in Figure 9 is the result of several phenomena at the molecular level. The addition of hydroxide ions on the system, promotes the ionization of the carboxyl groups of the diacetylene monomers and the electrostatic repulsion generated on the surface is sufficient to cause conformational changes in the copolymer structure containing chains of polymerized PCDA or TCDA monomers trapped. The conformational changes in the L64 structures are processes entropically driven, with endothermic curves, despite the ionization and neutralization reaction on the surface that results in exothermic enthalpy changes. Thus, these thermodynamic processes prevail at the start of titration for both PCDA and TCDA nanoblends until concentrations of 0.128 and 0.076 mM, respectively.

The abrupt decrease in the values of apparent enthalpy of interaction for the nanoblends is the result of possible aggregation processes of the copolymer chains containing diacetylene monomers adsorbed. All these molecular processes seek to achieve a more stable conformation, however, occurs the polydiacetylene backbone disturbance causing the colorimetric transition. In the case of nanoblends, the decrease in the coplanarity of the en-yne structure occurs by the same effects that cause the chromatic change in the vesicles, but these structures are formed on copolymer templates and the synergistic effect between the conformational changes of macromolecule and trapped chains of diacetylenes becomes very important. Thus, the difference between PCDA and TCDA nanoblends curves is justified by the greater number of hydrophobic interactions between PCDA monomers and PO units of L64. The increase of these interactions implies in a lower rotational freedom of copolymers molecules into the nanoblend structure, so that the energy required to overcome the rotational energy barrier in PCDA nanoblends is greater, and the concentration of NaOH needed to promote self-aggregation processes in nanoblends of TCDA is lower. Moreover, as in the microcalorimetric experiments for vesicles, the energy involved in the transition chromatic process of polydiacetylenes in nanoblends is negligible compared to other thermodynamic processes observed by ITC.

3.3. Effect of Na_2CO_3 addition on the PDA nanostructured systems

Aqueous solutions of Na_2CO_3 present a series of equilibria reactions that can be written as acid-base conjugated pairs of BrØnsted-Lowry governed by their dissociation constant, as shown in Figure 10.

$$\mathbf{Na_2CO_3 \rightarrow 2\ Na^+ + CO_3^{2-}}$$

$$\mathbf{CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-} \qquad K_1 = 4.5 \times 10^{-7}$$

$$\mathbf{HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-} \qquad K_2 = 4.5 \times 10^{-11}$$

$$\mathbf{H_2CO_3 \rightarrow CO_2 + H_2O}$$

Figure 10. Reactions equilibrium involved in aqueous solution of Na_2CO_3.

Na_2CO_3 solutions are considered basic salts due to the ability to originate hydroxide ions in solution, increasing the pH. Thus, an aqueous solution of this salt also promote the colorimetric transition in PDA structures. However, there is a greater number of ionic species with different sizes and charge distribution involved in these equilibria, which interacts differently with the blue nanostructures.

Figure 11 shows the colorimetric response of PCDA or TCDA vesicles and nanoblends as a function of the Na_2CO_3 concentration in the system, at 25 ºC. In the same way as done in the experiments with NaOH, the nanoblends used in this study were synthesized in the copolymer solution at various L64 concentrations.

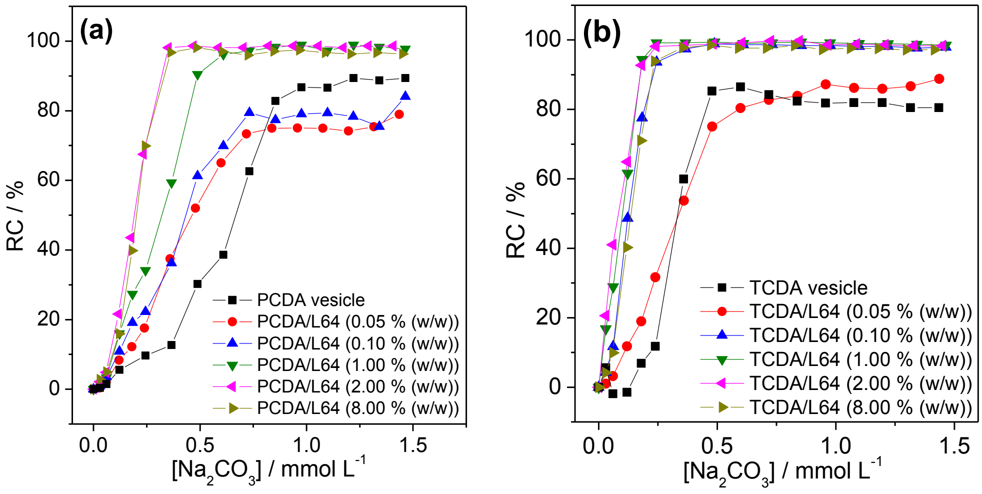

Figure 11. CR as a function NaOH concentration of the PCDA vesicle or PCDA/L64 nanoblends **(a)** and TCDA vesicle or TCDA/L64 **(b)** nanoblends made in different concentrations of L64, at 25 ºC.

At intervals from 0.0 to 1.5 mM, the aqueous solutions of Na_2CO_3 show the pH ranging from approximately 7.00 to 10.75. Therefore, these salt concentrations provide a number of hydroxyl ions sufficient to promote the ionization of the carboxyl groups of the vesicles and nanoblends. Figure 11 shows that the structures formed from the TCDA monomers are more sensitive to environmental stimulation comparing with the PCDA nanostructures as well as experimental results obtained with the addition of NaOH.

The abrupt change in the RC values of PCDA vesicles occurs between 0.24 and 0.98 mM of Na_2CO_3, while the TCDA vesicles occurs between 0.19 to 0.48 mM of Na_2CO_3. Regarding the nanoblends, these are again most sensitive to the salt addition in relation to the vesicles, and the sensitivity is greater with increasing the copolymer concentration. Immediately, at low concentration of 0.05 % (w/w) of L64, the PCDA and TCDA nanoblends have the abrupt range change in the of RC values starting at electrolyte concentrations less to 0.18 and 0.12 mM of Na_2CO_3, respectively. In high concentrations of copolymer, the chromatic transition range is approximately between 0.05 to 0.356 and 0.02 to 0.235 mm for PCDA and TCDA nanoblends, respectively.

It is interesting to note that when the vesicles and the nanoblends synthesized at low concentrations of L64 are exposed to the higher concentrations of Na_2CO_3, the transition chromatic becomes constant at values lower than 90%. However, the nanoblends formed in higher concentrations of L64 undergo a blue to red transition at extension of about 100%. This result is different from the results obtained from the RC curves as a function of concentration of NaOH. This shows that not only the hydroxide ion participates in the processes of intermolecular interaction with nanostructures, but also the curves of RC are not able to provide detailed information to the understanding of this phenomenon.

Therefore, microcalorimetric measurements were necessary for the investigation of the driving forces that govern the interactions of the PDA structures with different electrolytes. Figure 12 shows curves ΔH_{ap-int} versus [Na_2CO_3] obtained from the titration solution of Na_2CO_3 in PCDA or TCDA vesicles (a) and PCDA or TCDA nanoblends synthesized in a concentration of 1.0 % (w/w) of L64 (b).

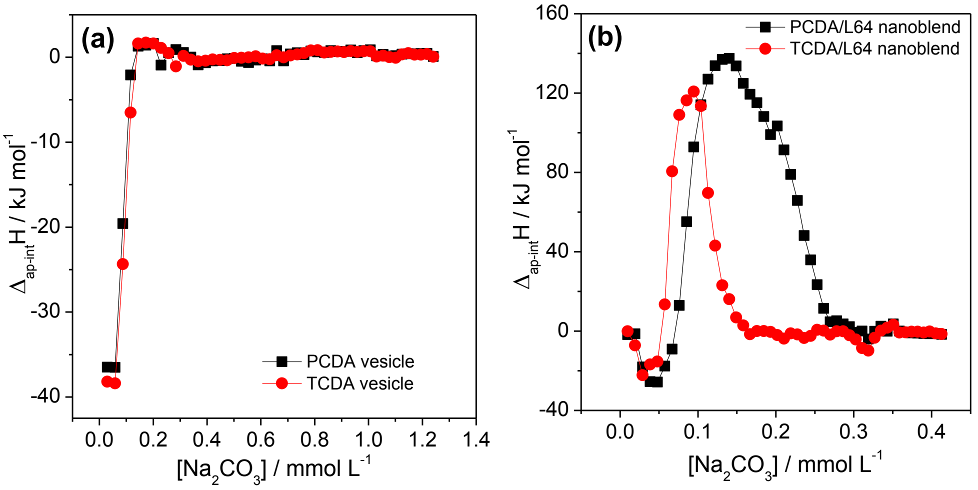

Figure 12. $\Delta \boldsymbol{H}_{ap-int}$ between (■) PCDA and (●) TCDA vesicles versus [Na_2CO_3], at 298.15 K **(a)**. $\Delta \boldsymbol{H}_{ap-int}$ between (■) PCDA/L64 and (●) TCDA/L64 nanoblends versus [Na_2CO_3], at 298.15 K **(b)**.

The titration curves obtained by titration of solutions of Na_2CO_3 in PCDA and TCDA vesicles have the profile very similar, when compared to the curves obtained by titration with NaOH. ΔH_{ap-int} at the start of titration correspond to -36.58 and -38.19 kJ mol^{-1} for the PCDA and TCDA vesicles, respectively. The result of these measures differ by more than 10 kJ mol^{-1} for the value found in the NaOH titration, indicating that this is not only due to the dissociation of the carboxylic acid groups on the surface of the vesicles and the neutralization reaction with the OH^- ions, but is certain that these process are predominant in this case. The isothermal titration curves are always exothermic and become less negative with increasing concentration of NaOH from 0.0 to 0.14 mM. The abrupt change in this range suggests the existence of a cooperative process similar to that observed to titration with NaOH. After 0.14 mM, ΔH_{ap-int} values are very small compared to the beginning of the titration, being negligible.

Moreover, the colorimetric transition induced by Na_2CO_3 occurs in concentrations greater than 0.14 mM, indicating again that the colorimetric transition is a result of the molecular processes that begin with the ionization of the heads on the surface of the bilayer and the energy involved in the thermodynamic process of blue to red transition is not significant.

Interestingly, the results obtained by titration of Na_2CO_3 in PCDA and TCDA nanoblends show a very different behavior with in relation to the titration with NaOH. Figure 12 (b) shows three regions with different behavior compared to the curve shown in Figure 9. The apparent enthalpy of interaction during the entire isothermal titration was associated with the contribution of three different main processes:

(i) The energy associated with the deprotonation of the carboxylic groups and the reaction of hydroxide ions with H^+ originating arising from the surface vesicle;

(ii) The conformational changes in the copolymer chains induced by increase of the distance between the diacetylene monomers deprotonated;

(iii) The hydrolysis of water molecules in the reaction with the carbonate ions dissociated.

These three processes can occur throughout the titration, but each one predominates at different carbonate concentrations. In the intervals from 0.00 to 0.03 and 0.00 to 0.04 mM of Na_2CO_3, the calorimetric curves are exothermic with minimum values of ΔH_{ap-int} equal to ~21 and ~26 kJ mol^{-1} for TCDA and PCDA nanoblends, respectively. In this range, the enthalpic contribution to the spontaneity of the process is favorable and the reactions on the surface of the nanostructures with the hydroxide ions are predominant. However, among 0.03 to 0.09 and 0.04 to 0.14 mM of Na_2CO_3, the ΔH_{ap-int} increases abruptly to TCDA and PCDA nanoblends, respectively, indicating that the conformational changes of macromolecule chains begin to prevail. However, the enthalpic energy from the process (ii) is not the main factor responsible for the observed results. The endothermic ΔH_{ap-int} has become higher than the ones observed in the titration of NaOH in nanoblends, where the process (ii) is primarily responsible. Thus, the energy involved in the formation of HCO_3^- ions from hydrolysis of water plays a central role in this stage, with $\Delta H_{ap-int} > 0$. The third region of Figure 12 (b) shows an abrupt drop in amounts of energy, becoming less endothermic until stabilization of the system with values of enthalpy change near zero for both nanoblends. At this stage, the conformational changes in the polymer chains cause the possible aggregation of monomers containing copolymer diacetylenes embedded, increasing the entropy of the system. In addition, during all stages of the titration, the curves of the nanostructures formed by PCDA and TCDA are different in magnitude and in concentration ranges that each region is dominant. All steps of the curve obtained by ITC for PCDA/L64 nanoblends begin and end in higher concentrations of Na_2CO_3 compared with TCDA/L64 nanoblends. It is noteworthy that the greatest differences occur in regions where the conformational change process in the copolymer structures is dominant, is this in the second and especially in the third region. This occurs because the interactions between the diacetylene monomers and copolymers directly influence in the conformational freedom of the copolymer molecules, and the hydrophobic interactions to PCDA-L64 are stronger than TCDA-L64, as previously discussed.

4. Conclusion

As described in this work, the hydrophobic templates formed by triblock copolymers provide a suitable environment for self-assembly of polydiacetylenes. The different interactions between diacetylene monomers and the amphiphilic macromolecules modify the packing state of the monomers, generating PDA/copolymer nanoblends with different chromatic transition ranges. The results show that different structures and concentrations of these copolymers used in the synthesis of nanoblends allows to modulate the chromatic transition these species induced by temperature increasing. This property can be useful in the development of irreversible colorimetric sensors for monitoring perishable products, for example.

The addition of NaOH and Na_2CO_3 also induces electronic transitions in nanostructures PDA. The PCDA/L64 and TCDA/L64 nanoblends shown to be more sensitive to stimulation of electrolytes compared with PCDA vesicles and TCDA respectively. Furthermore, nanoblends formed at higher concentrations of copolymer achieve the full blue-red conversion in smaller concentrations of electrolyte than nanoblends synthesized at low concentrations of L64.

ITC technique was successfully used to study the interaction of PDA nanostructures with different electrolytes. Measures of energy associated with the interaction of vesicles with NaOH and Na_2CO_3 support the hypothesis of colorimetric transition promoted by deprotonation of the carboxylic groups on the surface of the bilayers, generating conformational changes in conjugated monomers causing the rotation of the simple C-C bond on backbone. Differently, ΔH_{ap-int} values for polymer nanoblends show that the chromatic transition is caused not only by the ionization of adjacent monomers but also by the synergistic effect between the conformational changes of macromolecule and trapped chains of diacetylenes. Moreover, an additional effect on the interaction of Na_2CO_3 with nanoblends was observed in the microcalorimetric measurements due to hydrolysis of water molecules in the reaction with the carbonate ions dissociated.

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