CHAPTER IV

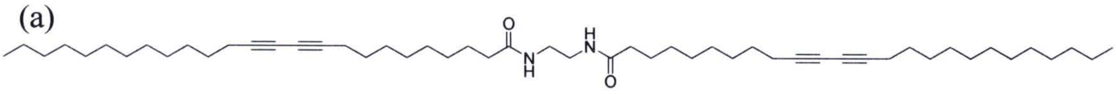
RESULTS AND DISCUSSION

In this study, we investigate the effect of structural modification on thermochromic and fluorescence properties as well as morphologies of PDA assemblies in aqueous solutions and other solvents. In addition, we explore the reversible and irreversible thermochromism of PDA assemblies in various thin films. The structures of PDA assemblies are modified by varying chemical structures of the linker between the diamide groups as shown in Fig. 20. Different linkers including hydrophobic alkyl chain, phenyl group and hydrophilic ethyleneoxide chain are used. Moreover, the linkers are modified by increasing length of hydrophobic alkyl linker and varying the substituted position of phenyl linker.

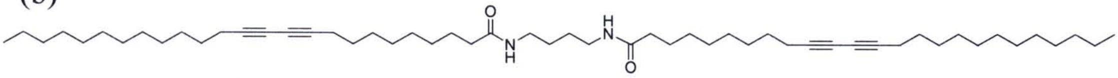
This chapter thus involves the detailed results and discussion in the following topics;

1. Thermal properties of DA monomers
2. Thermochromic properties and the morphologies of PDA assemblies in aqueous solutions
3. Thermochromic properties and the morphologies of PDA assemblies in other solvents
4. Effect of solvent on photo-polymerization of PDA assemblies
5. Effect of chain length on thermochromic properties
6. Thermochromic properties of PDA assemblies in polymeric thin films
7. Fluorescence properties of PDA assemblies

(a)



(b)



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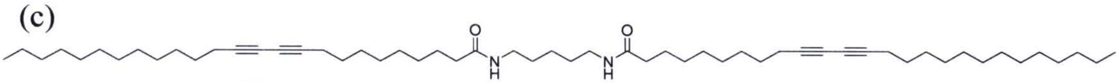

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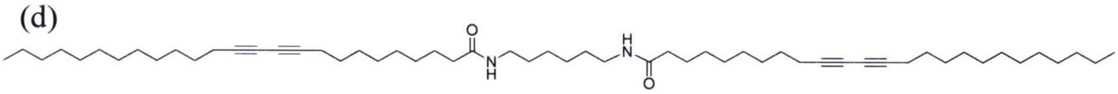

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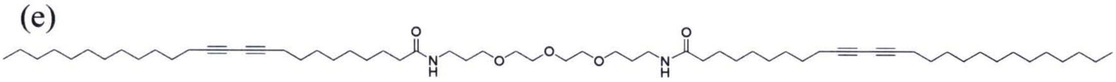

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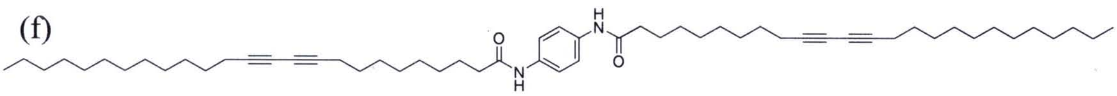
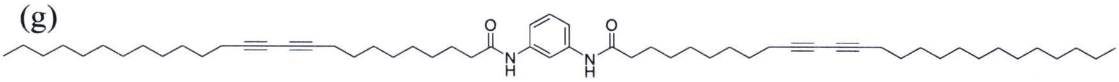


(g)



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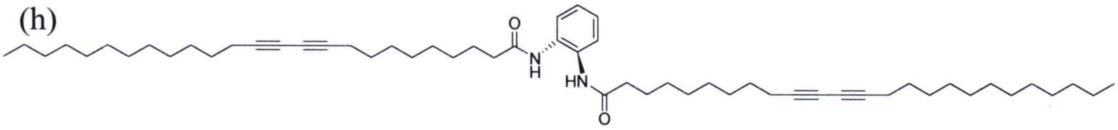


Figure 20 Chemical structures of diamidodiacetylene monomers

Note: (a) N,N′-ethylenebispentacosa-10,12-diynamide (EBPCDA-2DA)

(b) N,N′-(butane-1,4-diyl)dipentacosa-10,12-diynamide (BDPCDA-2DA)

(c) N,N′-(pentane-1,5-diyl)dipentacosa-10,12-diynamide (PDPCDA-2DA)

(d) N,N′-(hexane-1,6-diyl)dipentacosa-10,12-diynamide (HDPCDA-2DA)

(e) N,N′-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl)) dipentacosa-10,12-diynamide (APOEO-2DA)

(f) N,N′-(1,4-phenylene)dipentacosa-10,12-diynamide (*p*-PA-2DA)

(g) N,N′-(1,3-phenylene)dipentacosa-10,12-diynamide (*m*-PA-2DA)

(h) N,N′-(1,2-phenylene)dipentacosa-10,12-diynamide (*c*-PA-2DA)

Thermal properties of DA monomers

Since thermochromic properties of PDA assemblies are related to structural transition, it is important to study the phase transition of each DA monomers. Thermal properties of DA monomers are investigated by using Differential Scanning Calorimeter (DSC). The DSC curves obtained from 2nd heating and 1st cooling cycles of the DA monomers are illustrated in Fig. 21. The melting temperatures (T_m), crystallization temperatures (T_c) and enthalpy change (ΔH) of the transition are summarized in Table 1. We observe that the transition temperatures and ΔH vary with the linkers. The PCDA monomer exhibits the T_m and ΔH at 62.80 ^oC and 0.57×10^5 (J/mol), respectively. Most of diamidodiacetylene monomers exhibit higher T_m and ΔH compared to those of PCDA monomer. Increasing length of alkyl linker with even number of carbon (N=2,4,6) causes slight increase of ΔH values. The increase of ΔH values is attributed to the increase of dispersion interactions due to the longer alkyl linker. However, the PDPCDA-2DA monomer with even number of carbon (N=5) exhibits different thermal behavior. Two transition regions are detected at lower temperature. The DA with ethyleneoxide linker exhibits lower T_m at 92.47 ^oC compared to the DA with alkyl linker. For the system of phenyl linker, the T_m and ΔH vary with the substituted position of phenyl linker. The cis-substitution shows lowest T_m. The T_c and ΔH of the DA monomers are consistent with the melting T_m and ΔH.

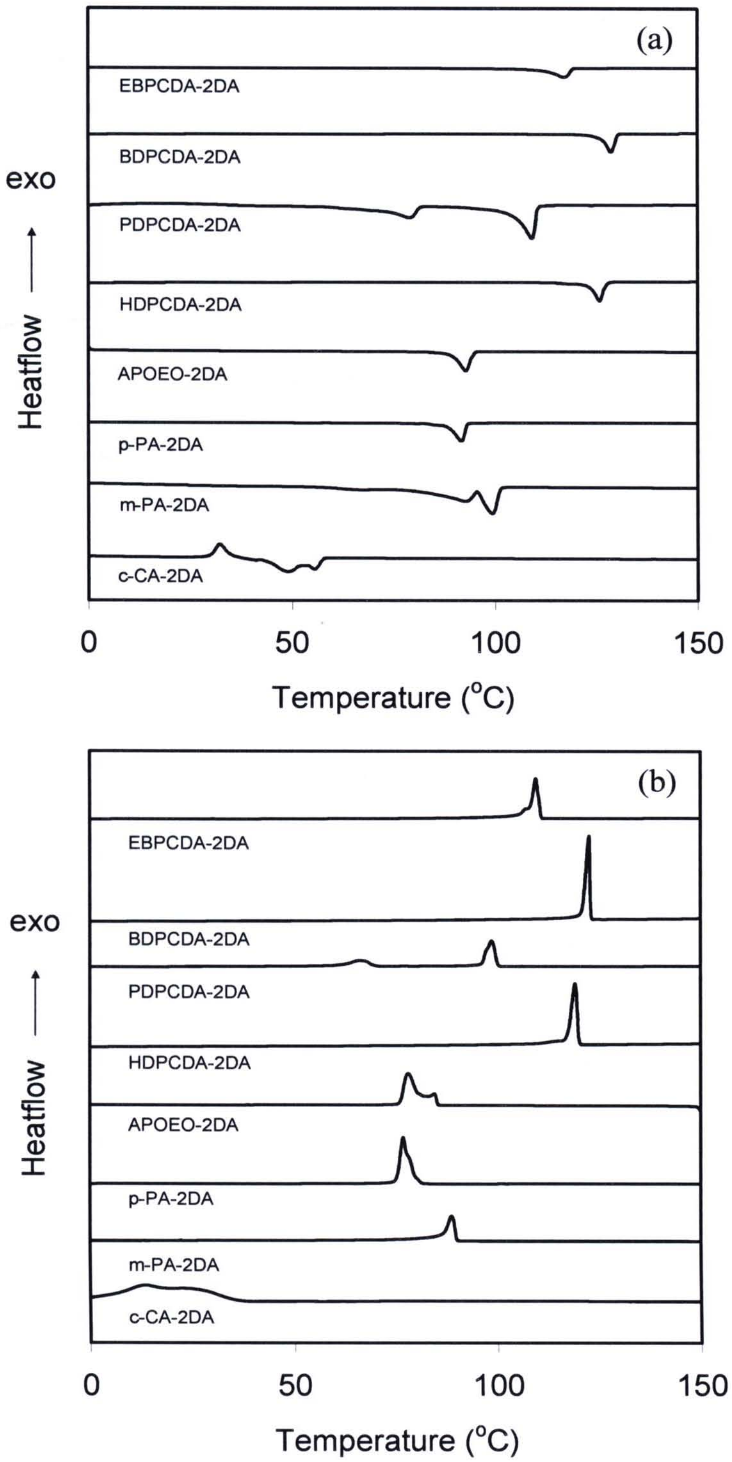


Figure 21 DSC thermograms measured upon (a) 2nd heating and (b) 1st cooling of diamidodiacetylene monomers. The thermograms were normalized to weight of the sample and shifted vertically for presentation

Table 1 Thermal properties of diamidodiacetylene monomers measured upon 1^{st} cooling and 2^{nd} heating cycles

Monomer	2^{nd} Heating		1^{st} Cooling	
	T_m(°C)	ΔH(J/mol)	T_c(°C)	ΔH(J/mol)
PCDA	62.80	0.57×10^5	58.20	0.58×10^5
EBPCDA-2DA	117.00	1.01×10^5	109.53	0.48×10^5
BDPCDA-2DA	128.56	1.02×10^5	122.64	1.10×10^5
PDPCDA-2DA	78.90	0.37×10^5	98.64	0.59×10^5
	109.02	0.60×10^5	66.12	0.33×10^5
HDPCDA-2DA	125.67	1.09×10^5	119.07	1.17×10^5
APOEO-2DA	92.47	1.35×10^5	78.03	1.39×10^5
p-PA-2DA	91.34	1.00×10^5	76.83	1.15×10^5
m-PA-2DA	99.22	0.71×10^5	88.73	0.91×10^5
c-CA-2DA	48.89	0.47×10^5	13.43	0.30×10^5

Thermochromic properties and the morphologies of PDA assemblies in aqueous solutions

In this section, we investigate the effect of structural modification on thermochromic and the morphologies of PDA assemblies prepared in aqueous solutions. Fig. 22 illustrates SEM images of PDA assemblies prepared by dropping aqueous suspensions on polished silicon wafer. We observe that size and shape of the assemblies vary with the linkers. The poly(EBPCDA-2DA) assemblies exhibit spherical shape with diameters about 100 nm. Some large assemblies with diameter of about 5 μm are also observed. The poly(BDPCDA-2DA) assemblies exhibit rod-like shape with diameters about 100 nm. The poly(PDPCDA-2DA) and poly(HDPCDA-2DA) assemblies exhibit sheet-like shape assembled together. The poly(APOEO-2DA) assemblies also exhibit the rod-like shape. For the system of PDA with phenyl linker, the shape of assemblies is not well-define.

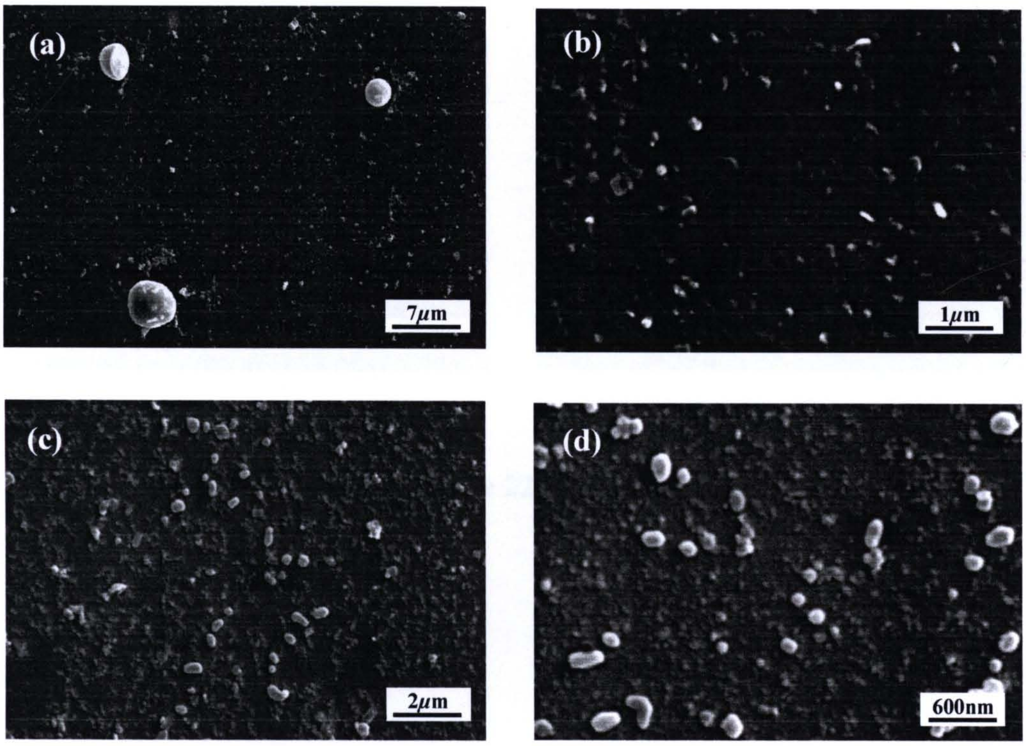


Figure 22 SEM images of (a,b) poly(EBPCDA-2DA), (c,d) poly(BDPCDA-2DA), (e,f) poly(PDPCDA-2DA), (g,h) poly(HDPCDA-2DA), (i,j) poly (APOEO-2DA), (k,l) poly(p-PA-2DA), (m,n) poly(m-PA-2DA) and (o,p) poly(c-CA-2DA) assemblies on polished silicon wafer

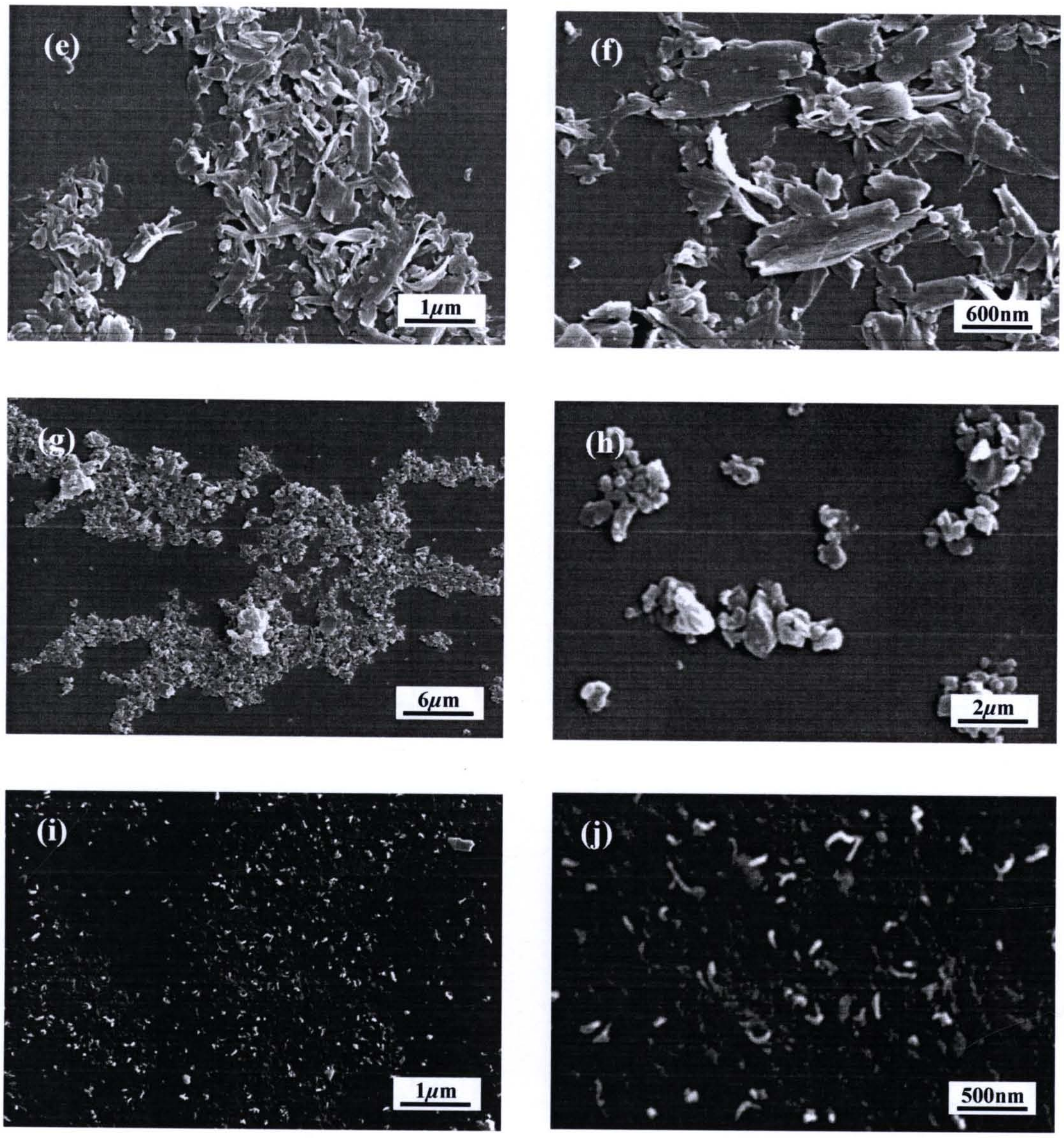


Figure 22 (cont.)

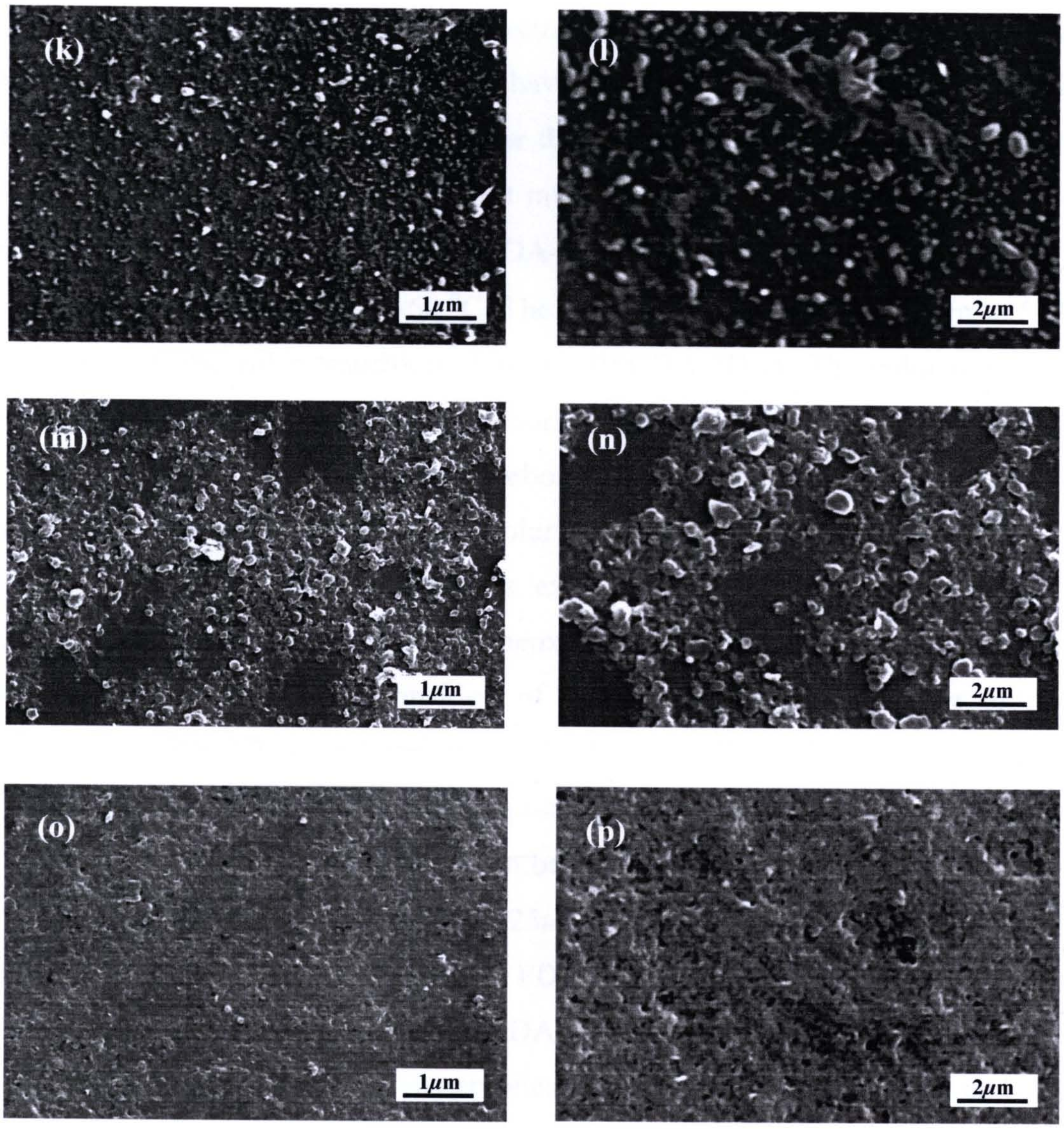


Figure 22 (cont.)

Fig. 23 illustrates absorption spectra of PDA assemblies in aqueous solution measured upon heating and cooling. We have found that the variation of linkers affects both color transition temperature and the thermochromic reversibility. Blue phase of poly(EBPCDA-2DA) assemblies exhibit maximum absorption at λ_{max} ~639 nm. The absorption spectrum of poly(EBPCDA-2DA) assemblies changes when the temperature is increased above ~60 °C. The blue-shift of λ_{max} from 639 nm to 538 nm corresponds to the color transition of poly(EBPCDA-2DA). The color transition of poly(EBPCDA-2DA) assemblies also occurs in a reversible fashion. Increasing length of alkyl linker with even number of carbon (N=2,4,6) causes slight increase of the transition temperature while the color reversibility remains. However, the poly(PDPCDA-2DA) (N=5) assemblies exhibit irreversible thermochromism. The change from alkyl linker to ethyleneoxide linker also results in irreversible thermochromism. The color transition of PDA assemblies constituting of phenyl linker, poly(p-PA-2DA) and poly(c-CA-2DA), (see Fig. 24) occurs irreversibly. However, the use of poly(m-PA-2DA) causes reversible color transition.

To investigate the color transition behavior in more details, the λ_{max} is plotted as a function of temperature (see Fig. 25a). It is observed that the color transition temperature varies with structure of PDA assemblies. The color transition of poly(EBPCDA-2DA), poly(BDPCDA-2DA), poly(PDPCDA-2DA), poly(HDPCDA-2DA) and poly(APOEO-2DA) assemblies occurs at 60, 80, 65, 80 and 55 °C respectively. For the system of phenyl linker (see Fig. 25b), color transition of the poly(c-CA-2DA), poly(p-PA-2DA) and poly(m-PA-2DA) assemblies occurs at 30, 45 and 80 °C, respectively. Color transition temperature and reversibility of the PDA assemblies in aqueous solution is summarized in Table 2.

The plots of colorimetric response (%CR) of alkyl linker and ethyleneoxide linker as a function of temperature are illustrated in Fig. 25c. We observe that the increasing length of alkyl linker causes the decrease of colorimetric response. The magnitude of %CR upon increasing temperature decreases in the order of poly(EBPCDA-2DA), poly(BDPCDA-2DA), poly(PDPCDA-2DA) and poly(HDPCDA-2DA), respectively. However, the use of ethyleneoxide linker results in highest changes of %CR. For the system of phenyl linker (see Fig. 25d), the results show that poly(c-CA-2DA) exhibits highest change the %CR.

We also investigate the sensitivity of colorimetric responses of PDA assemblies, studied by measuring absorption spectrum as a function of time when the samples are heated at 90 °C. The plots of colorimetric response (%CR) as a function of time are illustrated in Fig. 26. It is obvious that for the alkyl linker, the color change from blue to red of poly(BDPCDA-2DA) are most sensitive. The behaviors of poly(EBPCDA-2DA), poly(PDPCDA-2DA) and poly(HDPCDA-2DA) are similar. However, the use of ethyleneoxide linker causes highest sensitivity compared to the systems of the alkyl linker. For the system of phenyl linker, the sensitivity of PDA assemblies systematically decreases from poly(c-CA-2DA), poly(p-PA-2DA) and poly(m-PA-2DA), respectively.

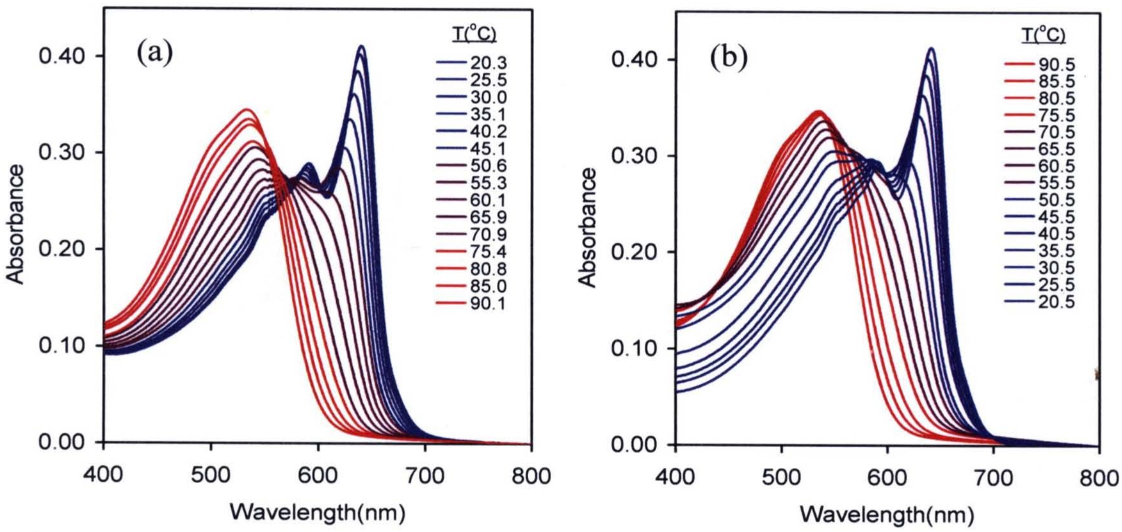


Figure 23 Absorption spectra of (a,b) poly(EBPCDA-2DA), (c,d) poly(BDPCDA-2DA), (e,f) poly(PDPCDA-2DA), (g,h) poly(HDPCDA-2DA) and (i,j) poly (APOEO-2DA) assemblies in aqueous solution measured upon heating (left) and cooling (right)

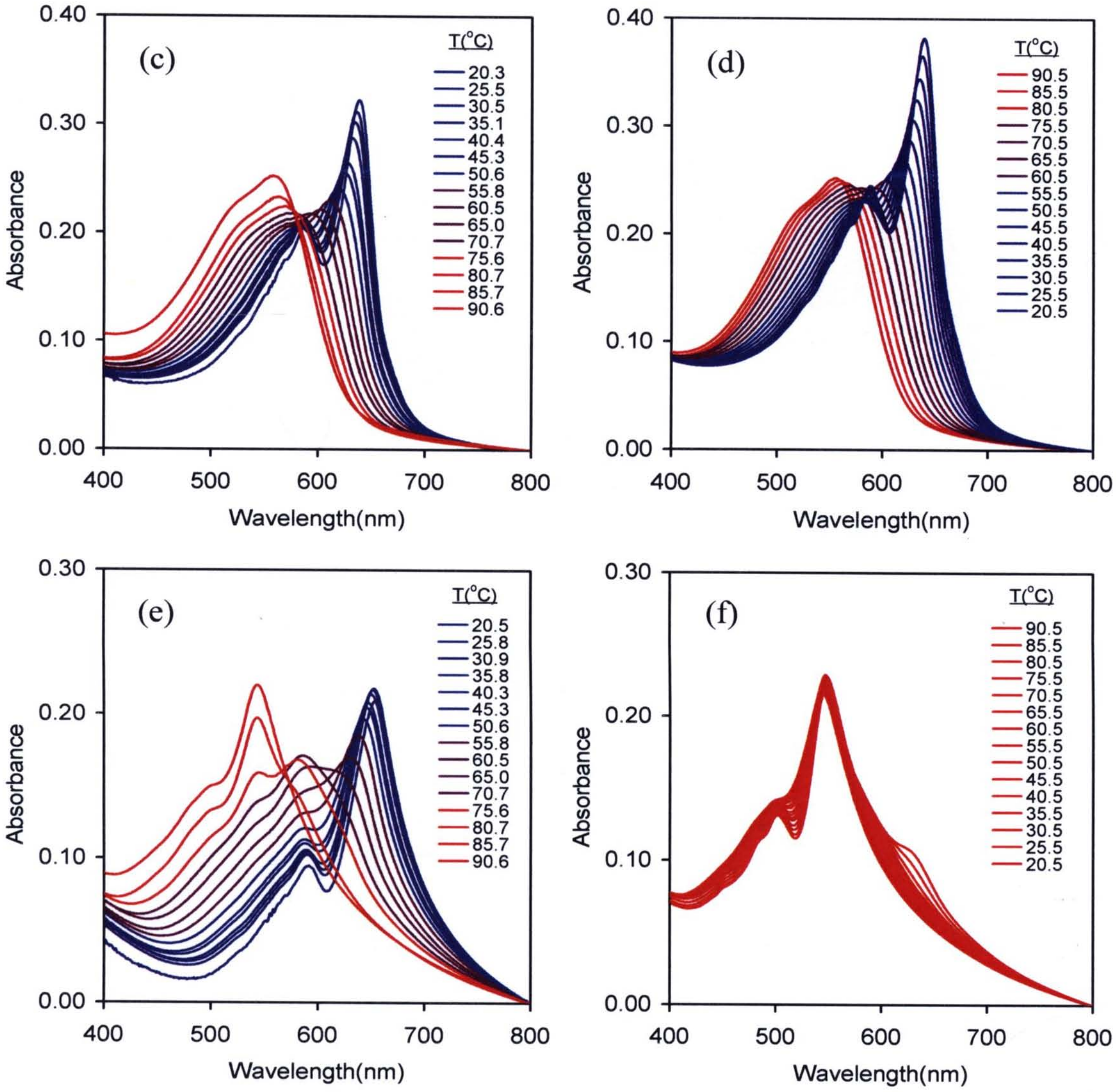


Figure 23 (cont.)

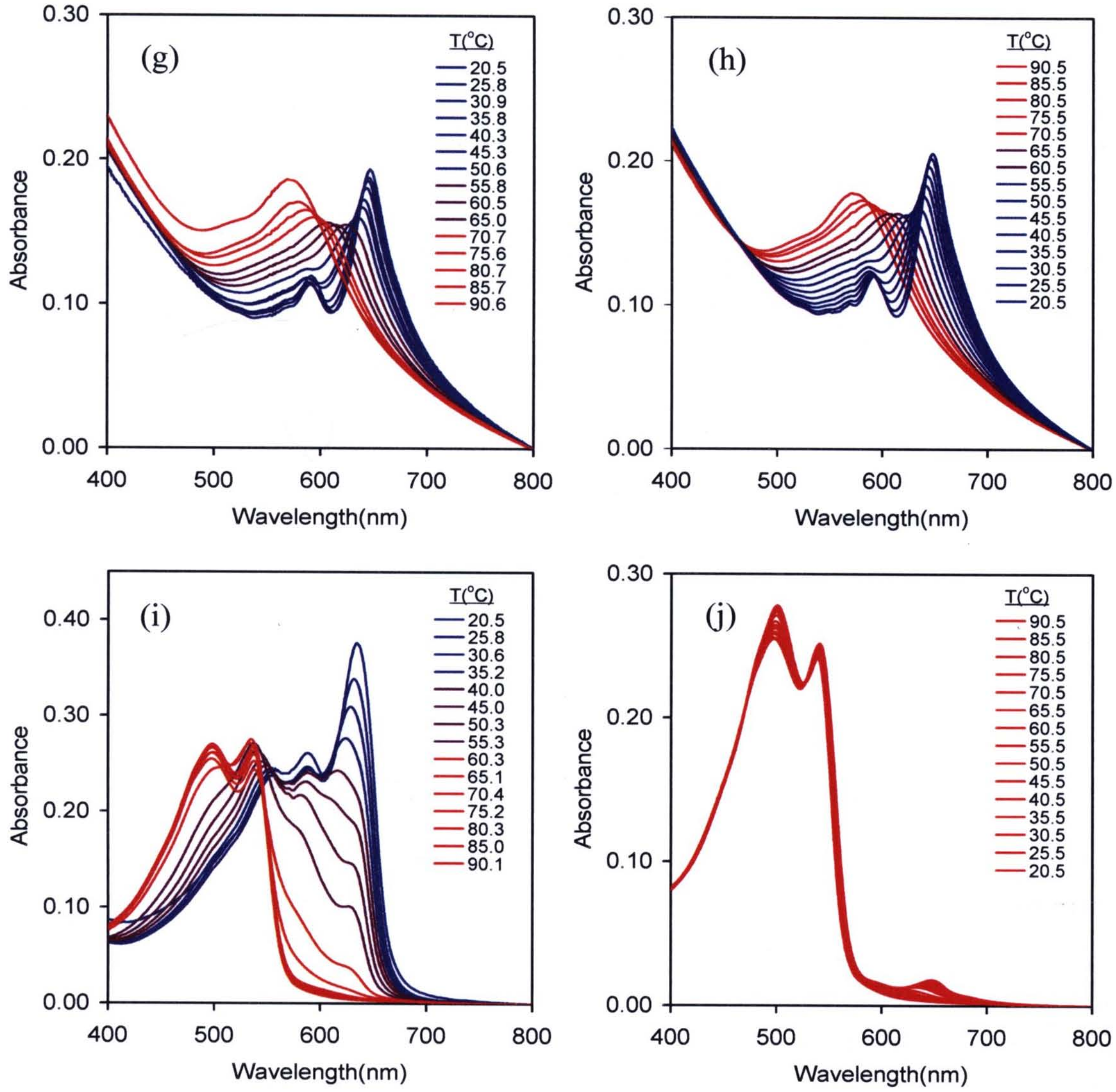


Figure 23 (cont.)

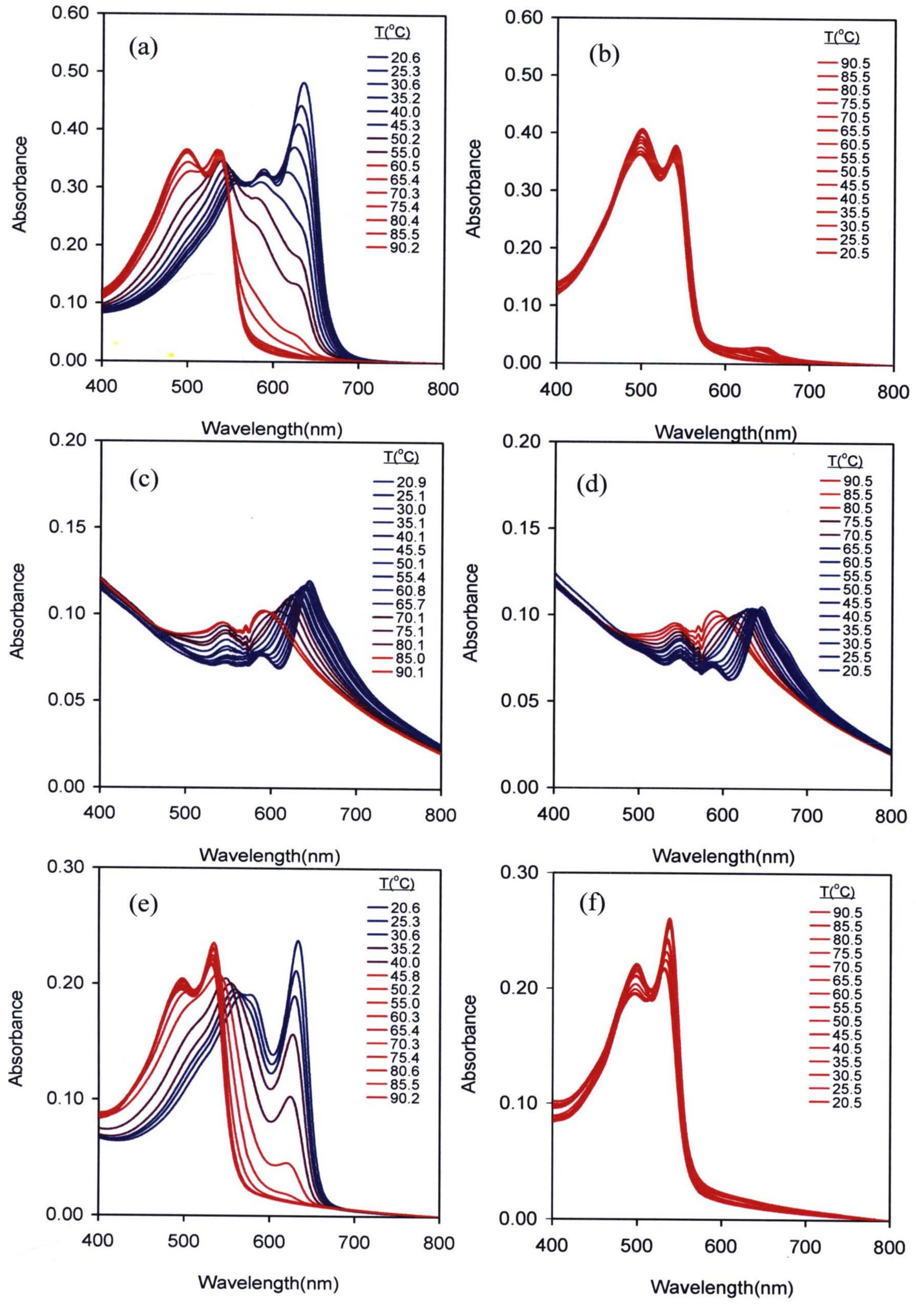


Figure 24 Absorption spectra of (a,b) poly(p-PA-2DA), (c,d) poly(m-PA-2DA) and (e,f) poly(c-CA-2DA) assemblies in aqueous solution measured upon heating (left) and cooling (right)

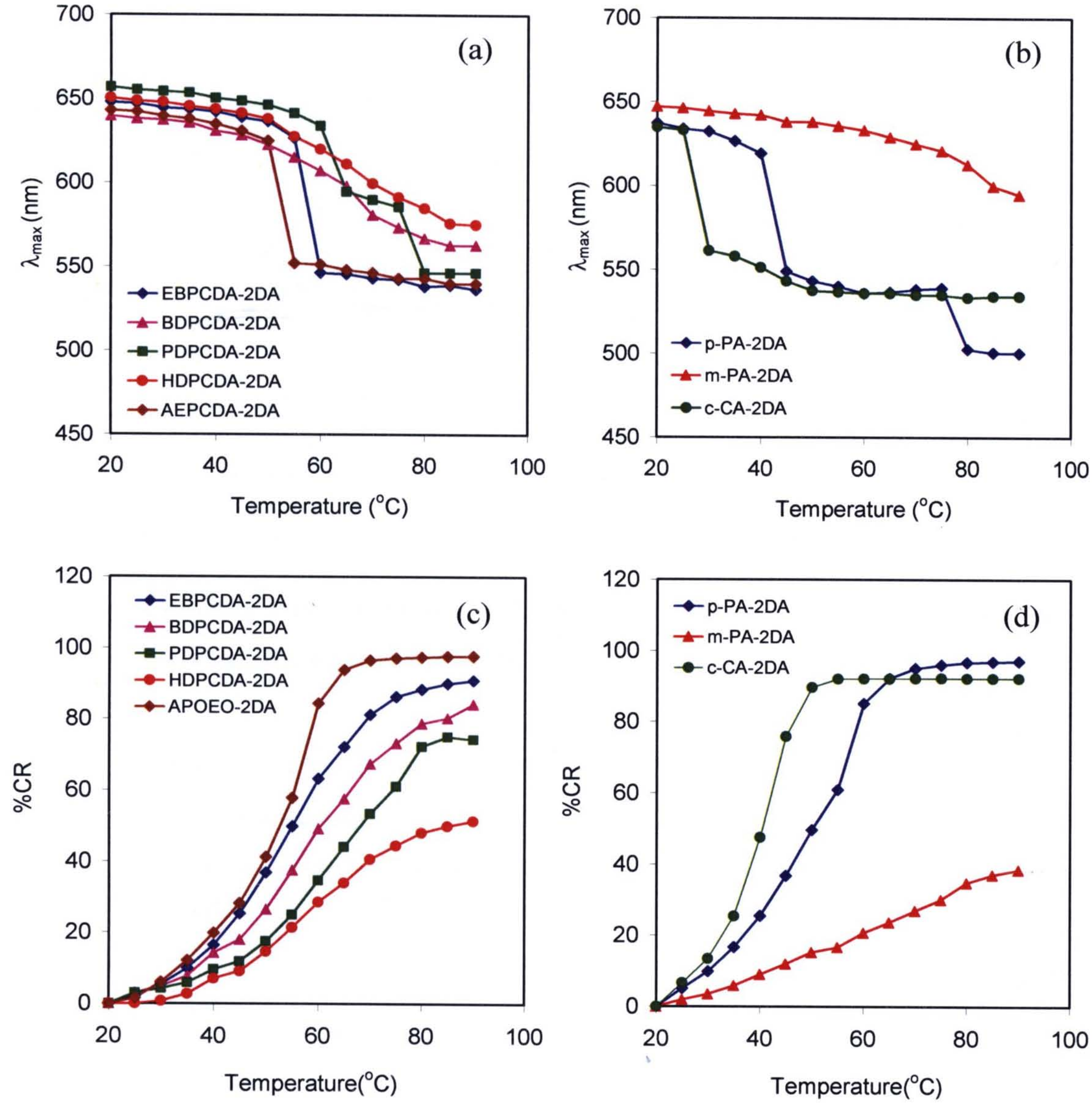
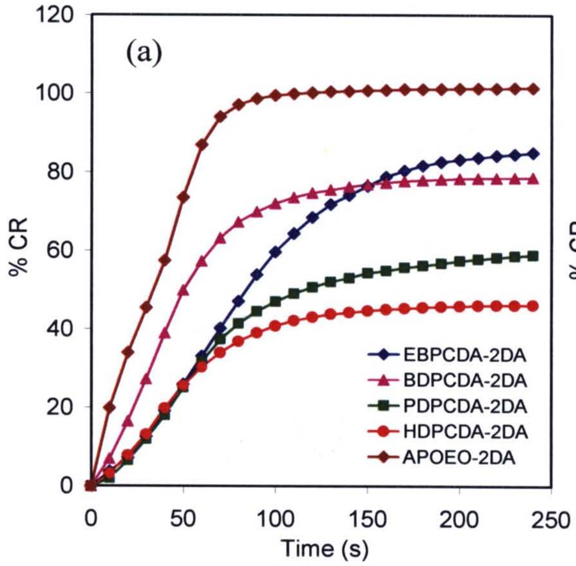


Figure 25 **(a,b) The change of λ_{max} absorption spectra of of PDA assemblies as a function of temperature and (c,d) colorimetric response. The samples are measured upon heating.**



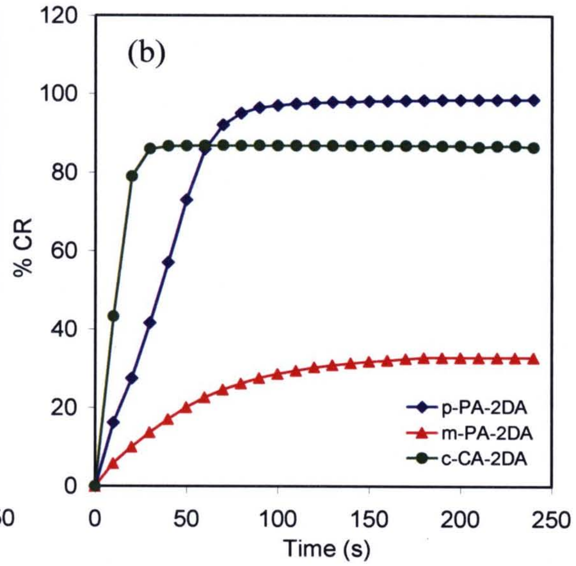


Figure 26 Colorimetric responses of PDA assemblies as a function of time when the samples are heated at 90 °C.

Table 2 Thermal color transition and reversibility of the PDA assemblies in aqueous solution

Monomer	Color transition temperature (°C)	Reversibility
PCDA	60	irreversible
EBPCDA-2DA	60	reversible
BDPCDA-2DA	65	reversible
PDPCDA-2DA	65	irreversible
HDPCDA-2DA	80	reversible
APOEO-2DA	55	irreversible
p-PA-2DA	45	irreversible
m-PA-2DA	80	reversible
c-CA-2DA	30	irreversible

In the following study, we investigate the color transition temperature and reversibility of PDA assemblies in drop cast film. The films of PDA assemblies on quartz slide are annealed for 5 minutes at different temperatures ranging from 30 to 250 °C. The photographs of PDA films at each temperature are recorded. When the films are cooled down to room temperature, the photographs and absorption spectra of the annealed film are measured to explore the color reversibility. Fig. 27 illustrates absorption spectra of PDA assemblies in drop cast film measured upon variation of annealing temperature. We observe that the PDA assemblies in drop cast film exhibits higher color transition temperature than that of the solution. The 1^{st} color transition (blue to purple) and 2^{nd} color transition (purple to red) of poly(EBPCDA-2DA) occurs at 65 °C and 110 °C. The poly(EBPCDA-2DA) assemblies exhibit complete reversible thermochromism in temperature range of 25 – 150 °C. However, when the temperature is increased above 150 °C, the PDA assemblies exhibit irreversible thermochromism (see Fig. 28). Increasing length of alkyl linker of carbon (N=2,4,5,6) causes slight increase of the 1^{st} transition temperature while the 2^{nd} transition temperature are about 110 °C. The temperature range of complete reversible thermochromism varies with length of alkyl linker. The poly(PDPCDA-2DA) (N=5) assemblies only exhibit irreversible thermochromism, which is similar to the behavior in aqueous solution. The change from alkyl linker to ethyleneoxide linker also results in irreversible thermochromism. The color transition of PDA assemblies constituting phenyl linkers, poly(p-PA-2DA) and poly(c-CA-2DA), occurs irreversibly (see Fig. 29). However, the use of (m-PA-2DA) causes complete reversible color transition at 25-65 °C. Color transition temperature and reversibility of the PDA assemblies in drop cast film is summarized in Table 3.

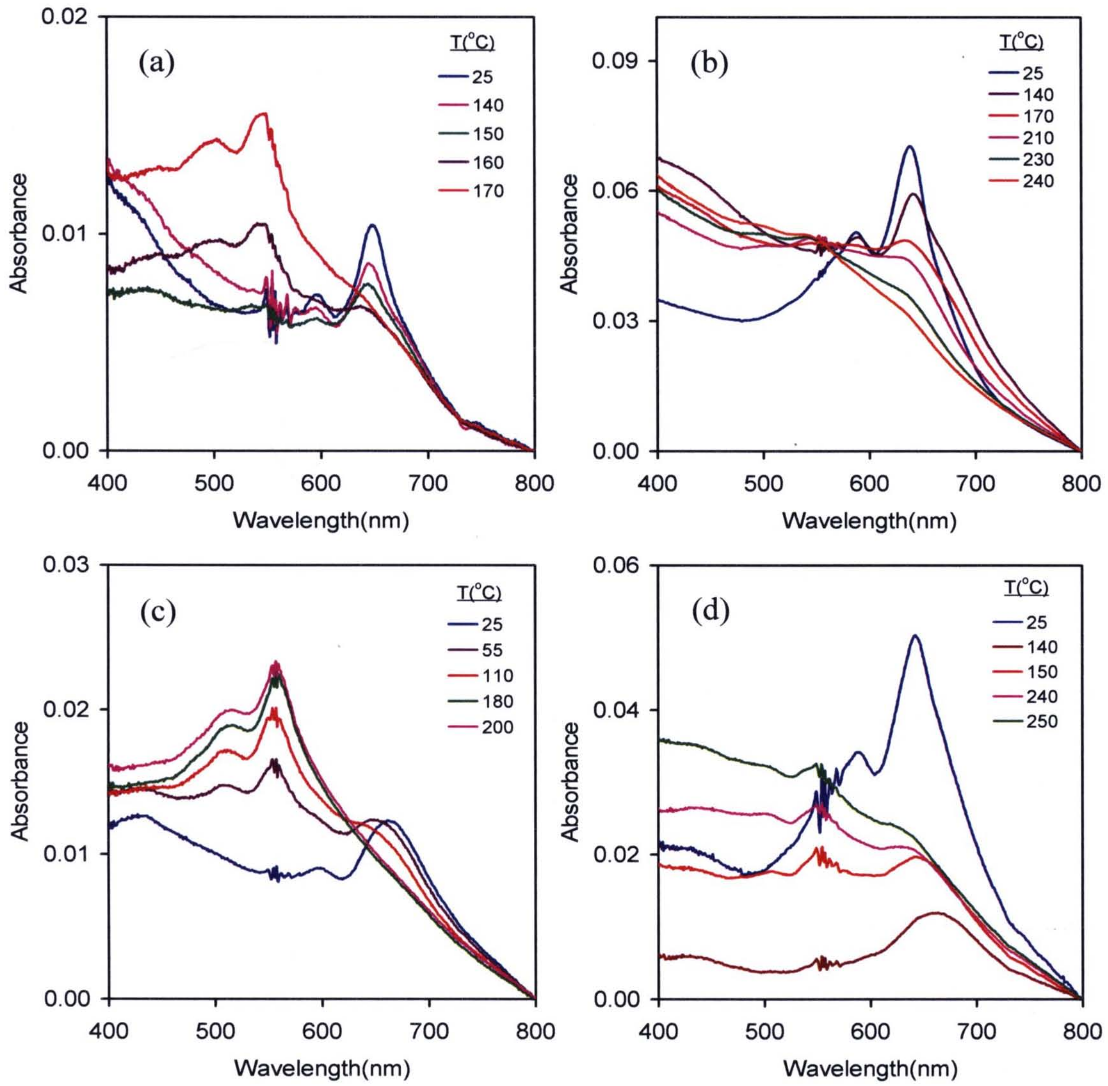


Figure 27 Absorption spectra of (a) poly(EBPCDA-2DA), (b) poly(BDPCDA-2DA), (c) poly(PDPCDA-2DA), (d) poly(HDPCDA-2DA), (e) poly (APOEO-2DA), (f) poly(p-PA-2DA), (i) poly(m-PA-2DA) and (j) poly(c-CA-2DA) assemblies in drop cast film measured upon varied temperature

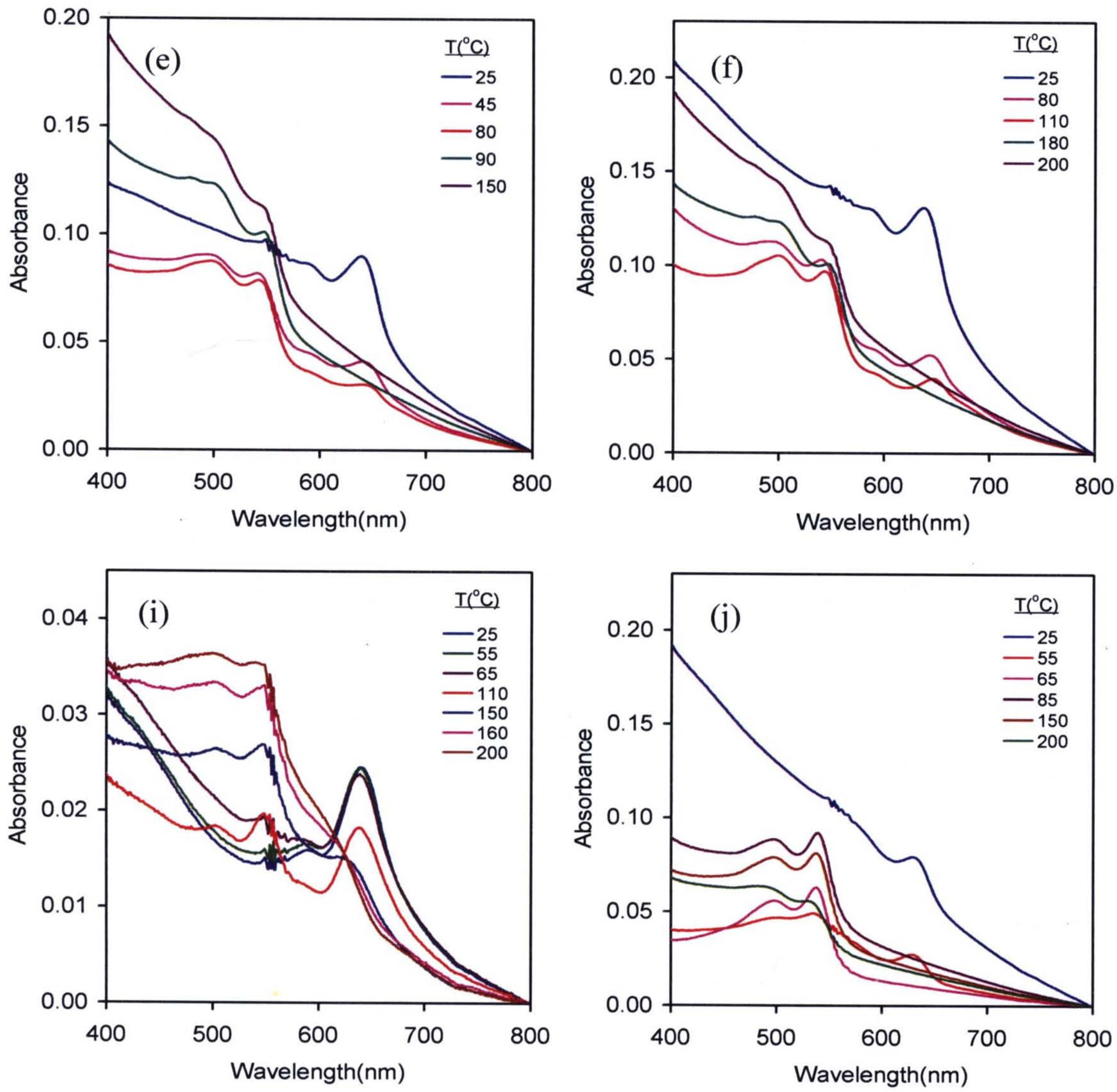


Figure 27 (cont.)

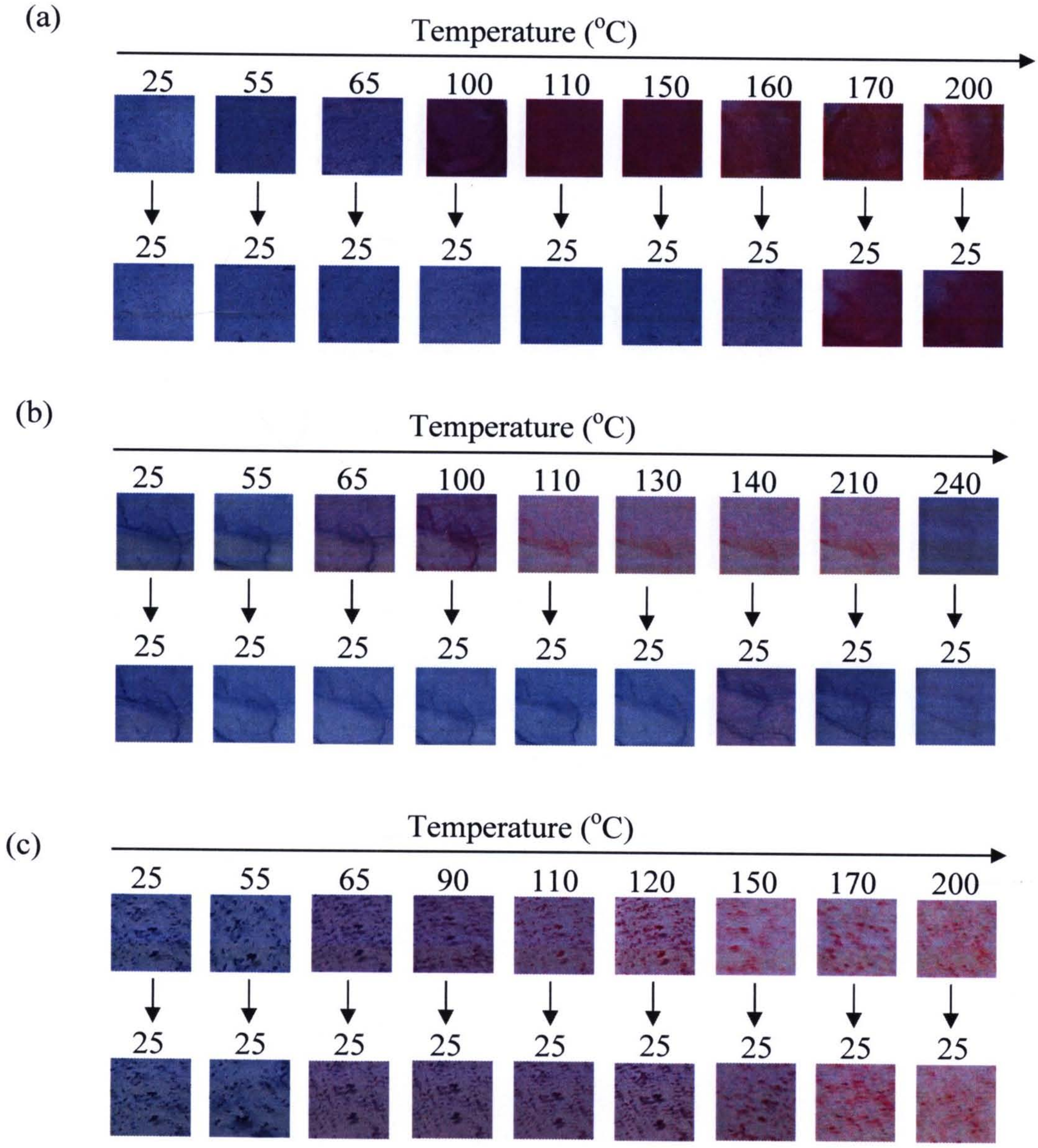
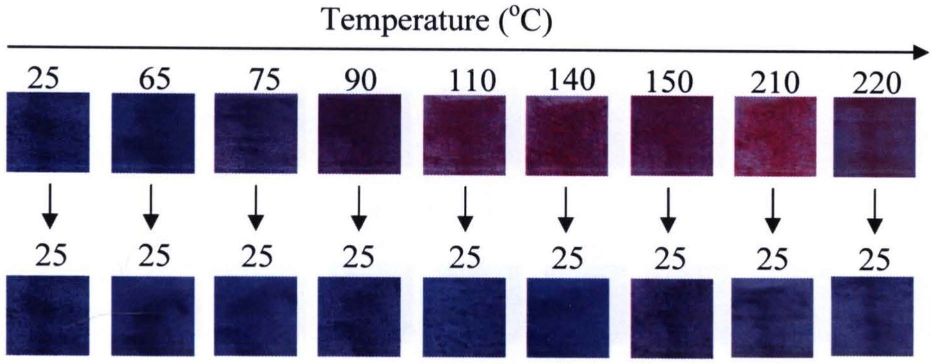


Figure 28 Color photographs of (a) poly(EBPCDA-2DA), (b) poly(BDPCDA-2DA), (c) poly(PDPCDA-2DA), (d) poly(HDPCDA-2DA) and (e) poly (AEPCDA-2DA) in drop cast film to taken upon heating and cooling at 25°C

(d)



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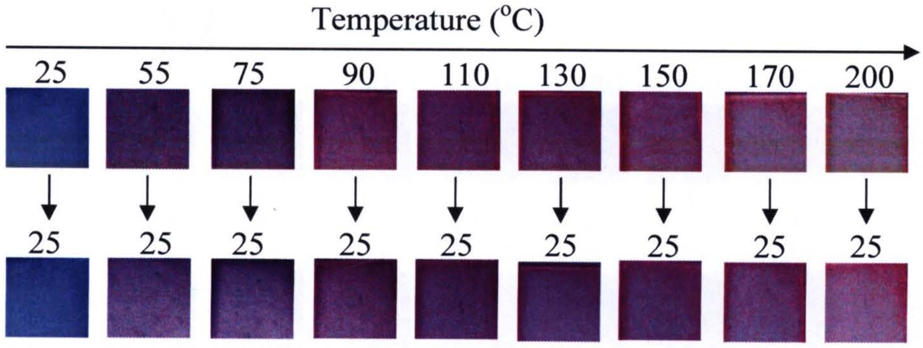


Figure 28 (cont.)

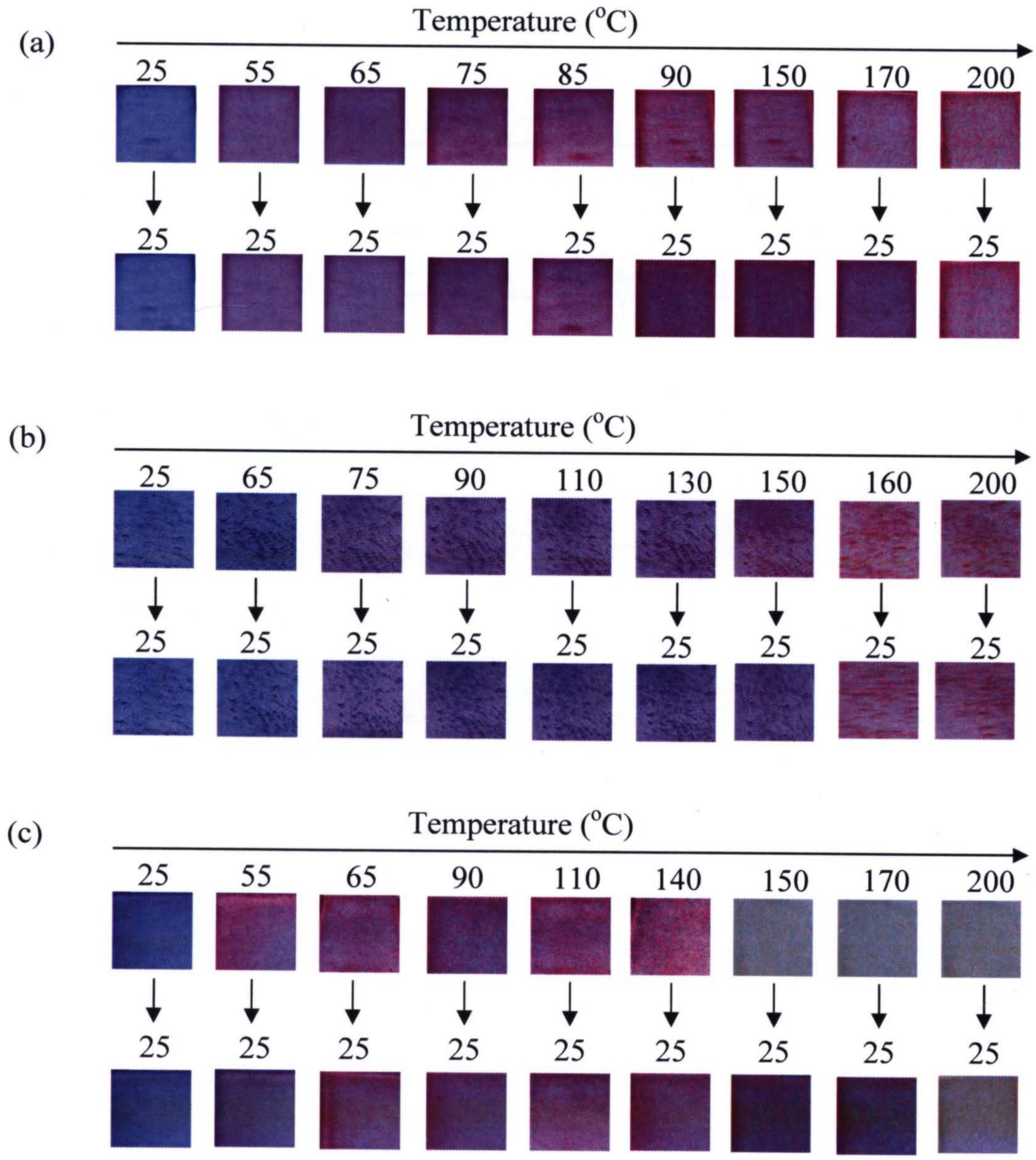


Figure 29 Color photographs of (a) poly(p-PA-2DA), (b) poly(m-PA-2DA) and (c) poly(c-CA-2DA) in drop cast film to taken upon heating and cooling at 25°C

Table 3 Color transition temperature and reversibility of the PDA assemblies in drop cast film

Monomer	Color transition temperature (°C)		Temperature range for complete reversibility
	1[st] transition Blue → Purple	2[nd] transition Purple → Red	
EBPCDA-2DA	65	110	25 - 150
BDPCDA-2DA	65	110	25 – 130
PDPCDA-2DA	55	110	irreversible
HDPCDA-2DA	75	110	25 - 140
APOEO-2DA	55	90	irreversible
p-PA-2DA	55	90	irreversible
m-PA-2DA	65	150	25-65
c-CA-2DA	55	65	irreversible

The interaction of PDA assemblies is explored by utilizing infrared (IR) spectroscopy. Fig. 30 illustrates FT-IR spectra of (a) poly(EBPCDA-2DA) and (b) poly(HBPCDA) assemblies measured upon variation of annealing temperature. The films of poly(EBPCDA-2DA) assemblies at 25 °C show ν(C=O),ν(CH_2) and ν(NH) at 1640, 2919 and 3282 cm^{-1}, respectively. The films of poly(EBPCDA-2DA) assemblies annealed at 110 °C show ν(C=O), ν(CH_2) and ν(NH) at 1642, 2923 and 3285 cm^{-1}, respectively, which are similar to the values at room temperature. This result indicates that the increase of temperature to 110 °C, causing reversible color transition, does not break the hydrogen bonding between the head group. The results obtained from the poly(HDPCDA-2DA) assemblies are consistent.

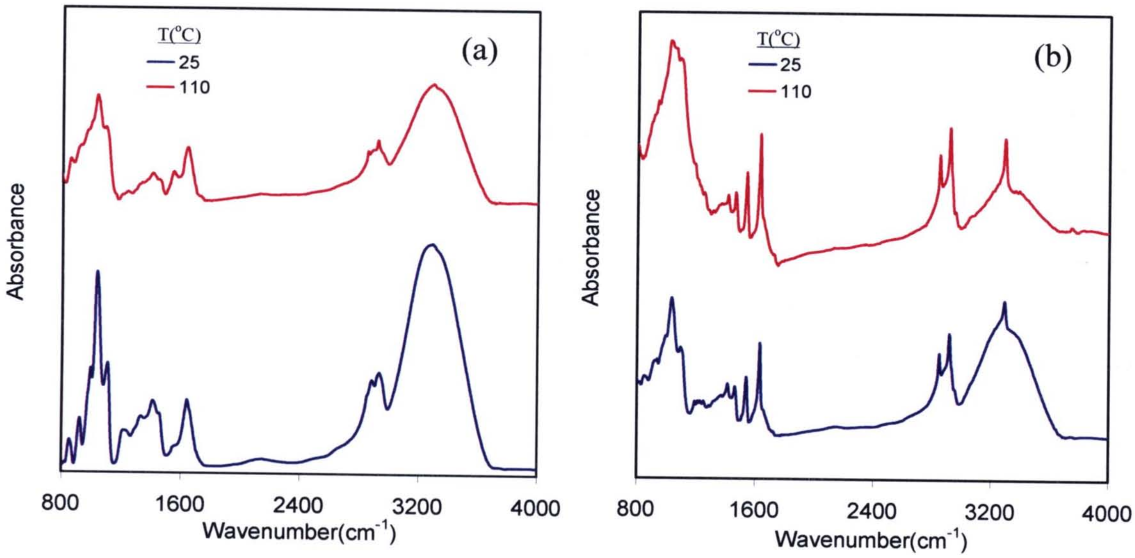


Figure 30 FT-IR spectra of drop cast film of (a) poly(EBPCDA-2DA) and (b) poly (HBPCDA-2DA) assemblies measured upon variation of annealing temperature

Table 4 FT-IR peak assignments of PDA assemblies measured in ATR mode

Peak Assignments (cm^{-1})	poly(EBPCDA-2DA)		poly(HDPCDA-2DA)	
	25 (°C)	110 (°C)	25 (°C)	110 (°C)
νC=O	1640	1642	1629	1631
ν_aCH_2	2919	2923	2914	2915
ν_sCH_2	2873	2877	2863	2877
νNH	3282	3285	3286	3290

Thermochromic properties and the morphologies of PDA assemblies in other solvents

In this section, we investigate the effect of structural modification on thermochromic and the morphologies of PDA assemblies prepared in other solvents. The PDA assemblies are prepared by dispersing in linear alkanes and alcohols solvent. Table 5 shows properties of solvents used in this study. Fig.31. illustrates photographs of poly(EBPCDA-2DA) assemblies in various solvents. We observe that the poly(EBPCDA-2DA) assemblies tend to precipitate in alkanes and alcohols.

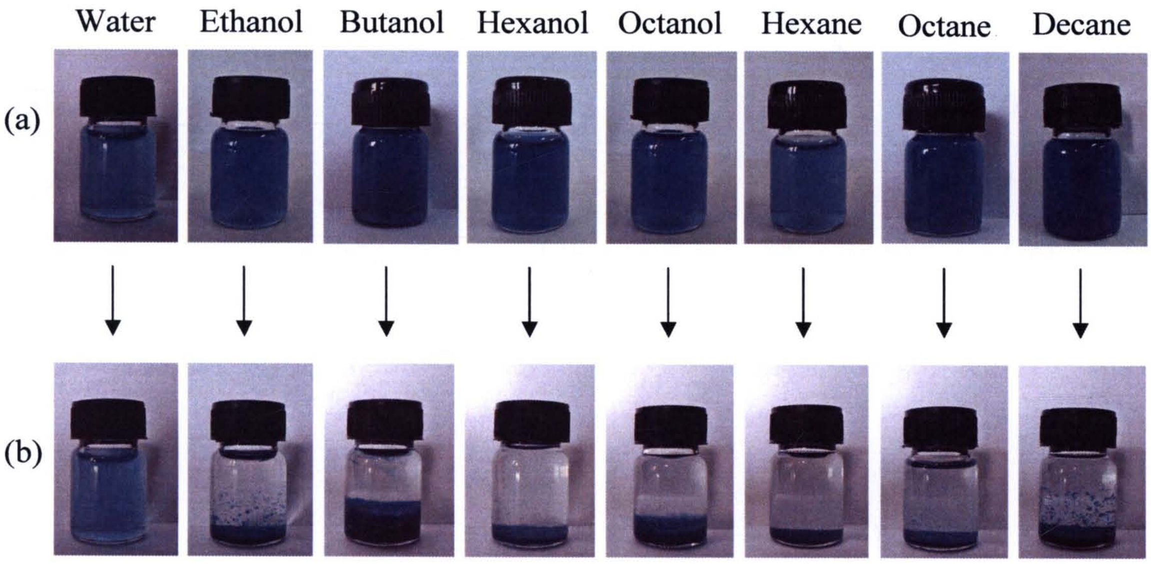
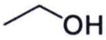


Figure 31 Photographs of poly(EBPCDA-2DA) assemblies in various solvents when (a) fresh solution and (b) stand over night at 25 °C

The morphologies of PDA assemblies prepared in various solvents are explored by utilizing SEM. Fig. 32 illustrates SEM images of poly(EBPCDA-2DA) assemblies prepared by dropping the suspensions on polished silicon wafer. The poly(EBPCDA-2DA) assemblies prepared in all solvents exhibit sheet-like shape. However, the shape of PDA assemblies prepared in alkanes and alcohols is much more well-defined compared to the PDA assemblies prepared in aqueous suspension.

Table 5 Properties of solvents including boiling point, melting point and dielectric constant

Solvents		Boiling point (°C)	Melting point (°C)	Dielectric constant
Water		100	0	78.30
Ethanol		78	-114	25.30
Butanol		118	-90	13.45
Hexanol		155	-53	13.03
Octanol		195	-16	10.30
Hexane		69	-95	1.89
Octane		126	-57	1.48
Decane		174	-28	1.99

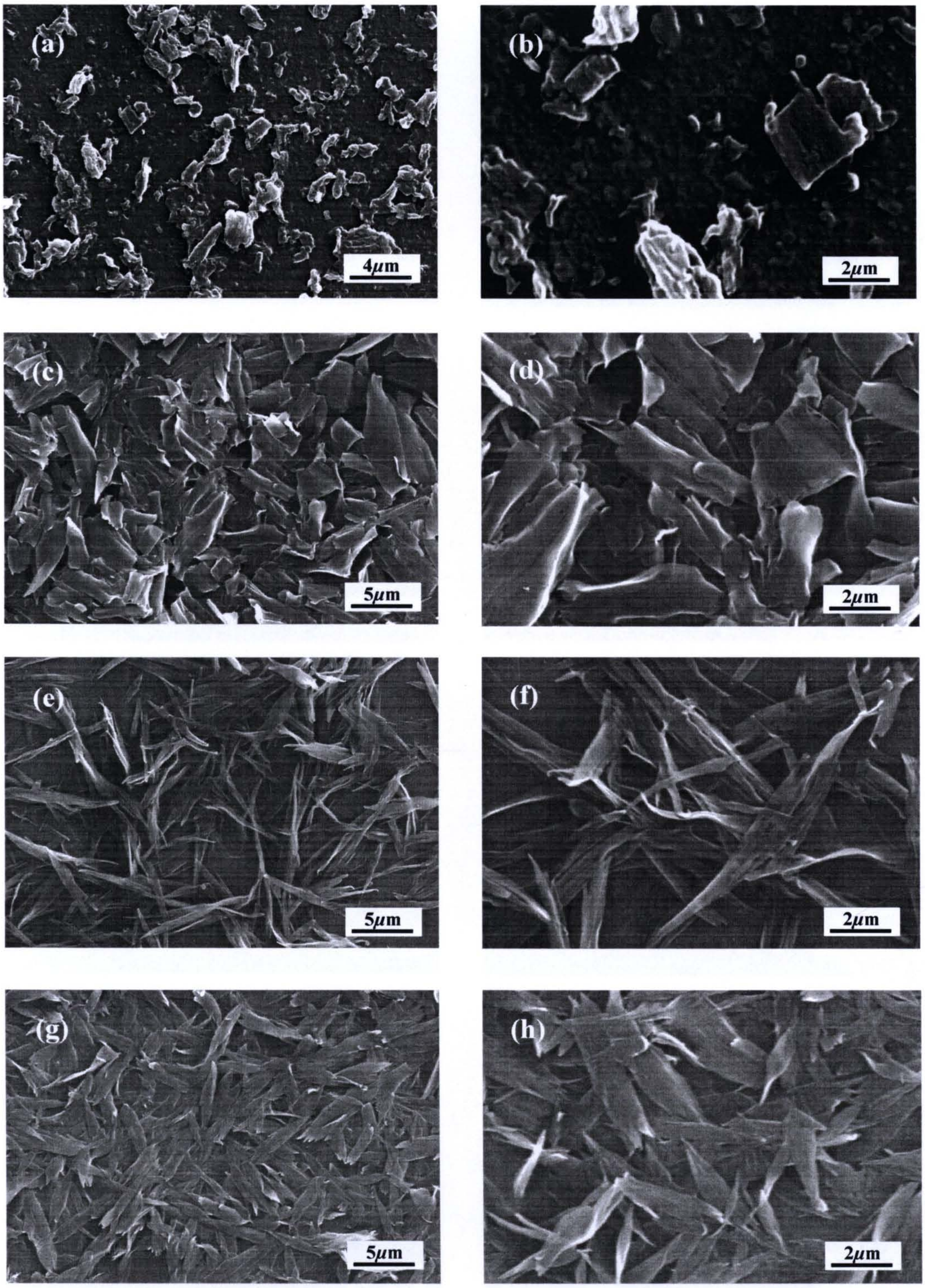


Figure 32 SEM images of poly(EBPCDA-2DA) assemblies in (a,b) water, (c,d) ethanol, (e,f) butanol, (g,h) hexanol, (i,j) octanol, (k,l) hexane, (m,n) octane and (o,p) decane on polished silicon wafer

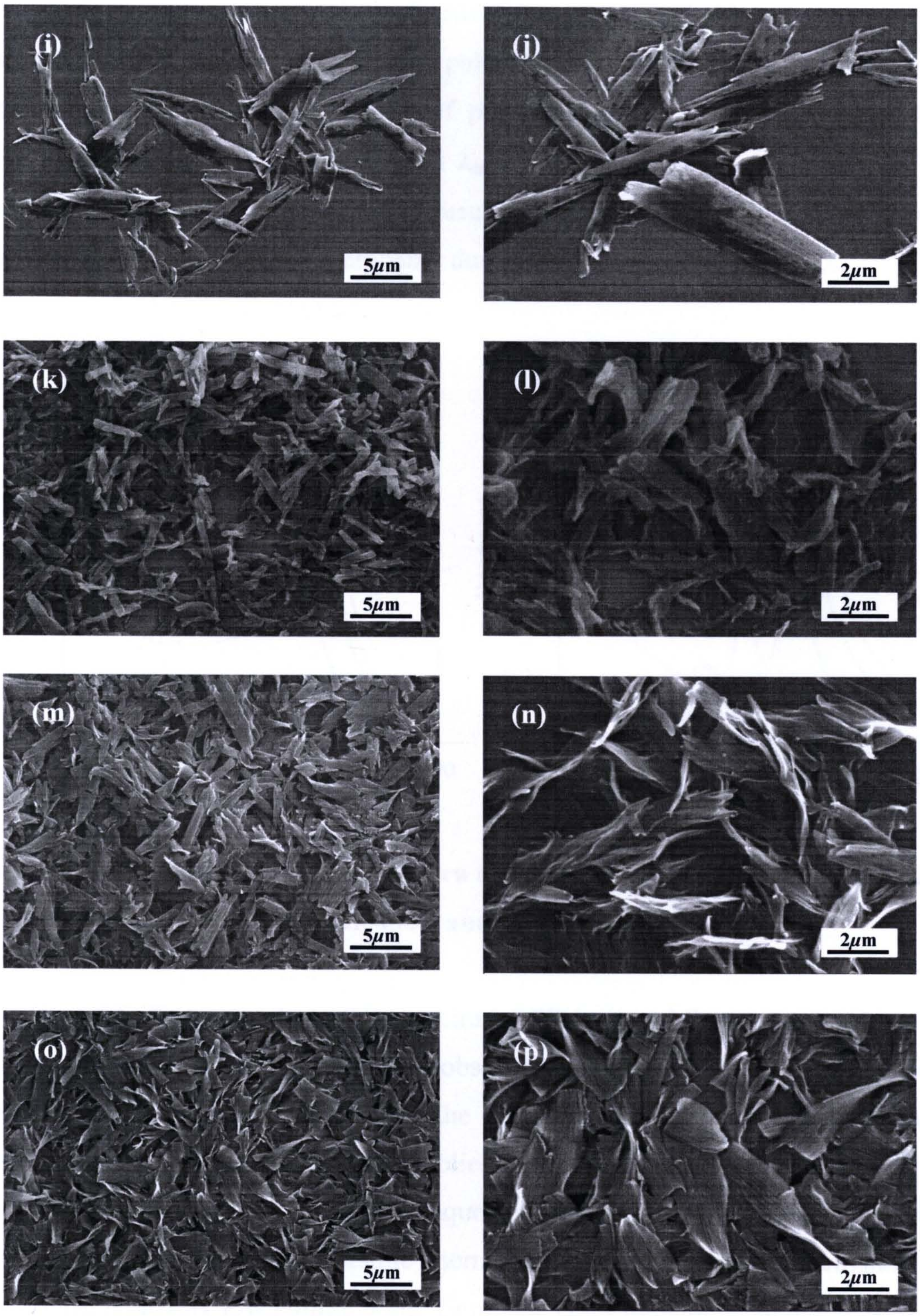


Figure 32 (cont.)

The absorption spectra of poly(EBPCDA-2DA) assemblies in alkanes and alcohols exhibit a red-shift compared to poly(EBPCDA-2DA) assemblies in aqueous suspension (see Fig. 33). Blue phase of poly(EBPCDA-2DA) assemblies in these solvents exhibit maximum absorption at λ_{max} ~655 nm while the λ_{max} of the PDA assemblies in water is at 639 nm. This result indicates the increasing of conjugation length of PDA in these solvents, probably due to the higher chain ordering.

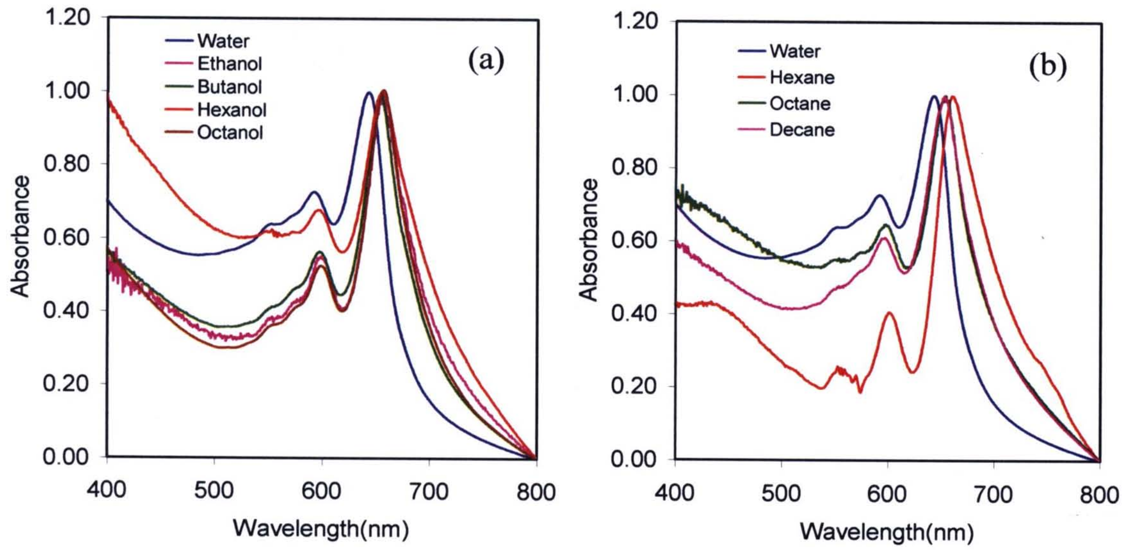


Figure 33 Normalized absorption spectra of poly(EBPCDA-2DA) assemblies in various solvents. (a) alcohols and (b) alkanes

Fig. 34 illustrates absorption spectra of PDA assemblies in various solvents measured upon heating and cooling. We observe that the variation of solvents affects both color transition temperature and the thermochromic reversibility. The color transition of poly(EBPCDA-2DA) assemblies in aqueous suspension occurs in a fully reversible fashion. The change from aqueous suspension to alkane and alcohol solvents results in partially reversible thermochromism. However, the ethanol and hexane have relatively low boiling point. Complete color transition can not be reached. Therefore, poly(EBPCDA-2DA) assemblies still exhibit reversible thermochromism in these two solvents. We believe that the alcohols and alkanes can penetrate into the outer layers of poly(EBPCDA-2DA) assemblies during the heating process, causing the partial irreversibility.

To investigate the color transition behavior in more details, the λ_{max} is plotted as a function of temperature (see Fig. 35a). It is clear that the color transition temperature varies with the solvents. The poly(EBPCDA-2DA) assemblies in water exhibit color transition at about 60 °C. The change of solvent from water to alcohols causes about 10 °C increase of the color transition. The variation of alcohol structure hardly affects the color transition. For the system of alkanes (see Fig. 35b), color transition of octane and decane takes place at 70 and 80 °C, respectively. Color transition temperature and reversibility of the PDA assemblies in various solvents are summarized in Table 6.

The plots of colorimetric response (%CR) as a function of temperature of alcohol system are illustrated in Fig. 35c. The poly(EBPCDA-2DA) assemblies in alcohols exhibit lower %CR value compared to that of the aqueous suspension. The decreasing of polarity of alcohols causes slight increase of %CR value. For the system of alkanes (see Fig. 35d), the poly(EBPCDA-2DA) assemblies in octane exhibits highest change of the %CR value.

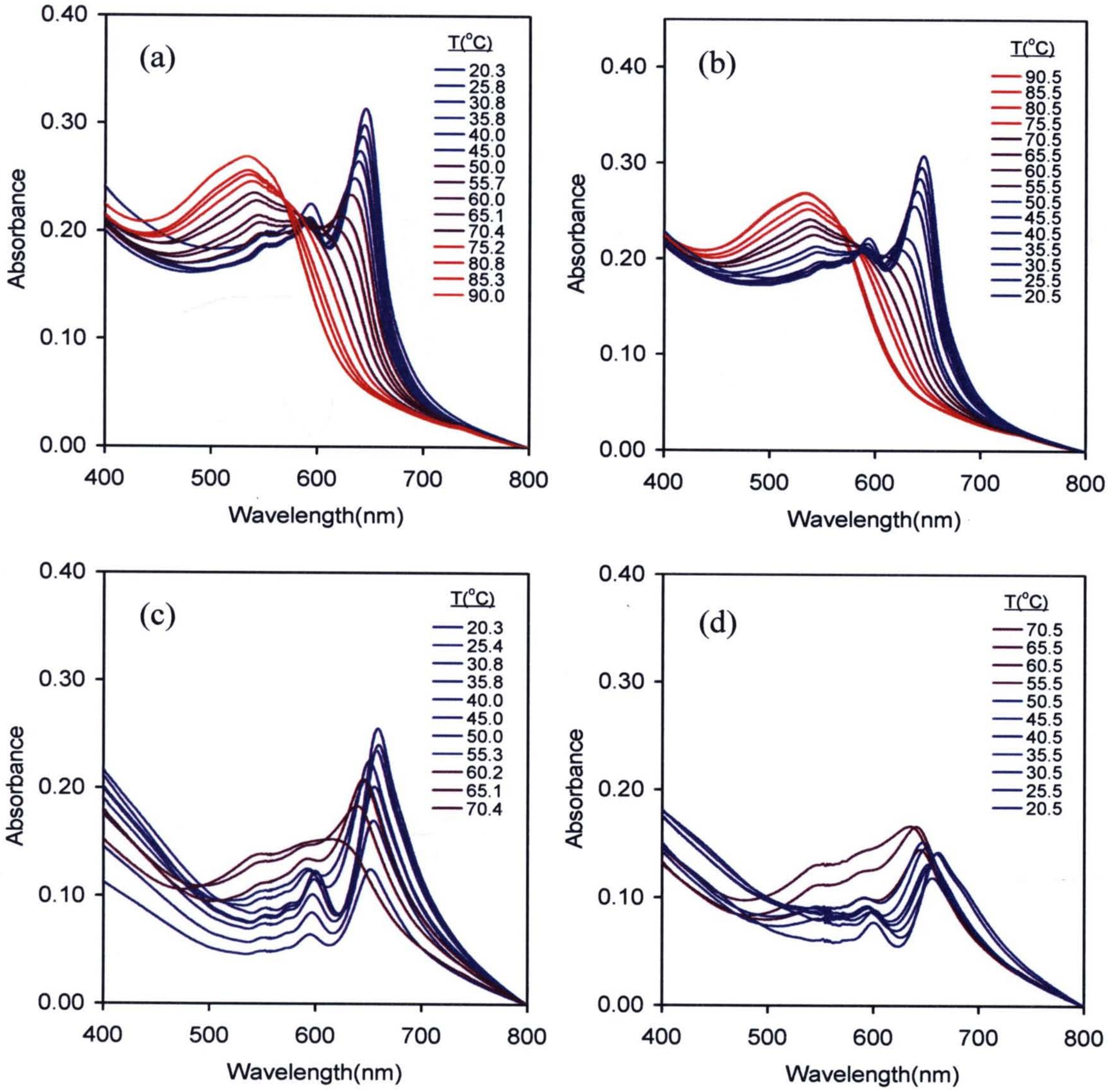


Figure 34 Absorption spectra of poly(EBPCDA-2DA) assemblies in (a,b) water, (c,d) ethanol, (e,f) butanol, (g,h) hexanol, (i,j) octanol, (k,l) hexane, (m,n) octane and (o,p) decane measured upon heating (left) and cooling (right)

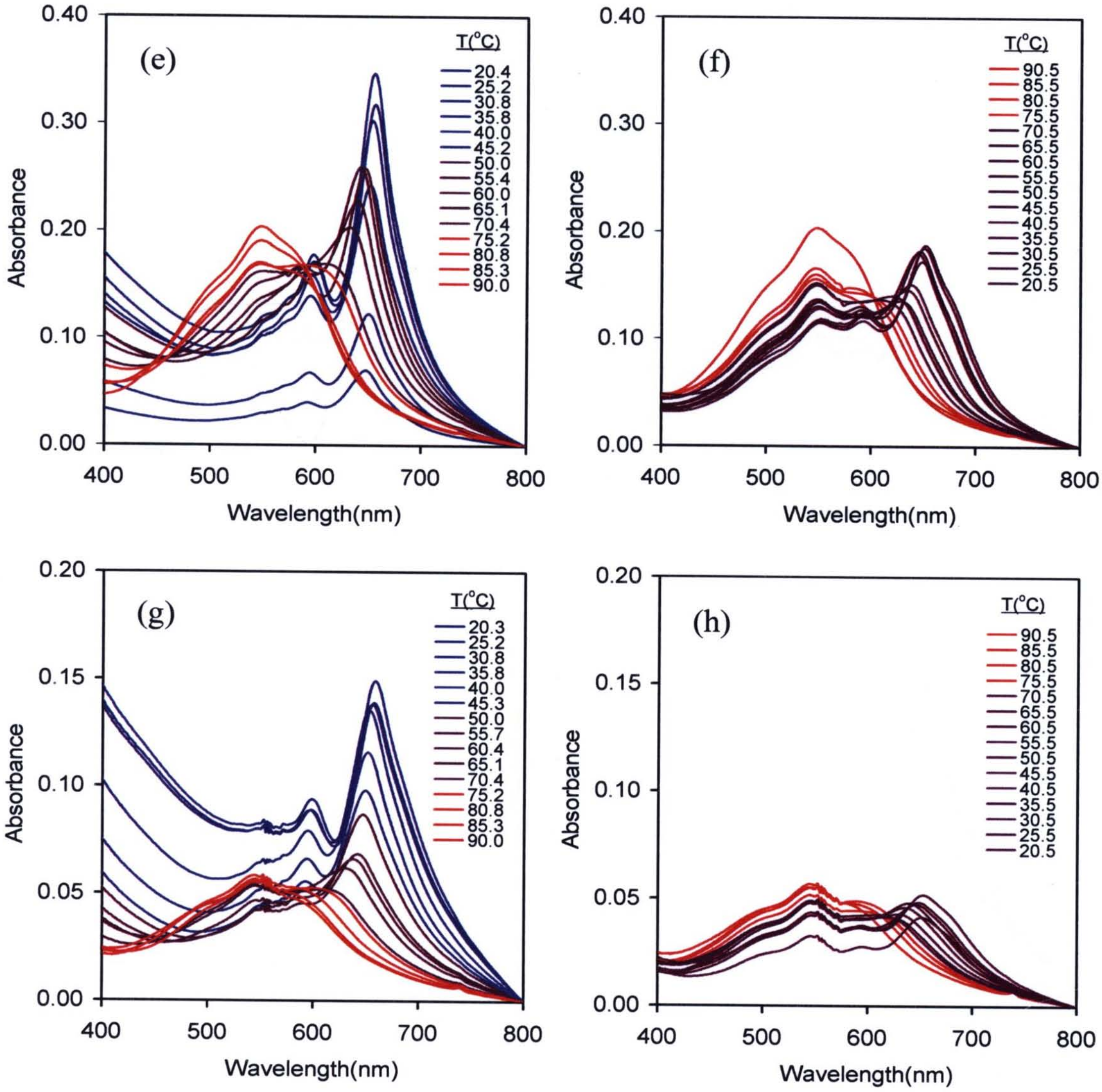


Figure 34 (cont.)

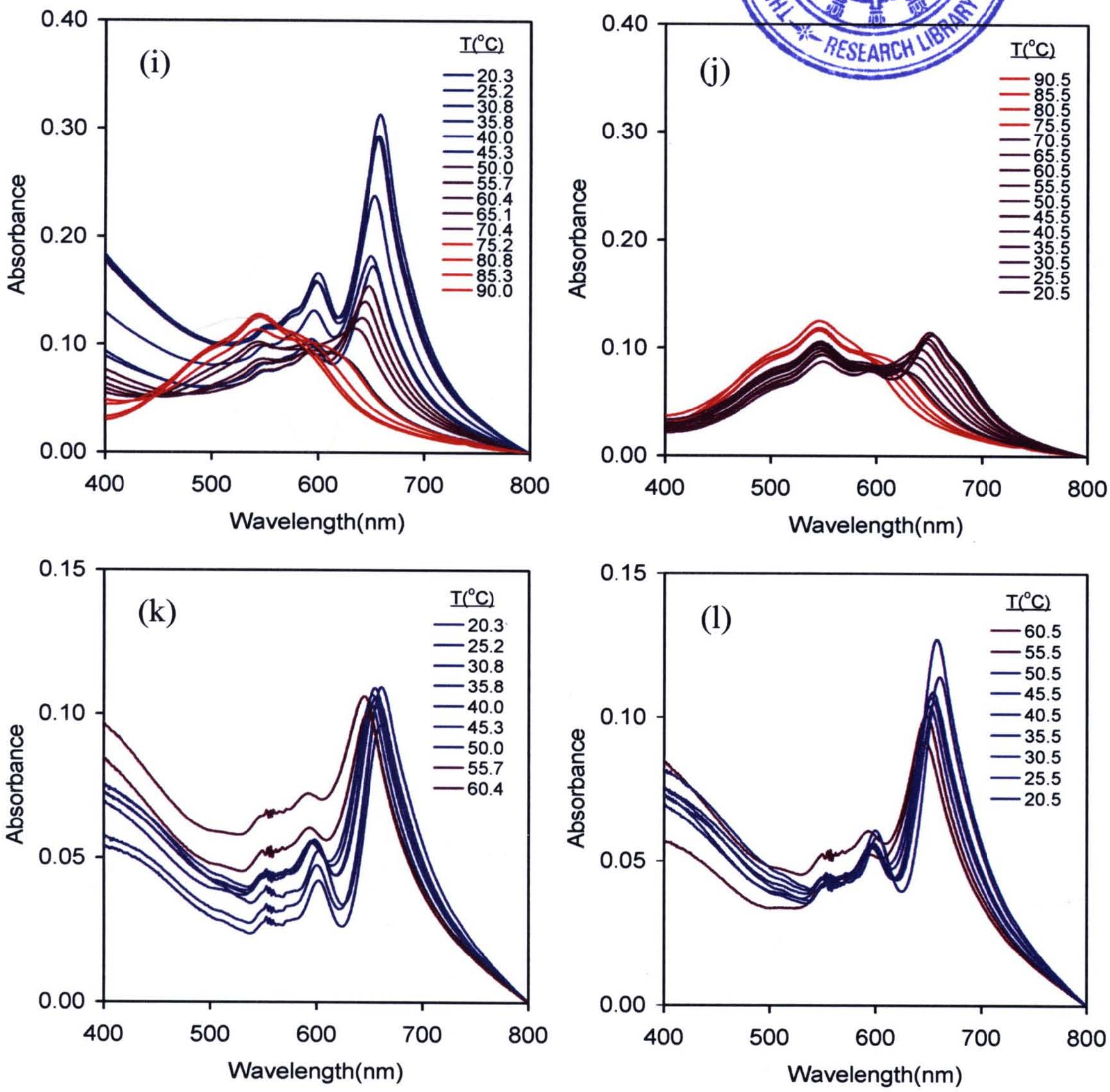


Figure 34 (cont.)

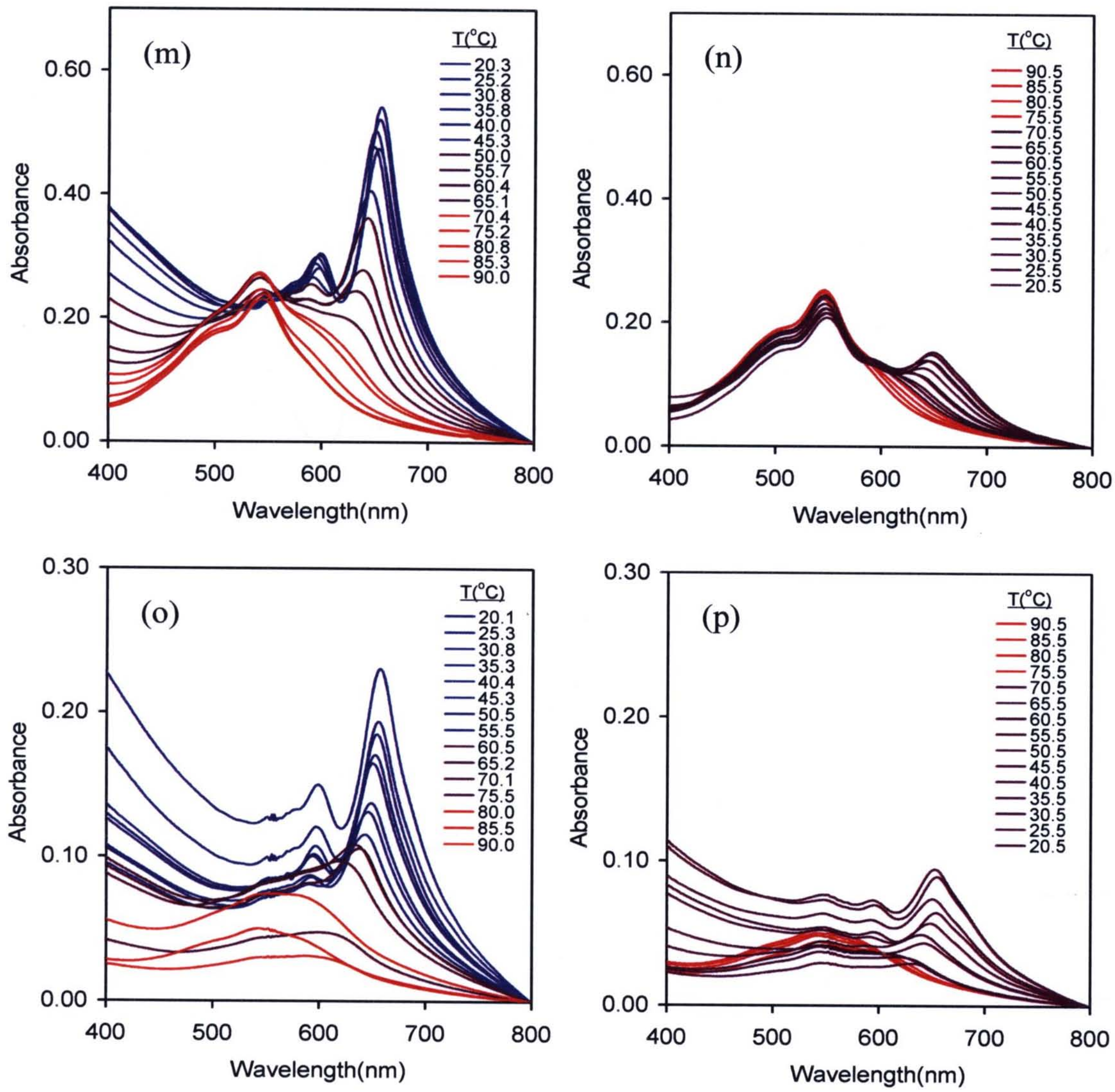


Figure 34 (cont.)

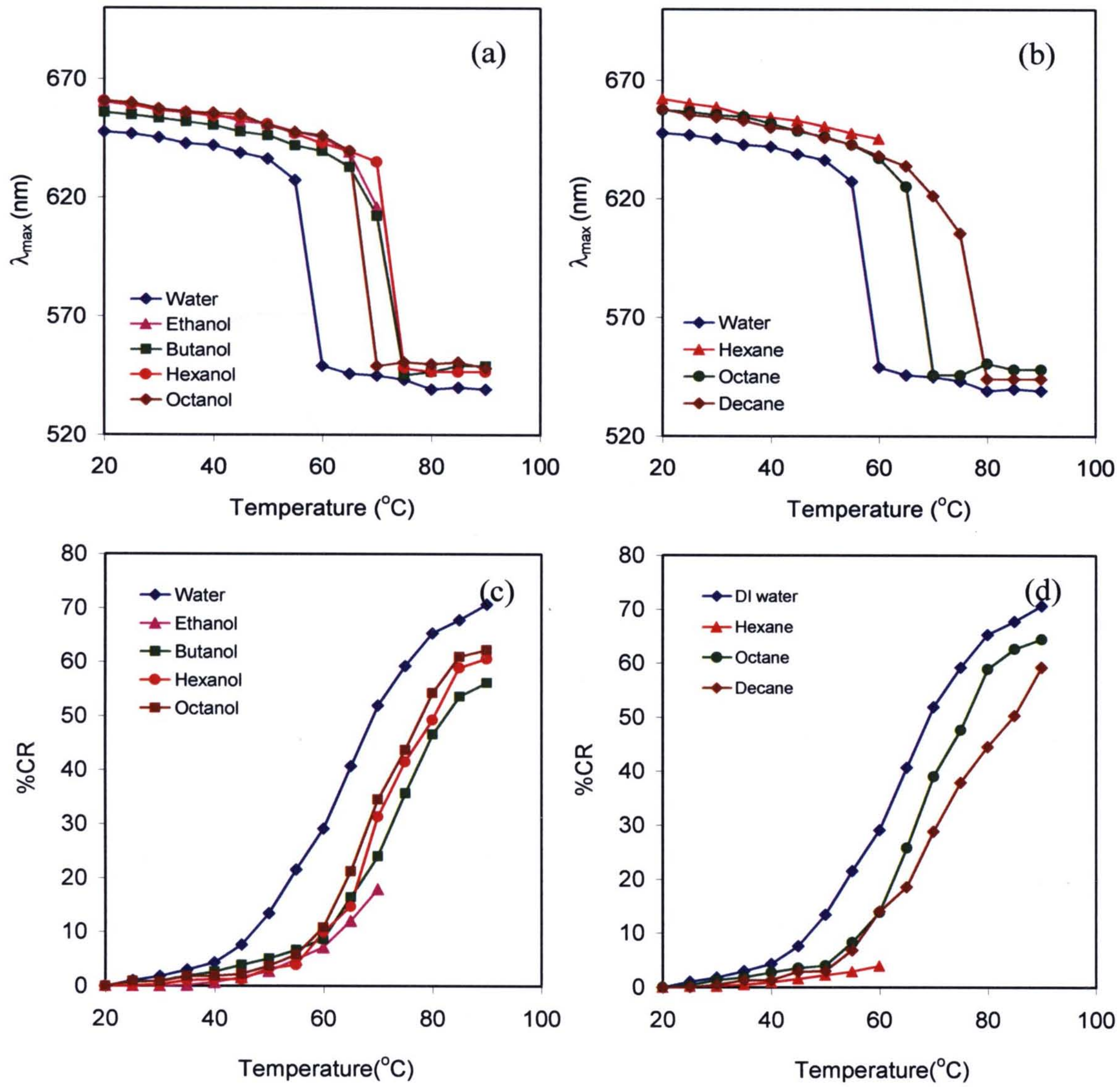


Figure 35 The change of (a,b) λ_{max} and (c,d) colorimetric response is plotted as a function of temperature. The samples are measured upon heating

Table 6 Color transition temperature and reversibility of poly(EBPCDA-2DA) assemblies in various solvents

Solvents	Color transition temperature (^{o}C)	Reversibility
Water	60	fully reversible
Ethanol	-	-
Butanol	70	partially reversible
Hexanol	70	partially reversible
Octanol	70	partially reversible
Hexane	-	-
Octane	70	partially reversible
Decane	80	partially reversible

In the following study, we investigate the color transition temperature and reversibility of PDA assemblies in drop cast films. The films of PDA assemblies on quartz slide are annealed for 5 minutes at different temperatures ranging from 30 to 200 °C. In the dried films, the penetration of solvents into layers of PDA can not take place. The color transition behaviors of PDA prepared in alcohols and alkanes are quite different from the results observed in the solution. The photographs of PDA films at each annealing temperature are recorded to follow the color transition. The photographs of the annealed films at room temperature are also measured to explore the color reversibility. Fig. 36 illustrates photographs of drop cast films of poly(EBPCDA-2DA) assemblies prepared from various solvents. The PDA assemblies in drop cast films exhibit higher color transition temperature than that of their respective solutions. The 1st color transition (blue to purple), 2nd color transition (purple to red) and 3rd transition (red to orange) poly(EBPCDA-2DA) assemblies obtained from aqueous solution occur at 65,110 and 160 °C, respectively. The drop cast films obtained from alcohols and alkanes also exhibit three-step color transition at 90, 120 and 160 °C, respectively. All of the poly(EBPCDA-2DA) assemblies exhibit complete reversible thermochromism in temperature range of 25 – 150 °C. However, when the temperature is increased above 150 °C, the PDA assemblies exhibit irreversible thermochromism. Color transition temperature and reversibility of the PDA assemblies in drop cast films are summarized in Table 7.

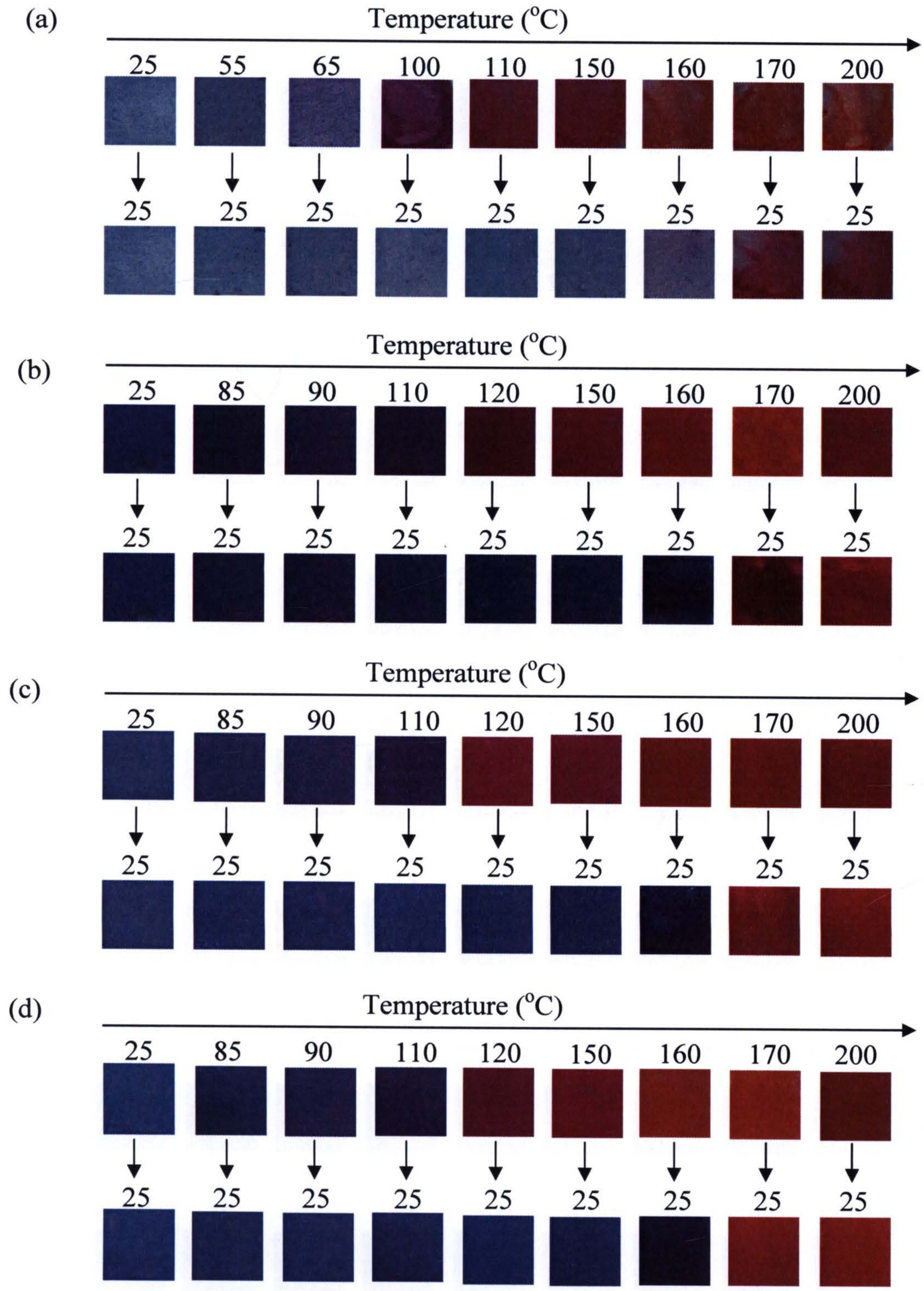


Figure 36 Color photographs of poly(EBPCDA-2DA) assemblies in (a) water, (b) ethanol, (c) butanol, (d) hexanol, (e) octanol, (f) hexane, (i) octane and (j) decane in drop cast film taken upon heating and then cooling to 25 °C

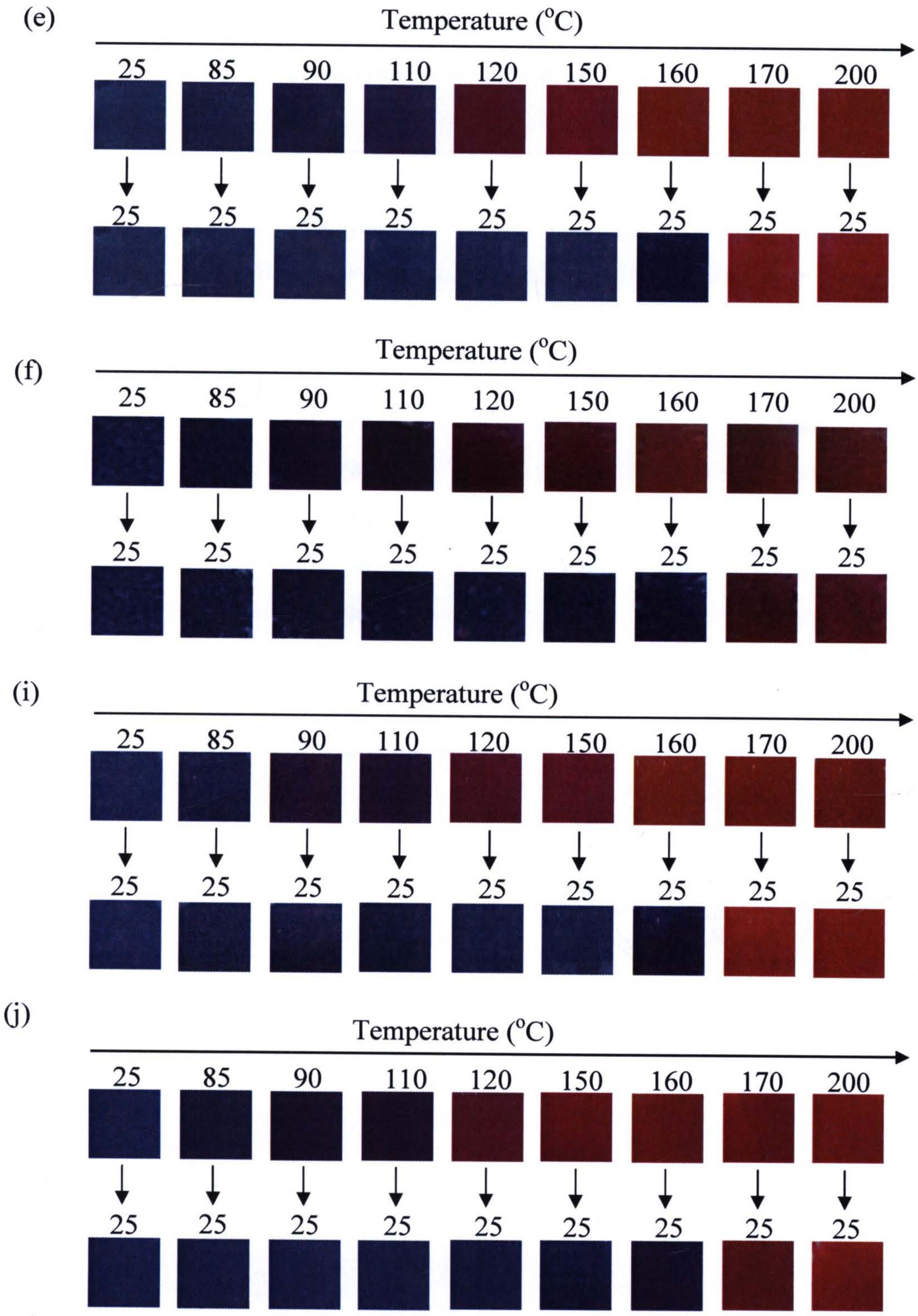


Figure 36 (cont.)

Table 7 Color transition temperature and reversibility of the poly(EBPCDA-2DA) assemblies in drop cast films prepared various solvents

Solvents	Color transition temperature (°C)		
	1st transition Blue → Purple	2nd transition Purple → Red	3rd transition Red → Orange
Water	65	110	160
Ethanol	90	120	160
Butanol	90	120	160
Hexanol	90	120	160
Octanol	90	120	160
Hexane	90	120	160
Octane	90	120	160
Decane	90	120	160

Thermal properties of poly(EBPCDA-2DA) assemblies in powder form prepared from various solvents are investigated by using Differential Scanning Calorimeter (DSC). The samples for DSC measurements were prepared by centrifuge the PDA suspensions to force the precipitation. The precipitates of PDA assemblies in water, butanol and decane were washed three times by using water, ethanol and hexane, respectively. The samples were dropped on Petri dish and dried at room temperature for one day. The DSC curves obtained from 1st and 2nd heating and cooling cycles are illustrated in Fig. 37. The melting temperatures (T_m), crystallization temperatures (T_c) and enthalpy change (ΔH) of the transition are summarized in Table 8 and 9. We observe that the transition temperatures and ΔH varies with the solvents. The poly(EBPCDA-2DA) assemblies prepared from all solvents exhibits the T_m at ~124 °C, which is close to the 2nd color transition temperature. However, we do not detect any transition in the DSC curves, which corresponds to the 1st and 3rd color transition temperatures. The poly(EBPCDA-2DA) assemblies in water exhibits the ΔH of 0.56×10^5 J/mol. When the solvent is changed to butanol and decane, the ΔH values are higher. This result indicates that there are higher fraction of order poly(EBPCDA-2DA) assemblies in butanol and decane, which is consistent with the SEM images in earlier discussion. The T_c of poly(EBPCDA-2DA) assemblies are consistent with the T_m. However, poly(EBPCDA-2DA) assemblies in butanol exhibits different thermal behavior upon cooling. It exhibits multiple transition regions. The origin of this crystallization behavior is not known. The T_m and ΔH values measured upon 2nd heating are lower than those of the 1st heating. This suggests that the original chain arrangement is not fully recovered during the 1st cooling cycle from 210 °C, which also corresponds to the partial reversibility of the color transition.

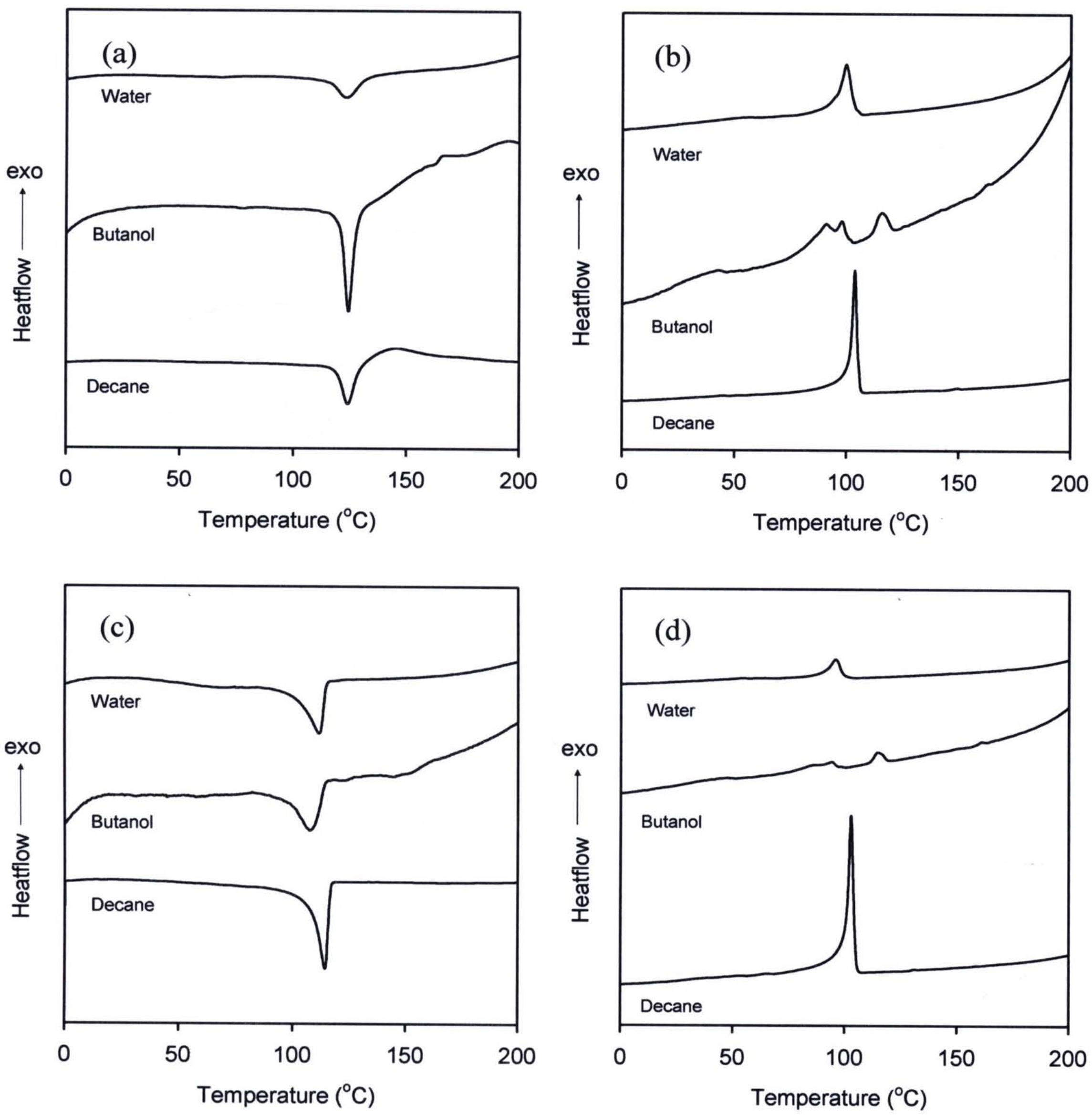


Figure 37 DSC thermograms measured upon (a) 1st heating, (b) 1st cooling, (c) 2nd heating and (d) 2nd cooling of poly(EBPCDA-2DA) assemblies. The thermograms were normalized to weight of the sample and shifted vertically for presentation.

Table 8 Thermal properties of poly(EBPCDA-2DA) assemblies in different solvent measured upon 1st heating and 1nd cooling cycles

Monomer	1nd Heating		1st Cooling	
	T_m(°C)	ΔH(J/mol)	T_c(°C)	ΔH(J/mol)
Water	123.16	0.56×10^5	99.93	0.39×10^5
Butanol	124.33	1.05×10^5	115.76	0.13×10^5
	-	-	91.01	0.37×10^5
Decane	124.03	1.28×10^5	103.82	0.51×10^5

Table 9 Thermal properties of poly(EBPCDA-2DA) assemblies in different solvent measured upon 2st heating and 2nd cooling cycles

Monomer	2nd Heating		2nd Cooling	
	T_m(°C)	ΔH(J/mol)	T_c(°C)	ΔH(J/mol)
Water	111.74	0.38×10^5	95.85	0.28×10^5
Butanol	107.75	0.44×10^5	114.67	0.12×10^5
	-	-	93.92	0.21×10^5
Decane	114.38	0.49×10^5	102.98	0.49×10^5

The segmental arrangement of poly(EBPCDA-2DA) assemblies in blue and red phases is explored by utilizing FT-IR spectroscopy. Fig. 38 illustrates FT-IR spectra of blue and red phase of poly(EBPCDA-2DA) assemblies prepared from butanol and octanol. The red phase is obtained by heating the powder form at 200 °C for 5 minutes and then cooled down to room temperature. The blue phase of poly(EBPCDA-2DA) assemblies show ν(C=O), $\nu_a(CH_2)$, $\nu_s(CH_2)$ and ν(NH) at 1640, 2918, 2848 and 3294 cm^{-1}, respectively. In the red phase, we observe the growth of new vibrational bands at 1688 and 3405 cm^{-1}. This corresponds to ν(C=O) and ν(NH) vibrational bands, which have no hydrogen bond. The other vibrational bands of ν(CH) (bending) (1461cm^{-1}), ν(CNH) (1553 cm^{-1}), νC=O (H-bond) (1640 cm^{-1}), $\nu_a(CH_2)$ (2918 cm^{-1}), $\nu_s(CH_2)$ (2848 cm^{-1}), $\nu(CH_3)$ (3063 cm^{-1}) and ν(NH) (H-bond) (3294 cm^{-1}) are still detected at the same wavenumber. This result indicates that the hydrogen bonds between the –C=O and –NH- of the head groups are partially broken. The arrangement of alkyl side chain remains the same. The results obtained from the poly(EBPCDA-2DA) in octanol assemblies are consistent.

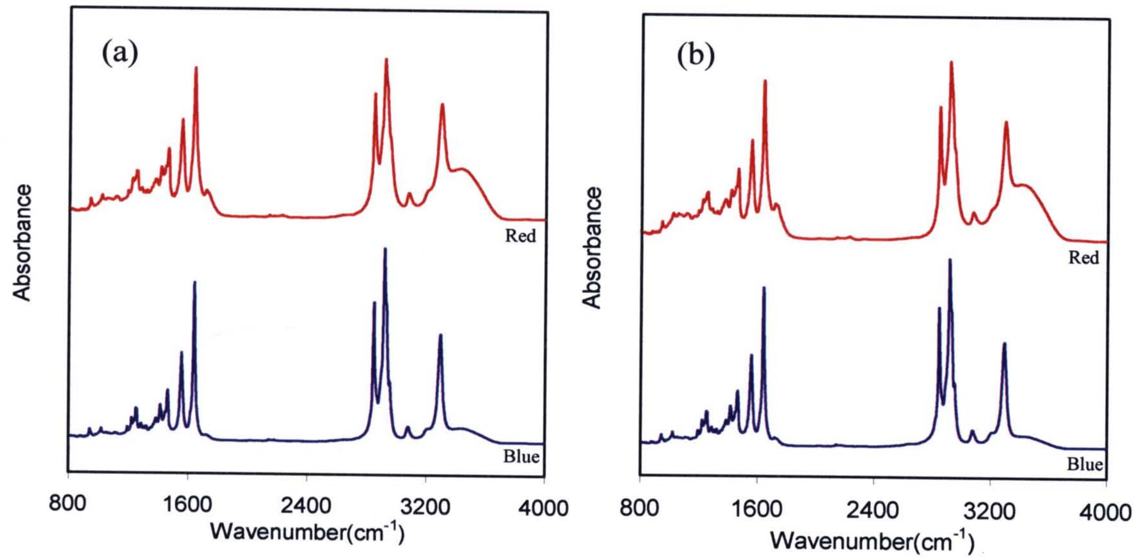


Figure 38 FT-IR spectra blue phase and red phase of poly(EBPCDA-2DA) assemblies prepared from (a) butanol and (b) octanol. The powder was compressed in the KBr disc for the measurement.

Table 10 FT-IR peak assignments of poly(EBPCDA-2DA) assemblies in various solvents

Peak Assignments	Butanol		Octanol	
	Blue (cm^{-1})	Red (cm^{-1})	Blue (cm^{-1})	Red (cm^{-1})
νCH (bending)	1461	1460	1461	1460
νCNH	1553	1550	1552	1550
νC=O (H-bond)	1640	1639	1640	1639
νC=O (no H-bond)	-	1688	-	1686
ν_aCH_2	2918	2918	2917	2918
ν_sCH_2	2848	2848	2848	2848
νCH_3	3063	3060	3065	3062
νNH (H-bond)	3294	3295	3289	3294
νNH (no H-bond)	-	3405	-	3409

In addition, we investigate the effect of structural modification on thermochromic and the morphologies of PDA assemblies prepared in various solvents. Increasing length of alkyl linker from N=2 to N=6 affects the solubility of the monomers in water, butanol and decane. Therefore, we expect different self-assembling behaviors in this system. Fig. 39 illustrates SEM images of poly(HDPCDA-2DA) assemblies prepared by dropping the suspensions on polished silicon wafer. We observe that the morphology of poly(HDPCDA-2DA) assemblies changes significantly with type of solvent. The assemblies in water exhibit irregular shape particles. This is probably due to the low solubility of monomer in the polar medium. The decrease of polarity in butanol causes the formation of flower-like particles. The high magnification image clearly reveals the assemblies of sheet-like aggregates. When the non polar solvent, i.e., decane, is used, the sheet-like aggregates are obtained.

Fig. 40 illustrates absorption spectra of poly(HDPCDA-2DA) assemblies in various solvents measured upon heating and cooling. We found that blue phase of poly(HDPCDA-2DA) assemblies in all solvents exhibit maximum absorption at λ_{max} ~648 nm. The absorption spectrum of poly(HDPCDA-2DA) assemblies changes when the temperature is increased above ~85 °C. The λ_{max} of poly(HDPCDA-2DA) in water, butanol and decane shifts from 648 nm to 598, 576 and 606 nm, respectively. We also note that the absorption spectrum of the red phase varies with type of solvent, indicating the difference of chain arrangement within the assemblies. However, all of the poly(HDPCDA-2DA) assemblies exhibit reversible thermochromism, which is different from the behavior of poly(EBPCDA-2DA) assemblies discussed earlier. We suggest that the molecular packing in poly(HDPCDA-2DA) assemblies is denser, preventing the penetration of solvent during the heating process.

To investigate the color transition behavior in more details, the λ_{max} is plotted as a function of temperature (see Fig. 41a). It is observed that the color transition temperature of poly(HDPCDA-2DA) assemblies in all solvents occurs at 85 °C. The plots of colorimetric response (%CR) of of poly(HDPCDA-2DA) assemblies in various solvents as a function of temperature are illustrated in Fig. 41b. The magnitude of %CR upon increasing temperature decreases in the order of poly(HDPCDA-2DA) in decane, water and butanol, respectively.

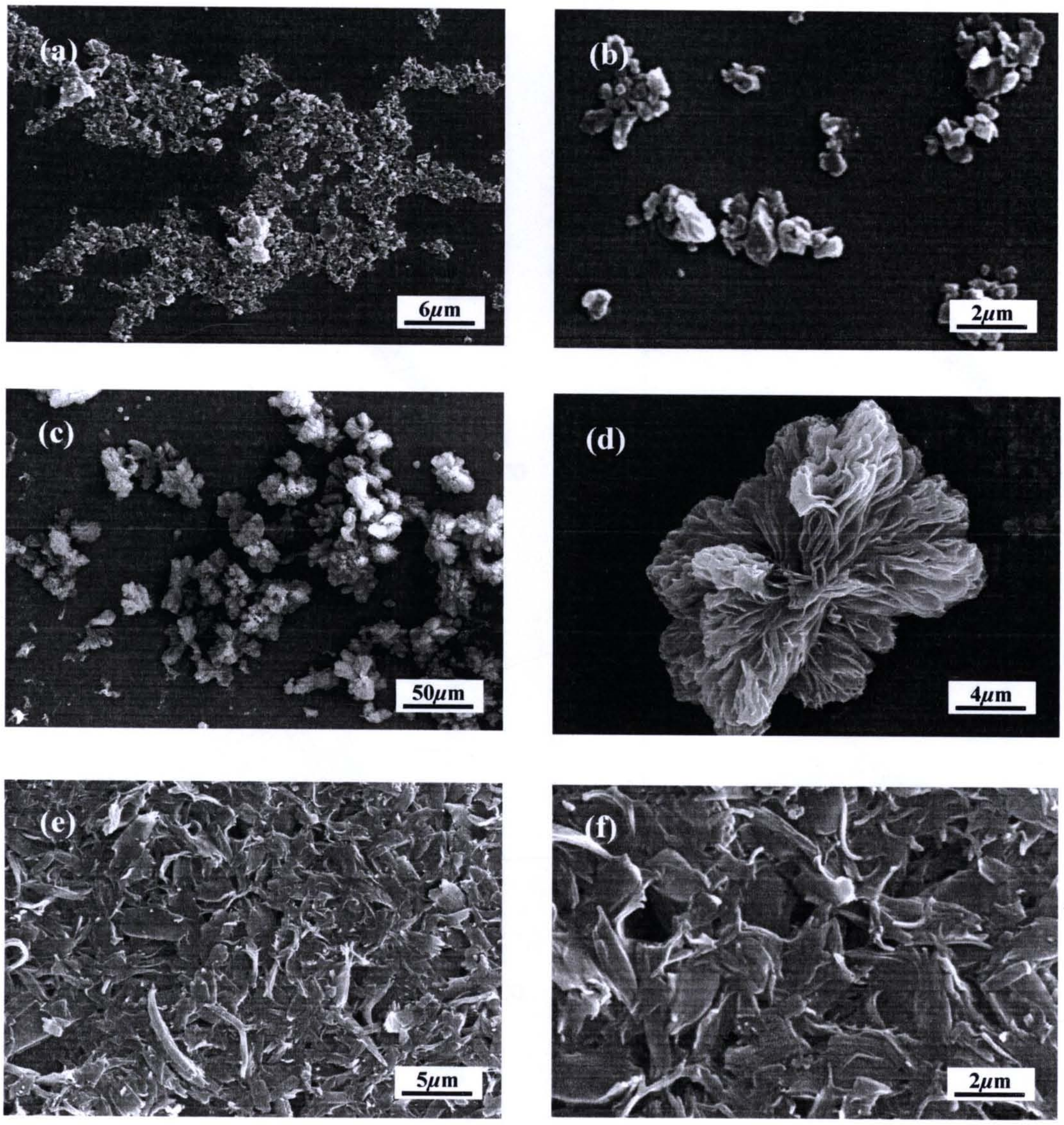


Figure 39 SEM images of poly(HDPCDA-2DA) assemblies in (a,b) water, (c,d) butanol and (e,f) decane on polished silicon wafer

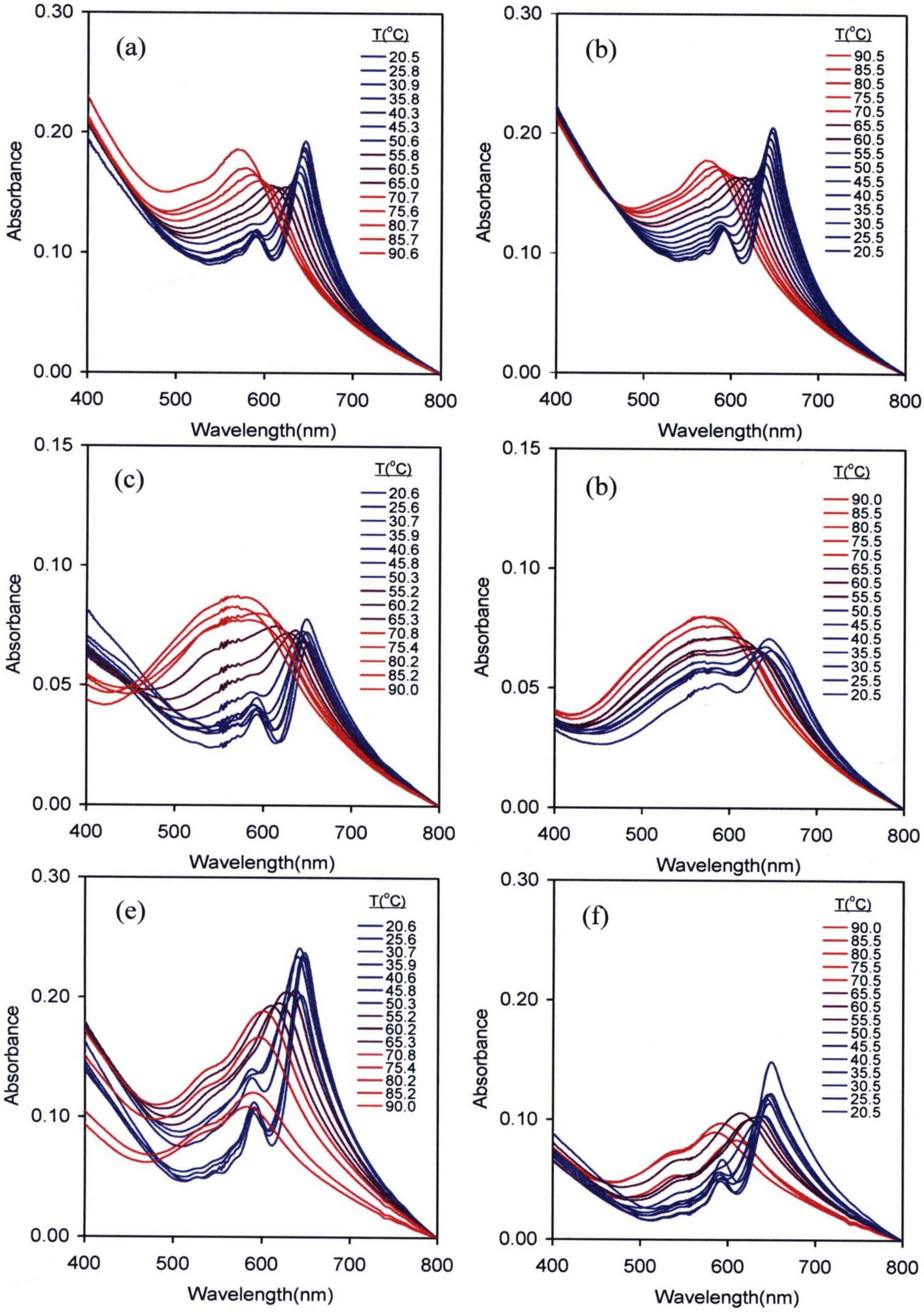


Figure 40 Absorption spectra of poly(HDPCDA-2DA) assemblies in (a,b) water, (c,d) butanol, (e,f) decane measured upon heating (left) and cooling (right)

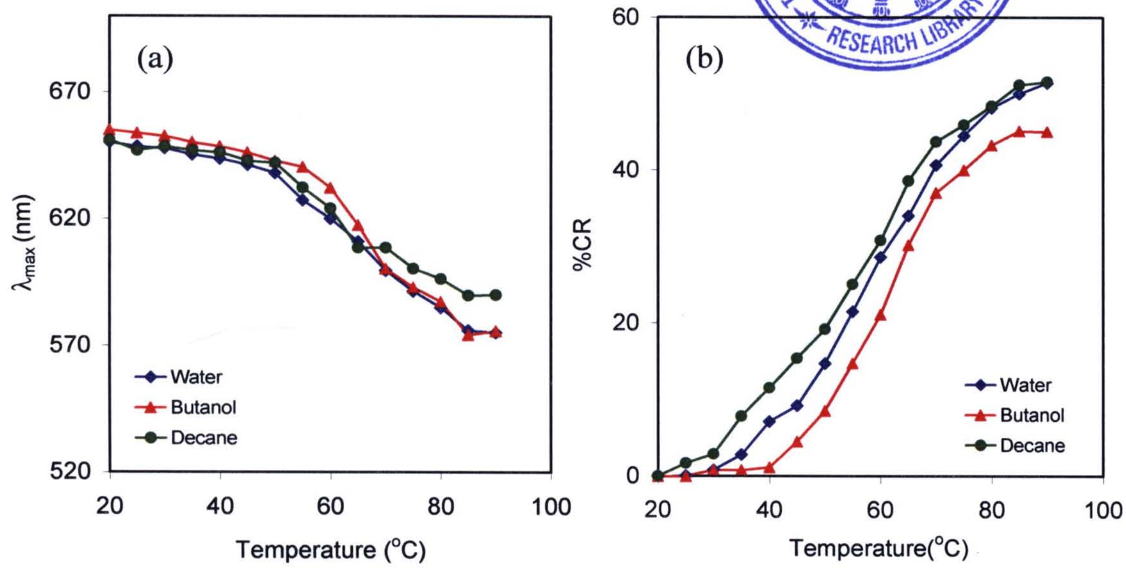


Figure 41 (a) The change of λ_{max} absorption spectra of poly(HDPCDA-2DA) assemblies as a function of temperature and (b) colorimetric response. The samples are measured upon heating.

The color transition temperature and reversibility of poly(HDPCDA-2DA) assemblies in drop cast films are shown in Fig 42. We observe that the color transition temperature of poly(HDPCDA-2DA) assemblies varies with the solvents. The 1st color transition (blue to purple), 2nd color transition (purple to red) and 3rd transition (red to orange) of poly(EBPCDA-2DA) in water occurs at 80, 110 and 220 °C, respectively. The change from aqueous solution to butanol and decane causes the shift of 2nd and 3rd transition temperature to 140 and 180 °C, respectively. Color transition temperature and reversibility of the poly(HDPCDA-2DA) assemblies in drop cast film is summarized in Table 11.

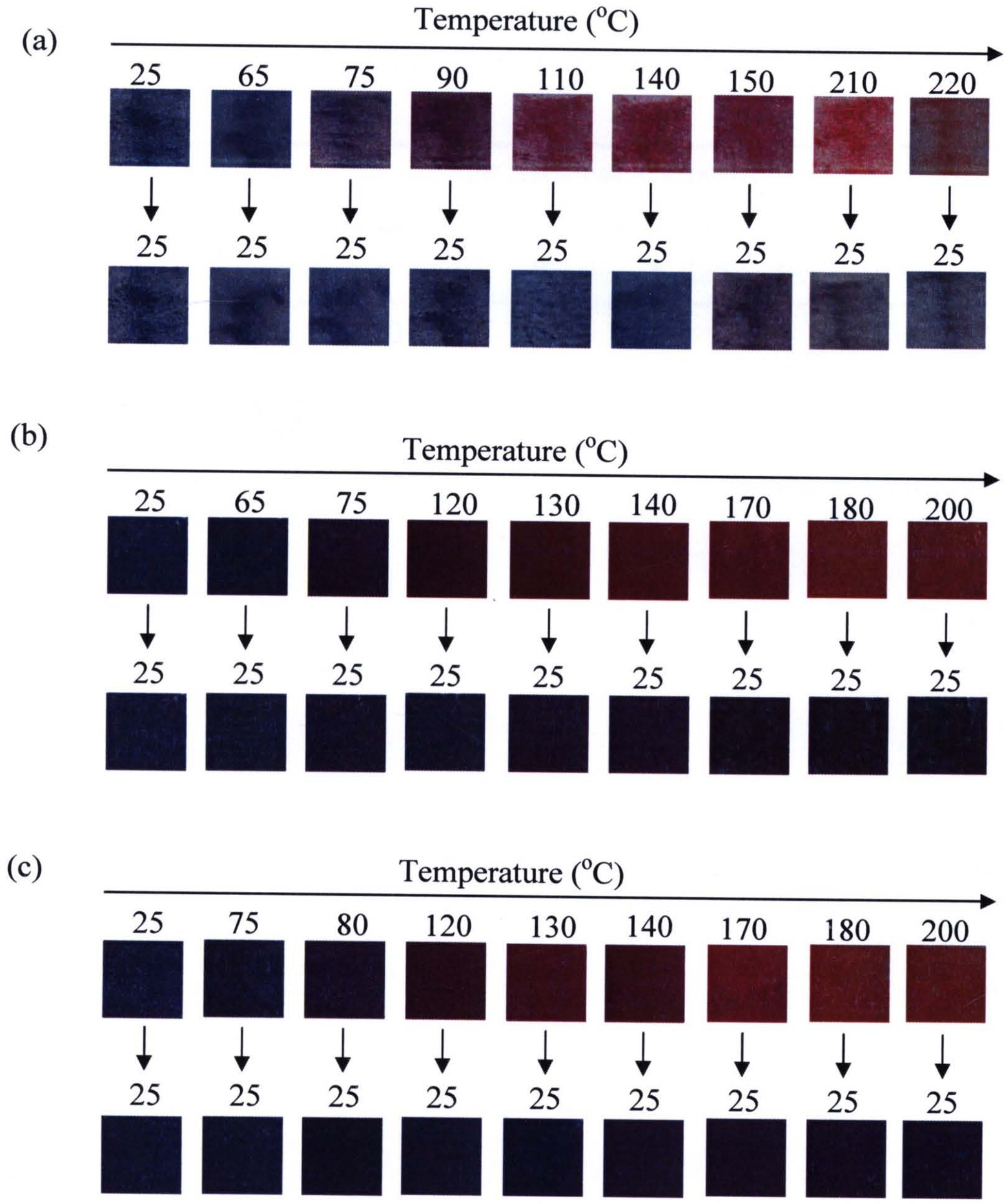


Figure 42 Color photographs of poly(HDPCDA-2DA) in (a) water, (b) butanol and (c) decane in thin film taken upon heating and then cooling to 25°C

Table 11 Color transition temperature and reversibility of the poly(HDPCDA-2DA) assemblies in other solvents prepared from drop cast film

Solvents	Color transition temperature (°C)		
	1st transition Blue → Purple	2nd transition Purple → Red	3rd transition Red → Orange
Water	80	110	220
Butanol	80	140	180
Decane	80	140	180

Effect of solvent on photo-polymerization of PDA assemblies

In the previous section, we observe the effect of solvents on the molecular organization and color-transition behaviors of PDA assemblies. In this section, the photo-polymerization behaviors of DA assemblies in different solvents are investigated. The solutions of DA assemblies were prepared as described in chapter 3. The solutions were diluted 10 times. The solution was irradiated by UV light. The irradiation time was varied from 10 seconds to 120 minutes. The change of solution color was followed by using UV–vis spectrometer. Fig. 43 illustrates absorption spectra of poly(EBPCDA-2DA) assemblies in various solvents measured as a function of polymerization time. In aqueous suspension, the absorption spectrum exhibits a λ_{max} at 646 nm after 10 second of the polymerization. The increase of polymerization time results in the increase of absorbance, corresponding to the increase of absorbing chromophores. The λ_{max} value systematically decreases with the increase of the polymerization time, indicating the decrease of conjugation length. This is attributed to the increase of chain flexibility during the chain growth process. In addition, we observe the decrease of λ_{max} in a step-wise process. The poly(EBPCDA-2DA) assemblies exhibit two transitions at 40 and 120 minutes where the λ_{max} shifts to 570 and 503 nm, respectively.

The photo-polymerization behaviors of DA assemblies in alcohols are rather different. In early stage, the increase of polymerization time causes slight decreases of the λ_{max}. Interestingly, further increasing of polymerization time results in an abrupt increase of λ_{max}, which indicates the increase of conjugation length. We suggest that the higher molecular ordering of DA monomers in alcohols allows the higher planarity of conjugated backbone. However, when the polymerization time becomes very long, the λ_{max} value quickly drops due to the increase of chain flexibility. In the systems of alkanes (see Fig 44), we also observe the abrupt increase of λ_{max} upon increasing polymerization time. However, we do not detect the drop of λ_{max} even after the polymerization time is increased to 120 minutes. This indicates the high rigidity of conjugated backbone, which is probably due to high molecular packing within the assemblies. The polymerization behaviors and the λ_{max} transition of poly(EBPCDA-2DA) assemblies in various solvents are summarized in Table 12.

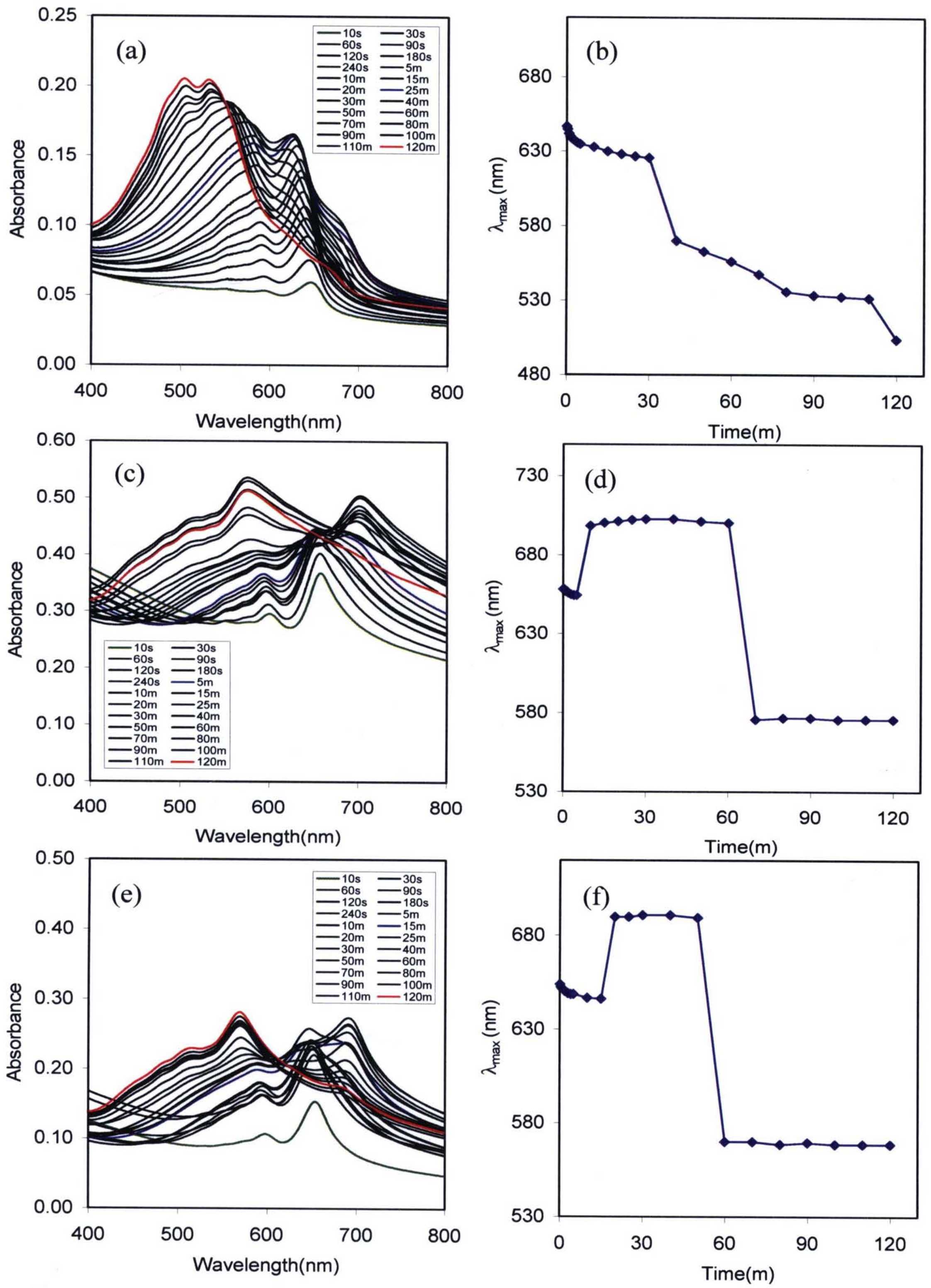


Figure 43 (left) Absorption spectra of poly(EBPCDA-2DA) assemblies measured as a function of polymerization time and (right) the change of λ_{max} is plotted as a function of polymerization time. (a,b) water, (c,d) ethanol, (e,f) butanol, (g,h) hexanol and (i,j) octanol

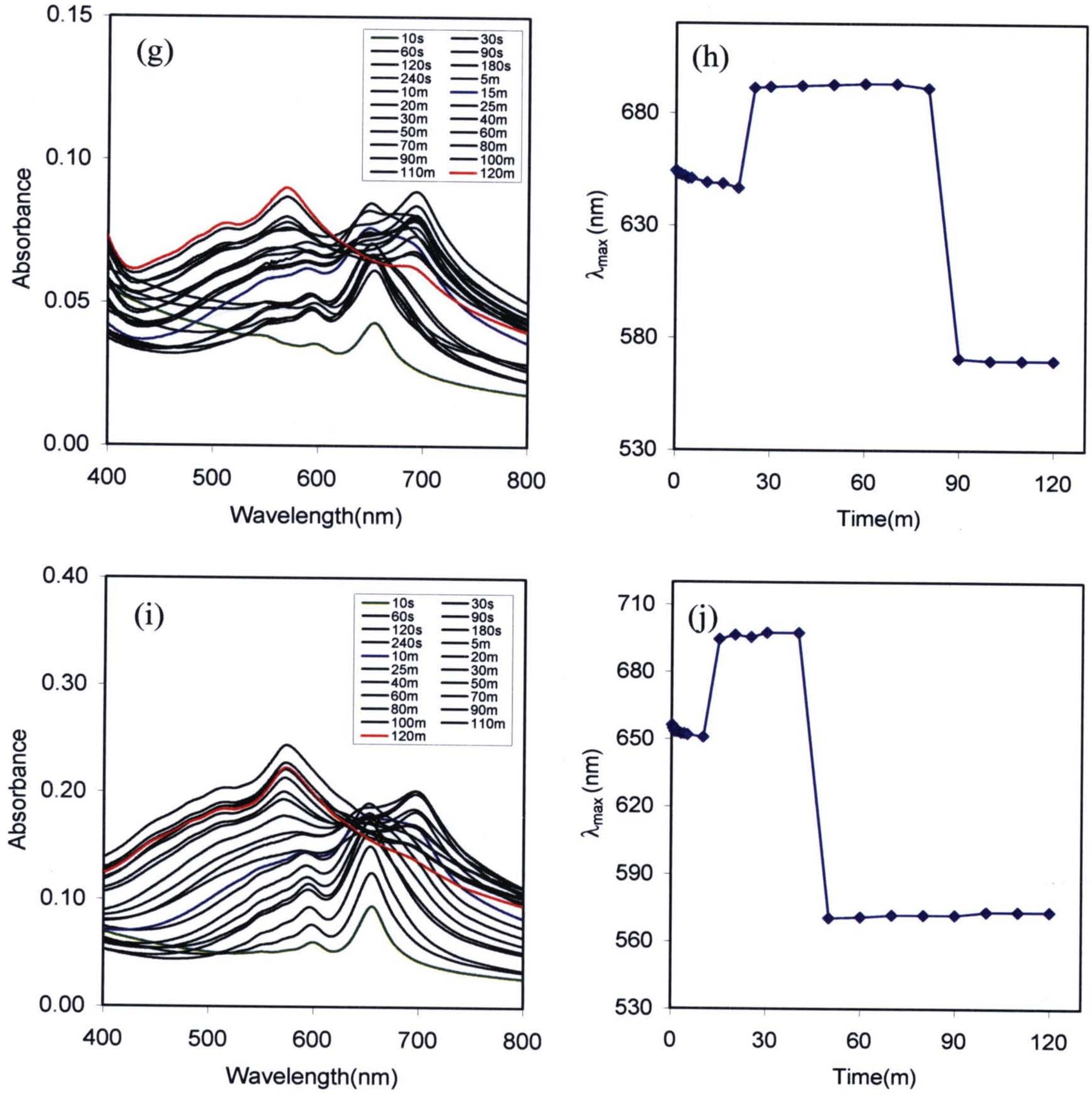


Figure 43 (cont.)

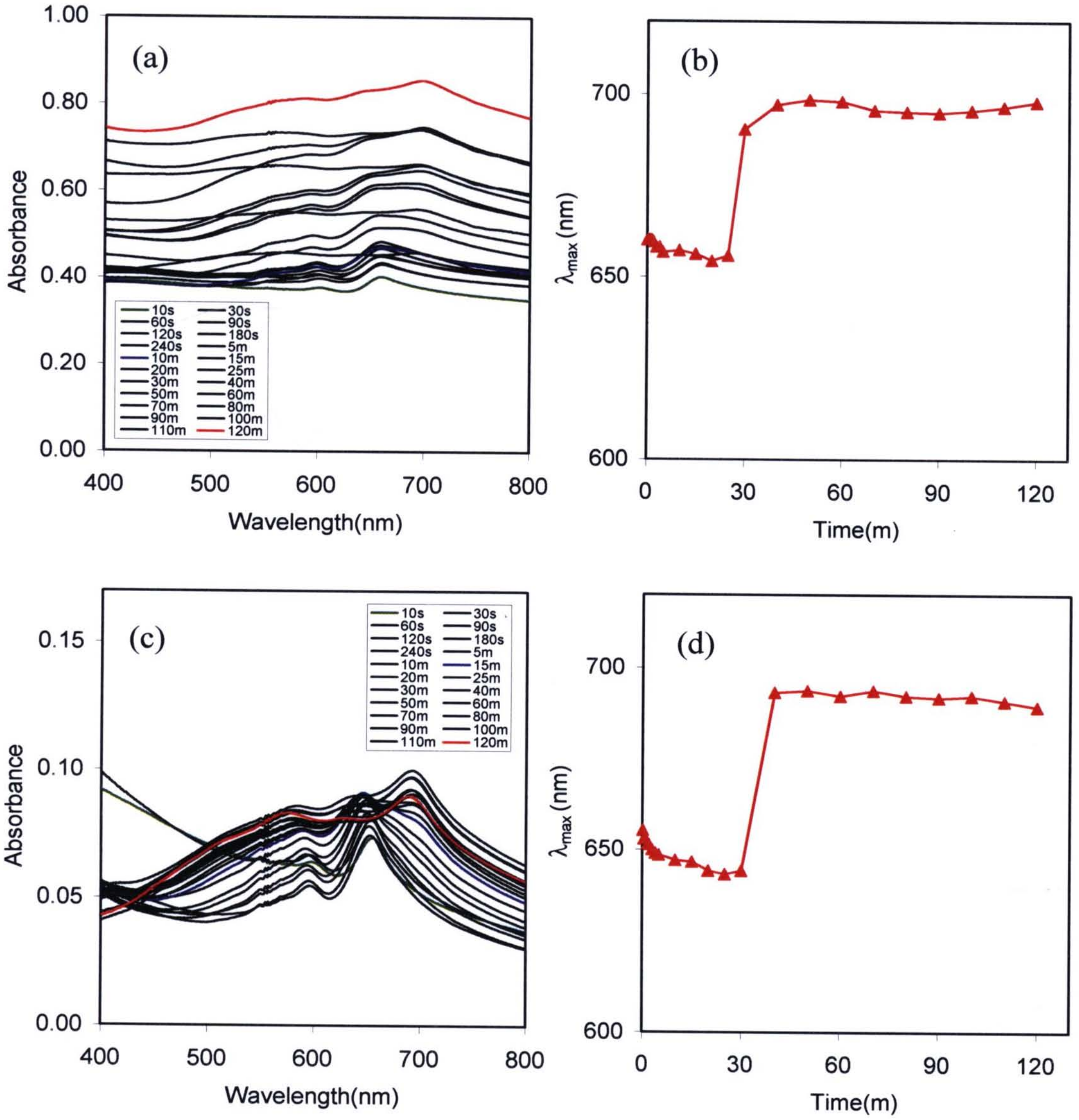


Figure 44 (left) Absorption spectra of poly(EBPCDA-2DA) assemblies measured as a function of polymerization time and (right) the change of λ_{max} is plotted as a function of polymerization time. (a,b) hexane and (c,d) octane.

Table 12 The polymerization time and transition of poly(EBPCDA-2DA) assemblies in various solvents

Solvents	Initial λ_{max} (nm)	Transition of λ_{max}			
		1[st] transition		2[nd] transition	
		Time (m)	λ_{max} (nm)	Time (m)	λ_{max} (nm)
Water	646	40	570	120	503
Ethanol	658	10	698	70	575
Butanol	652	20	689	60	570
Hexanol	654	25	691	90	571
Octanol	654	15	694	50	570
Hexane	660	30	690	-	-
Octane	655	40	693	-	-

Effect of chain length on thermochromic properties

The increase of chain length affects the chain flexibility and entropy of the system. Therefore, we investigate the effect of chain length on color-transition behaviors of DA assemblies. The chain length of PDA is varied by controlling the polymerization time. Fig. 45a illustrates photographs of poly(EBPCDA-2DA) assemblies in water obtained by varying the polymerization time. We observe that the color of solution changes with polymerization time. At relatively short polymerization time, the blue solutions are obtained. The solutions exhibit purple color at 20 minutes of irradiation time. The solutions gradually change to the red color at relatively long irradiation time. These poly(EBPCDA-2DA) assemblies exhibit different color transition temperature and reversibility. Fig. 45b shows that the poly(EBPCDA-2DA) assemblies exhibit irreversible thermochromism when the polymerization time is relatively long. Detailed investigation is given in the following discussion.

(a) 0 10s 1m 5m 10m 20m 30m 40m 50m 60m

(b) 0 10s 1m 5m 10m 20m 30m 40m 50m 60m

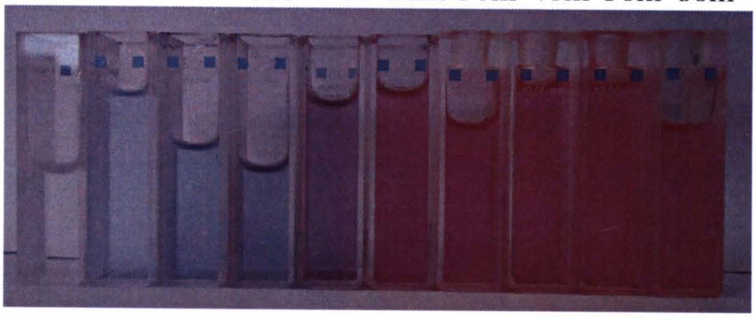


Figure 45 Photographs of poly(EBPCDA-2DA) assemblies in water obtained by varying polymerization time. (a) fresh solution and (b) after cooling from 90 °C

Fig. 46 illustrates absorption spectra of poly(EBPCDA-2DA) assemblies in aqueous solution measured as a function of temperature. We found that the variation of polymerization time affects both the color transition temperature and the thermochromic reversibility. In addition, the temperature of color transition decreases when the chain length is increased. The color transition of poly(EBPCDA-2DA) assemblies obtained at polymerization time of 10 second and 1 minute occurs in a fully reversible fashion. The increase of polymerization time to 5 and 10 minutes causes partial reversible thermochromism. For the polymerization times of 20, 30 and 40 minutes, the poly(EBPCDA-2DA) assemblies exhibit irreversible thermochromism. The poly(EBPCDA-2DA) assemblies obtained at longer polymerization time already exhibit a red color. Therefore, we do not detect any color transition upon increasing temperature.

To investigate the color transition behavior in more details, the λ_{max} is plotted as a function of temperature (see Fig. 47a). It is clear that the color transition temperature varies with the polymerization time. The increase of polymerization time causes the decrease of color transition temperature. For relatively short polymerization times at 10 second, 1 and 5 minutes, the color transition takes place at about 70 ^{o}C. The increase of polymerization time to 10, 20 and 30 minute minutes results in the drop of color transition to 55 ^{o}C, 45 ^{o}C and 45 ^{o}C, respectively. The plots of colorimetric response (%CR) as a function of temperature are illustrated in Fig. 47b. We observe that the increase of polymerization time causes the decrease of %CR. Color transition temperature and reversibility of the PDA assemblies obtained at different polymerization time are summarized in Table 13.

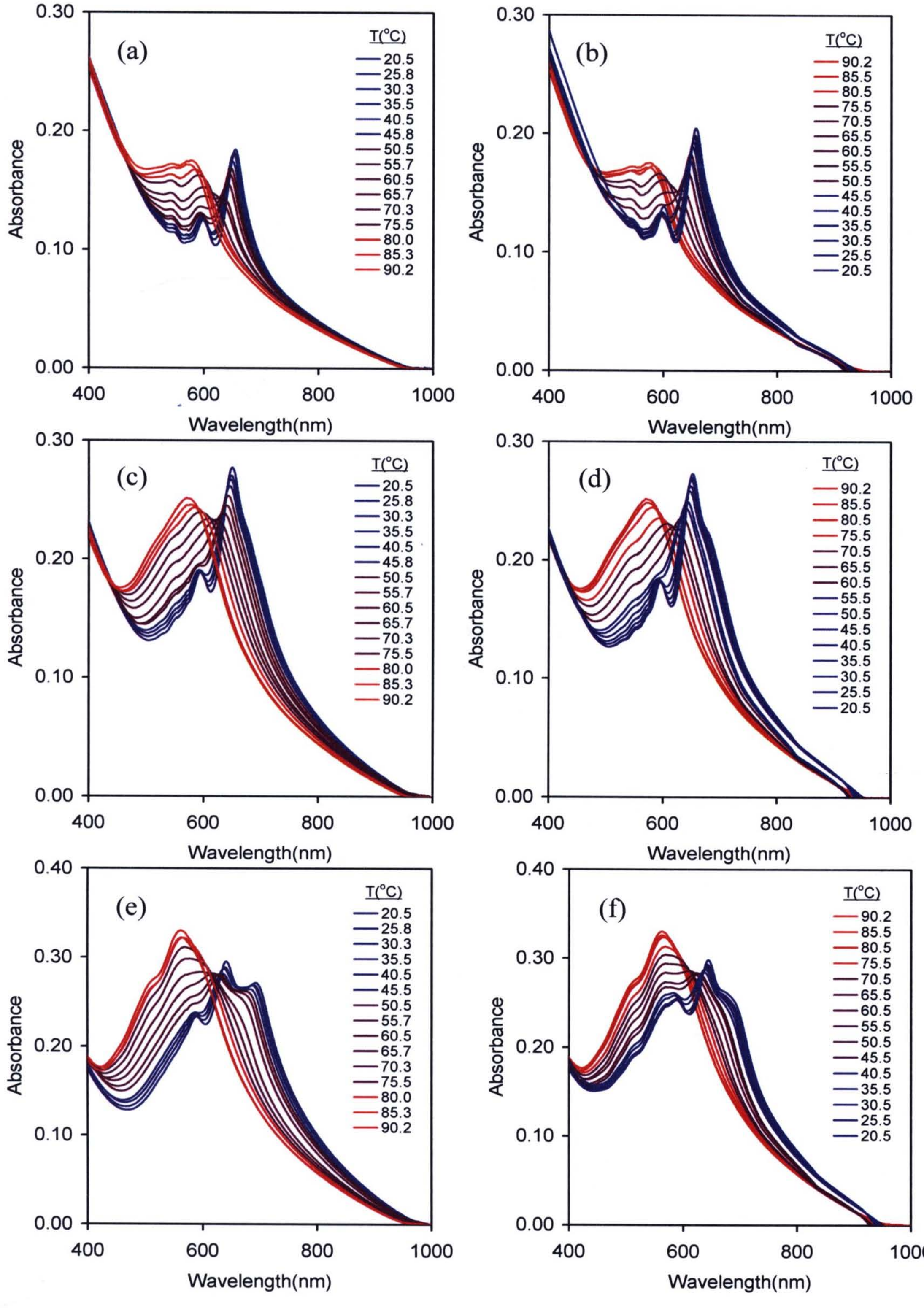


Figure 46 Absorption spectra of poly(EBPCDA-2DA) assemblies in aqueous solution measured upon heating (left) and cooling (right). The polymerization time is (a,b) 10 second, (c,d) 1, (e,f) 5, (g,h) 10, (i,j) 20, (k,l) 30, (m,n) 40, (o,p) 50 and (q,r) 60 minute.

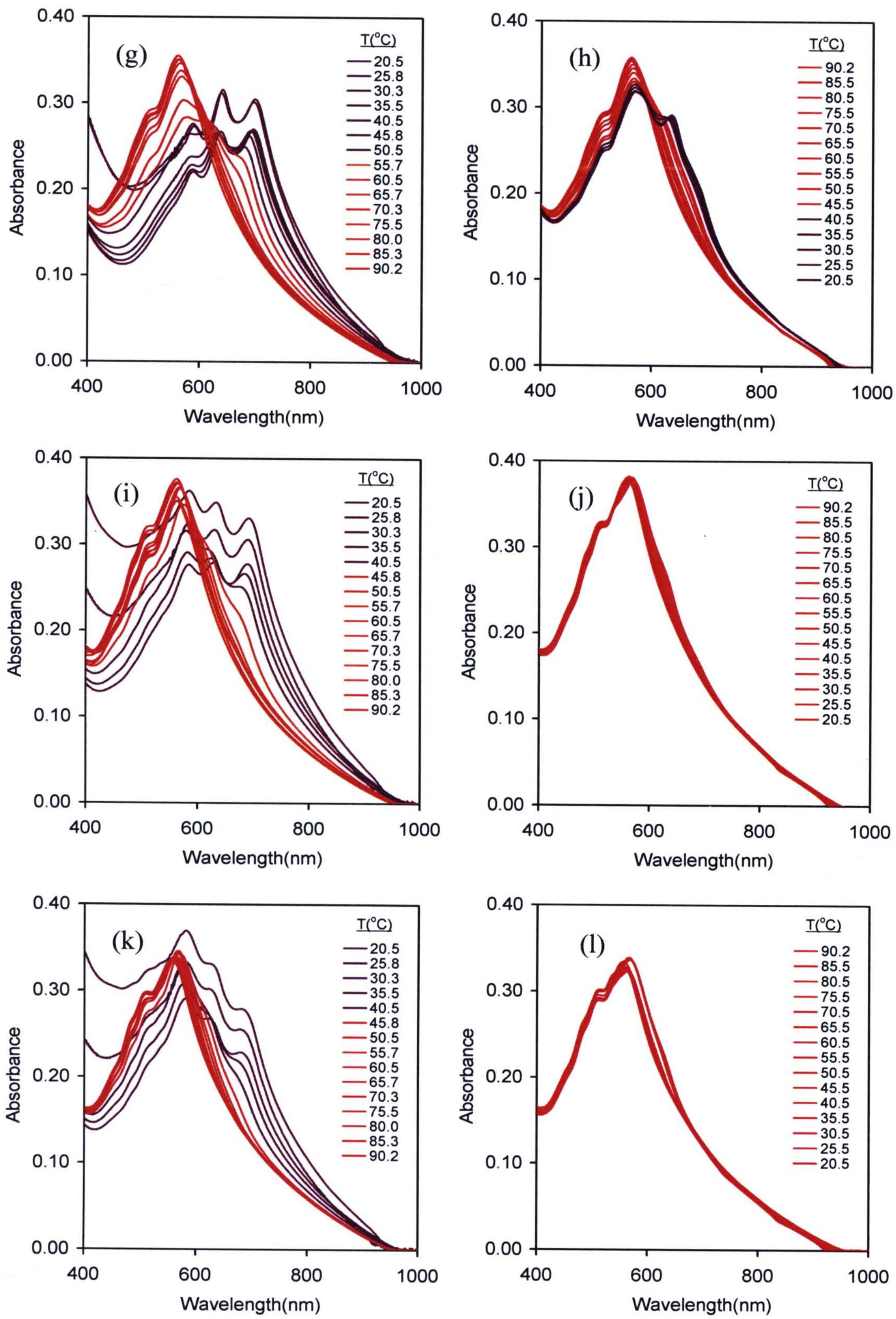


Figure 46 (cont.)

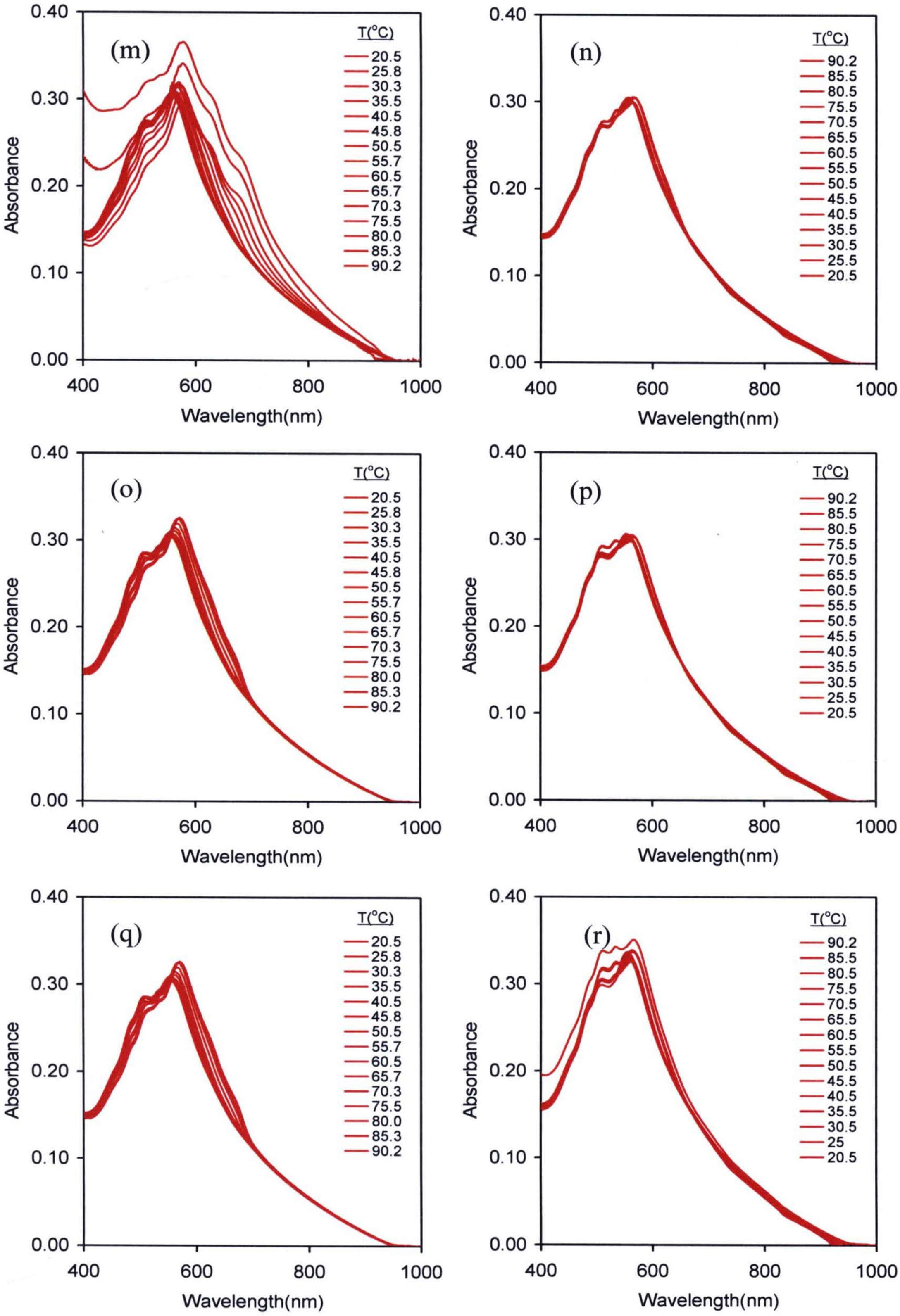


Figure 46 (cont.)

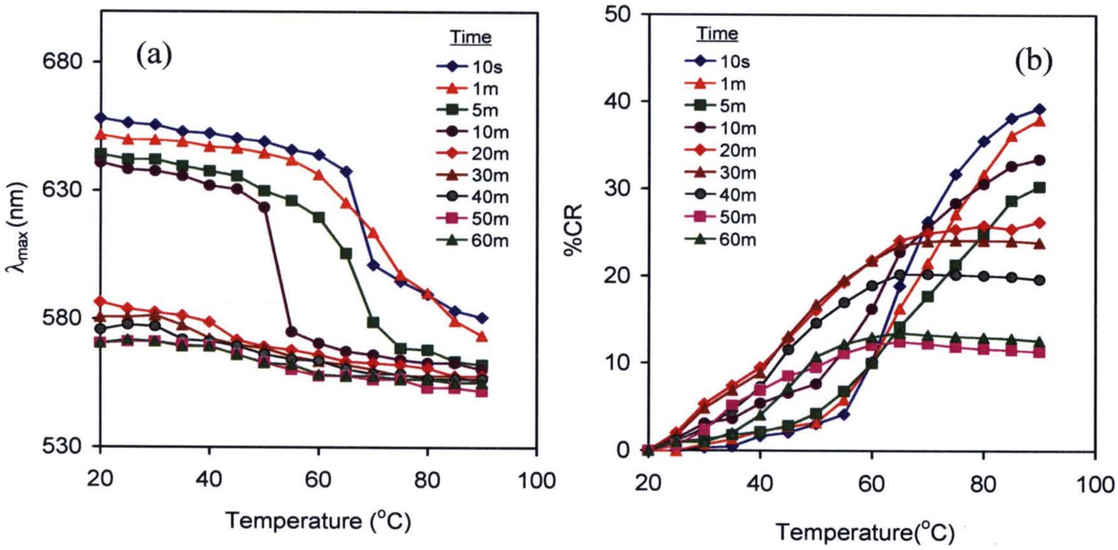


Figure 47 (a) The change of λ_{max} and (b) colorimetric response of poly(EBPCDA-2DA) assemblies in aqueous solution are plotted as a function of temperature. The samples are measured upon heating.

Table 13 Color transition temperature and reversibility of poly(EBPCDA-2DA) assemblies in aqueous solution measured as a function of temperature

Polymerization time	Color transition temperature (°C)	Reversibility
10 second	70	fully reversible
1 minute	75	fully reversible
5 minute	75	partially reversible
10 minute	55	partially reversible
20 minute	45	irreversible
30 minute	45	irreversible
40 minute	-	-
50 minute	-	-
60 minute	-	-

For the alcohol system, the color transition behavior of poly(EBPCDA-2DA) assemblies also varies with polymerization time. However, we detect major discrepancies between the alcohol and water systems. Fig. 48 illustrates absorption spectra of poly(EBPCDA-2DA) assemblies in butanol measured as a function of temperature. All PDA assemblies in butanol exhibit partial reversible thermochromism. In addition, the magnitude of color reversibility varies with the polymerization time. The magnitude of color reversibility systematically increases when the polymerization time is increased from 10 second to 10 minutes. However, the magnitude of color reversibility decreases at longer polymerization time. This observation is due to the change of molecular packing and chain rigidity upon increasing the polymerization time. The change of color transition temperature is consistent. The λ_{max} and %CR are plotted as a function of temperature as shown in Fig. 49. The increase of polymerization time from 10 second to 10 minutes causes systematic increase of color transition temperature. Further increase of polymerization time to 40 minutes results in the decrease of color transition temperature. The results are summarized in Table 14.

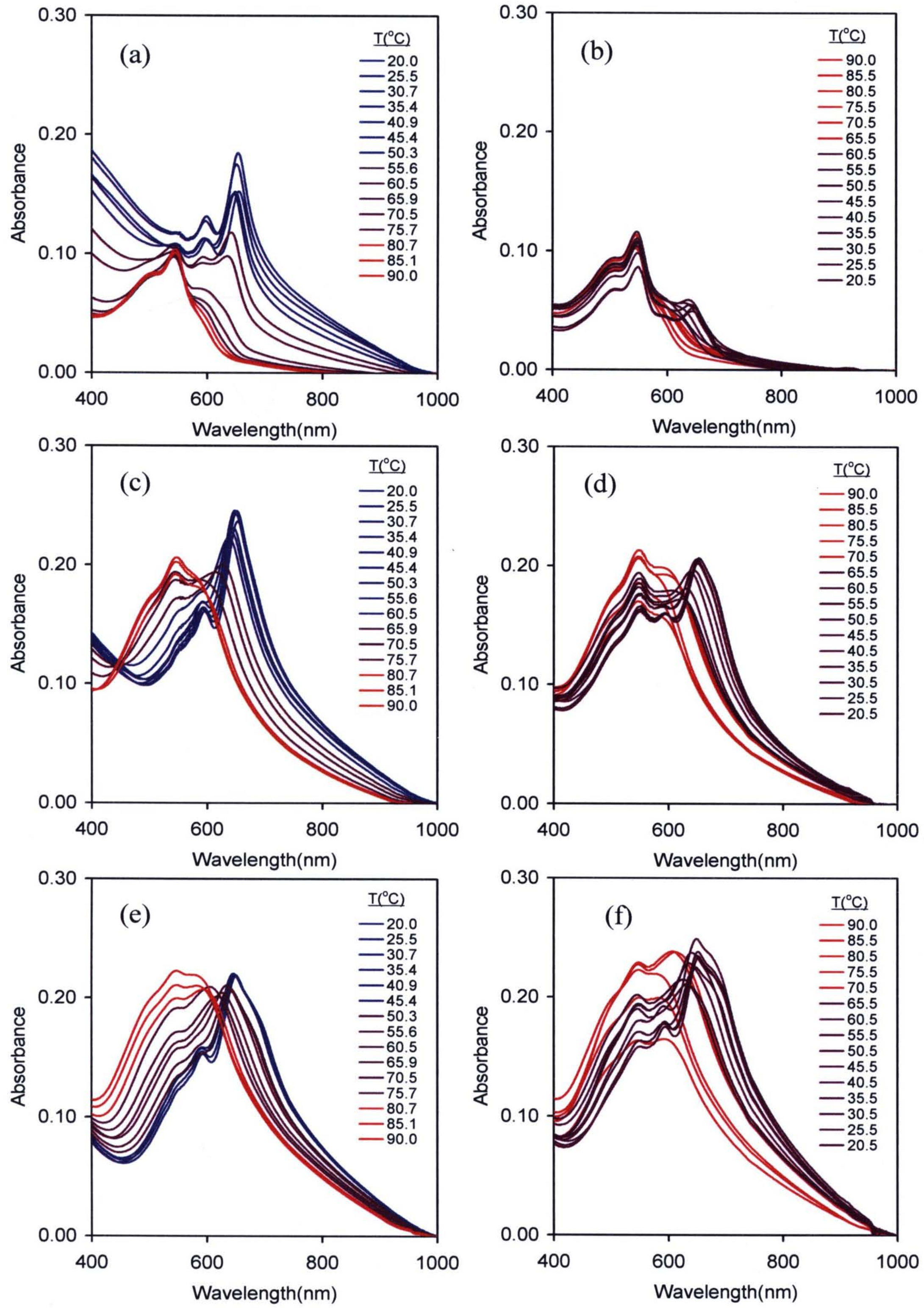


Figure 48 Absorption spectra of poly(EBPCDA-2DA) assemblies in butanol measured upon heating (left) and cooling (right). The polymerization time is (a,b) 10 second, (c,d) 1, (e,f) 5, (g,h) 10, (i,j) 20, (k,l) 30, (m,n) 40, (o,p) 50 and (q,r) 60 minute.

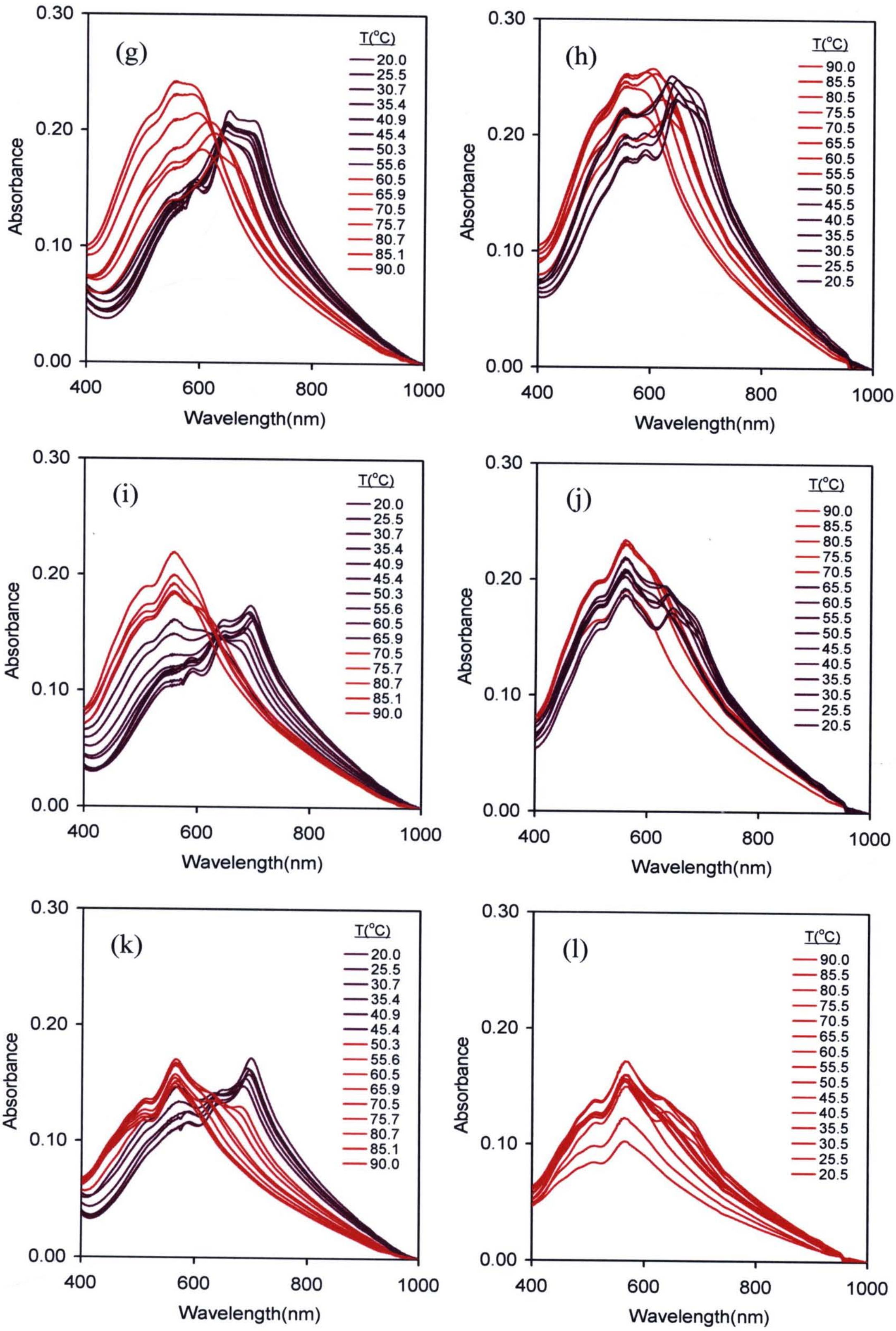


Figure 48 (cont.)

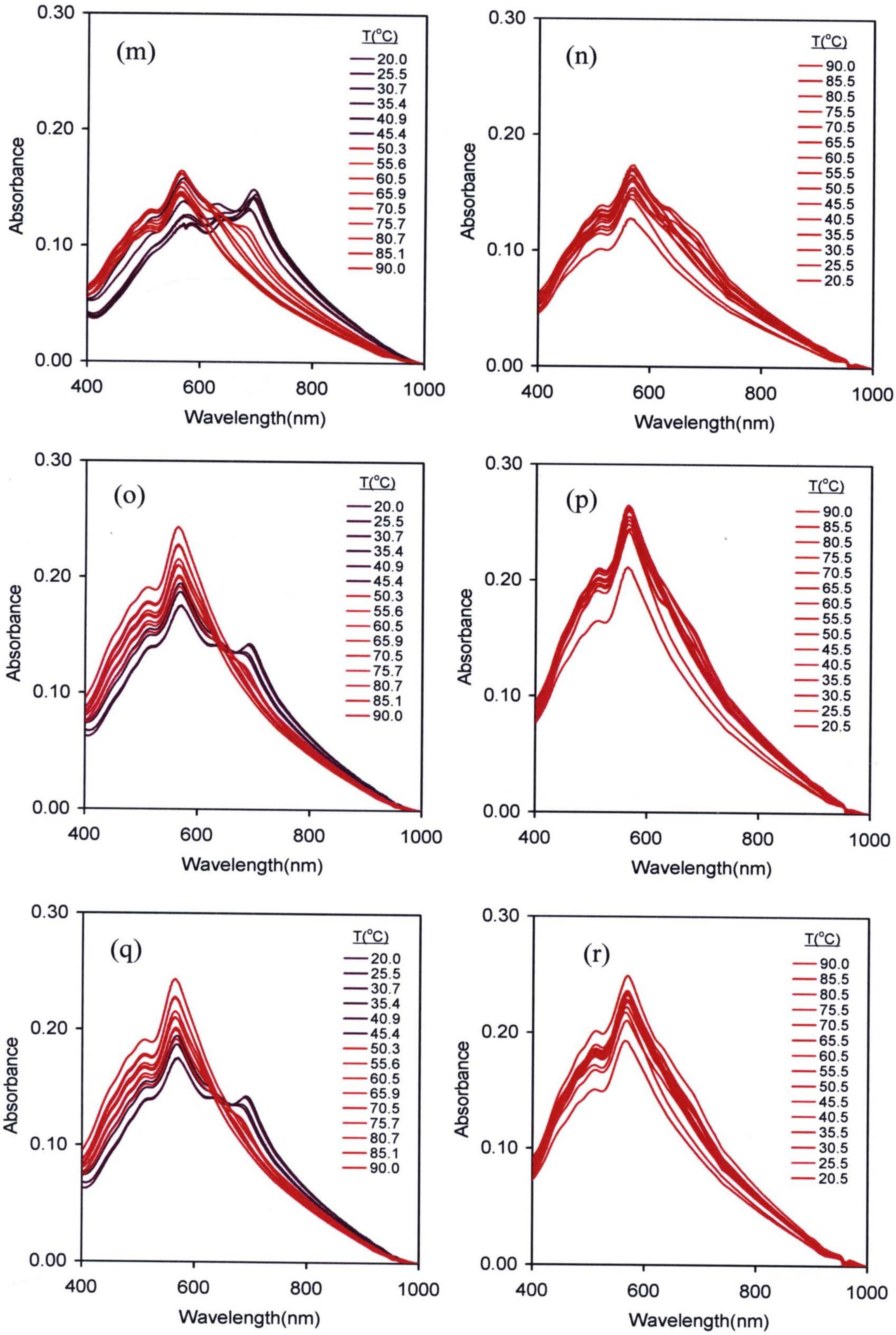
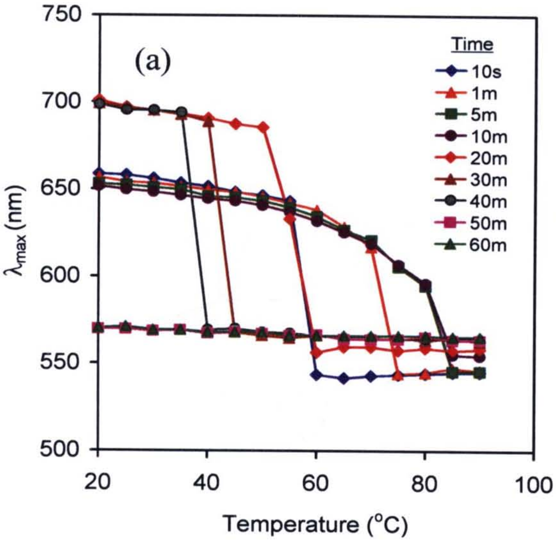


Figure 48 (cont.)



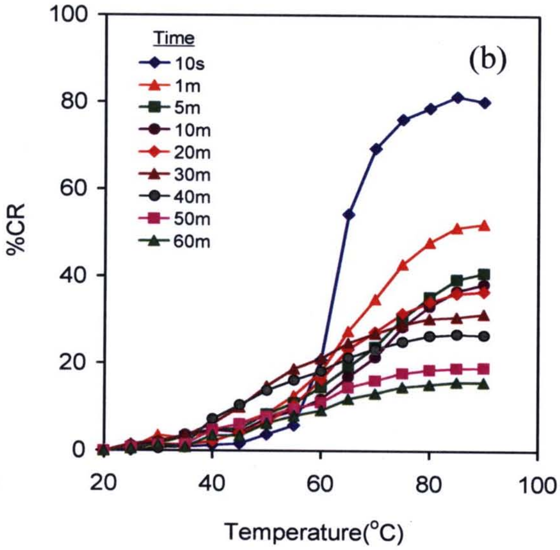


Figure 49 (a) The change of λ_{max} and (b) colorimetric response of poly(EBPCDA-2DA) assemblies in butanol are plotted as a function of temperature. The samples are measured upon heating.

Table 14 Color transition temperature and reversibility of poly(EBPCDA-2DA) assemblies in butanol measured as a function of temperature

Polymerization time	Color transition temperature (°C)	Reversibility
10 second	60	partially reversible
1 minute	75	partially reversible
5 minute	85	partially reversible
10 minute	85	partially reversible
20 minute	60	partially reversible
30 minute	45	irreversible
40 minute	40	irreversible
50 minute	-	-
60 minute	-	-

The color-transition behaviors of poly(EBPCDA-2DA) assemblies prepared in decane are consistent with those of the butanol system. Fig. 50 illustrates absorption spectra of poly(EBPCDA-2DA) assemblies in decane measured as a function of temperature. The color transition of poly(EBPCDA-2DA) assemblies obtained at polymerization time of 10 second, 1, 5, 10 and 20 minutes occurs in a partial reversible thermochromism. The magnitude of color reversibility also depends on the polymerization time similar to the butanol system. For the polymerization time of 30 and 40 minutes, the PDA assemblies exhibit irreversible thermochromism. The color transition is not detected after 50 minutes of the polymerization time. To investigate the color transition behavior in more details, the λ_{max} and %CR are plotted as a function of temperature (see Fig. 51). The increase of polymerization time from 10 second to 10 minutes does not affect the color transition temperature. The color transition of all samples is detected at 80 °C. The increase of polymerization time to 20, 30 and 40 minutes cause the decrease of transition temperature to 55, 50 and 45 °C, respectively. The results are summarized in Table 15.

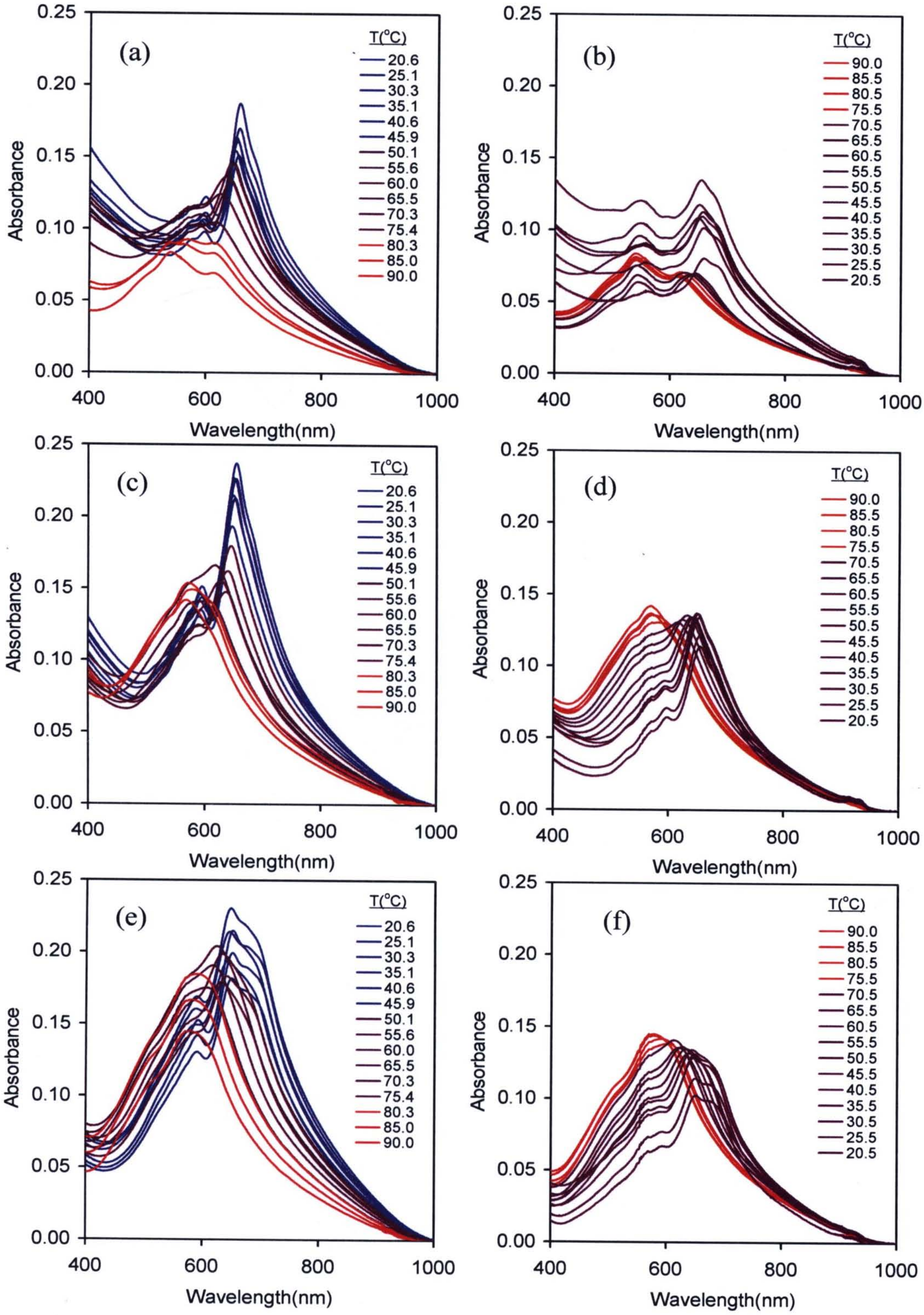


Figure 50 Absorption spectra of poly(EBPCDA-2DA) assemblies in decane measured upon heating (left) and cooling (right). The polymerization time is (a,b) 10 second, (c,d) 1, (e,f) 5, (g,h) 10, (i,j) 20, (k,l) 30, (m,n) 40, (o,p) 50 and (q,r) 60 minute.

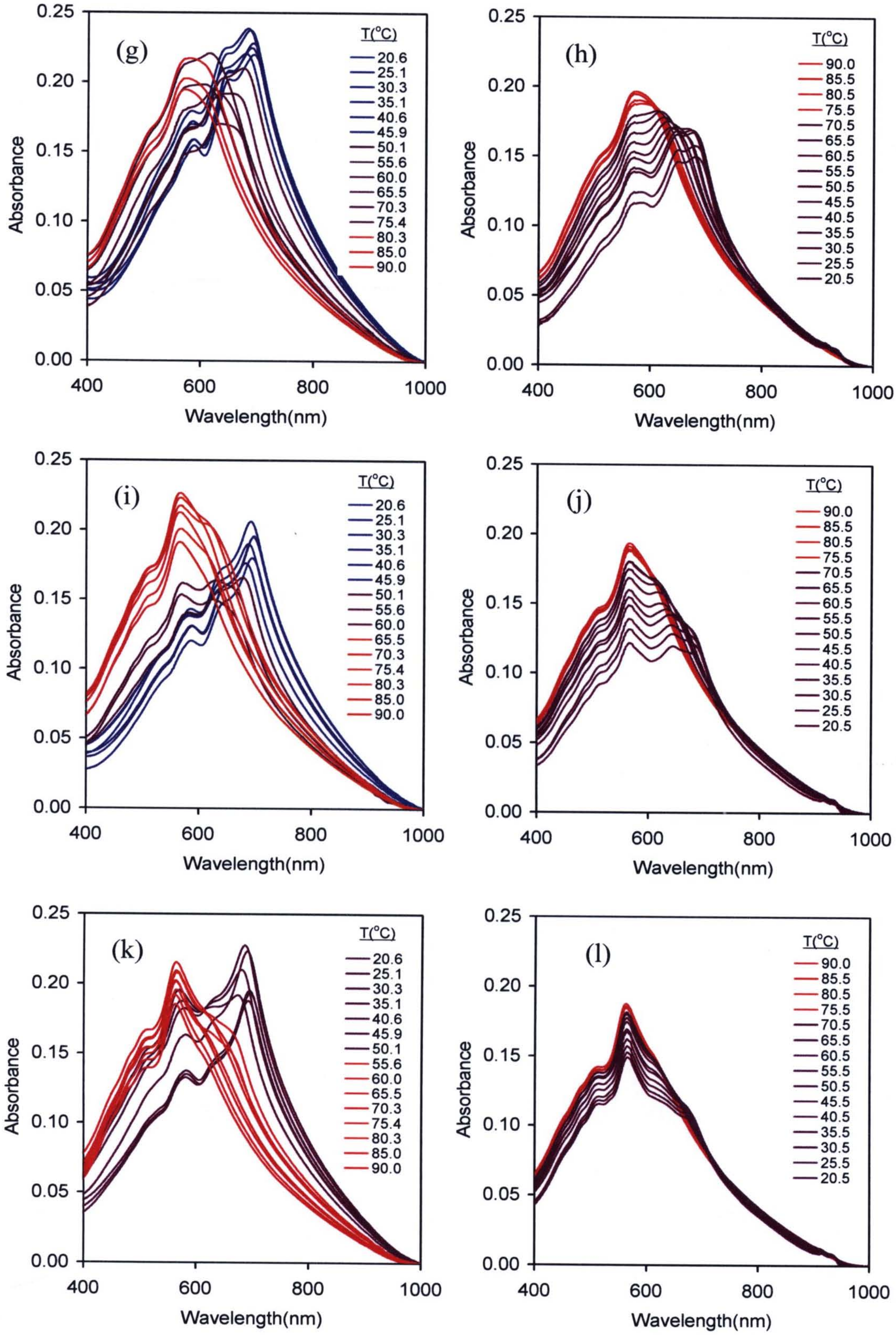


Figure 50 (cont.)

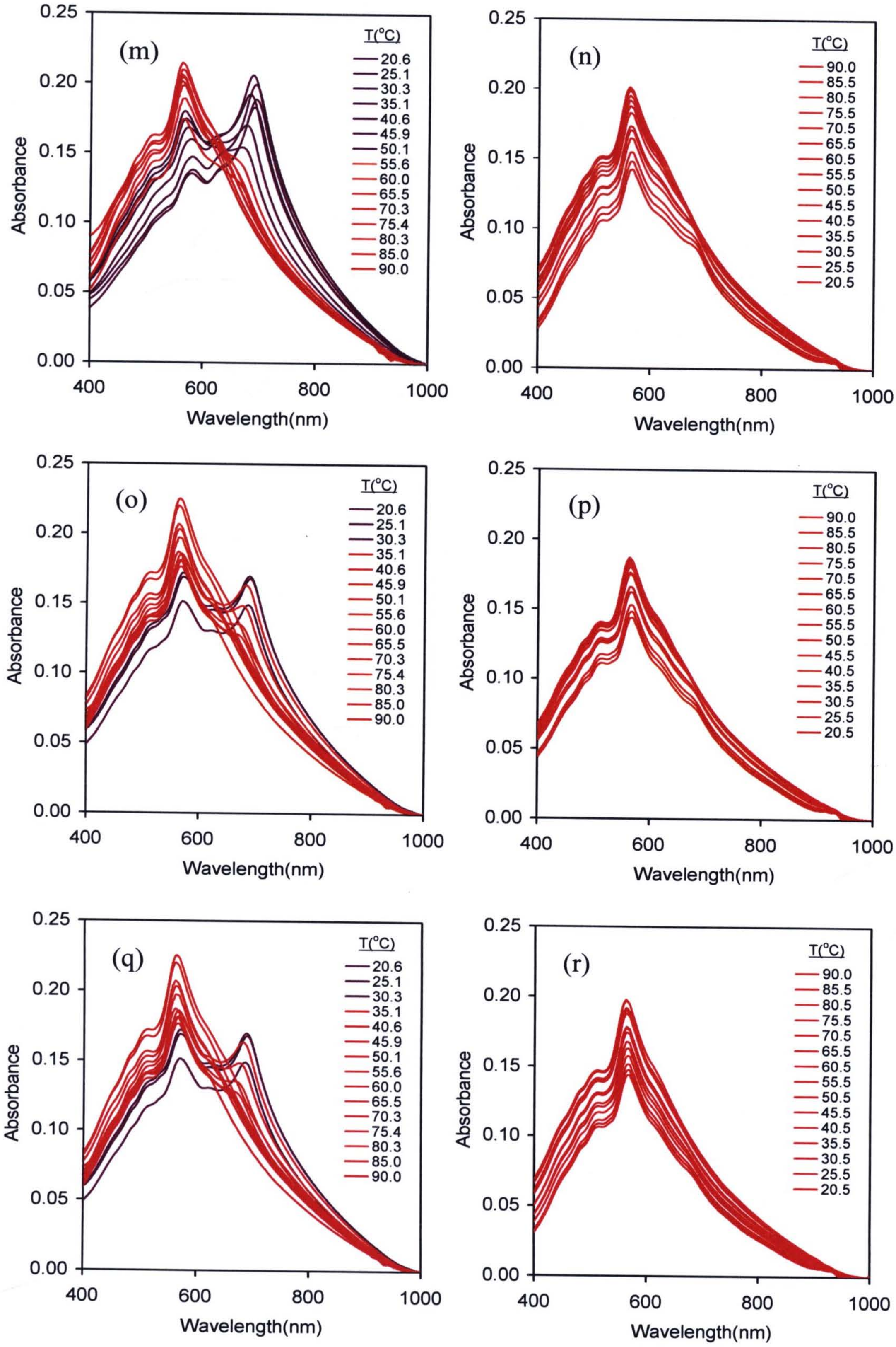
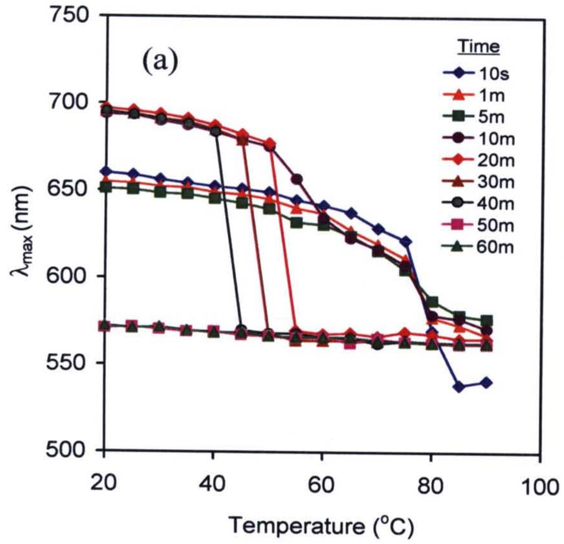


Figure 50 (cont.)



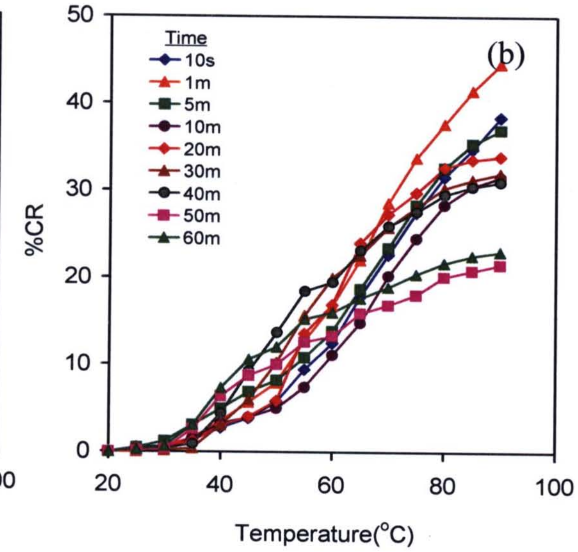


Figure 51 (a) The change of λ_{max} and (b) colorimetric response of poly(EBPCDA-2DA) assemblies in decane are plotted as a function of temperature. The samples are measured upon heating.

Table 15 Color transition temperature and reversibility of poly(EBPCDA-2DA) assemblies in decane measured as a function of temperature

Polymerization time	Color transition temperature (°C)	Reversibility
10 second	80	partially reversible
1 minute	80	partially reversible
5 minute	80	partially reversible
10 minute	80	partially reversible
20 minute	55	partially reversible
30 minute	50	partially reversible
40 minute	45	irreversible
50 minute	-	-
60 minute	-	-

Thermochromic properties of PDA assemblies in polymeric thin films

In addition to the preparation of PDA assemblies in aqueous solution, it can be prepared in polymeric thin films, which allow their utilization in wider range applications. In this study, we investigate the color-transition temperature and reversibility of PDA assemblies in thin films prepared by mixing with different types of polymers. The polymers used in this study include poly(vinyl alcohol) (PVA), poly(styrene) (PS) and poly(methylmethacrylate) (PMMA), which exhibit different polarity. The utilization of each polymer depends on solvents used for preparation of the PDA assemblies. The poly(EBPCDA-2DA) assemblies in aqueous solution are mixed with PVA while the poly(EBPCDA-2DA) assemblies in ethanol and hexane are mixed with PMMA in chlorobenzene and PS in toluene, respectively. The films of PDA assemblies embedded in the polymeric matrices are annealed for 5 minutes at different temperatures ranging from 50 to 200 °C. The photographs of PDA films at each temperature are recorded. When the films are cooled down to room temperature, the photographs and absorption spectra of the annealed film are measured to explore the color reversibility. Fig. 52 illustrates absorption spectra of PDA assemblies in thin film measured upon variation of annealing temperature. The PDA assemblies in various polymeric media exhibit different color transition temperature. All of the thin film exhibit 1st color transition (blue to purple) at 90 °C, which is the reversible one. The 2nd color transition (red to orange) of poly(EBPCDA-2DA) in thin films of PVA, PS and PMMA is detected at about 180 °C, respectively. The transition in this temperature range is irreversible. To investigate the irreversible color transition behavior in more details, the %CR of the annealed films is measured at room temperature and plotted as a function of temperature (see Fig. 52d). We observe that the %CR of PDA in PMMA film increases at relatively low temperature compared to the other films. The discrepancy of the color transition behavior is probably due to nature of each polymer. All of the poly(EBPCDA-2DA) assemblies thin films exhibit complete reversible thermochromism in temperature range of 25 – 120 °C as shown in Fig. 53. Color transition temperature and reversibility of the PDA assemblies in thin film are summarized in Table 16.

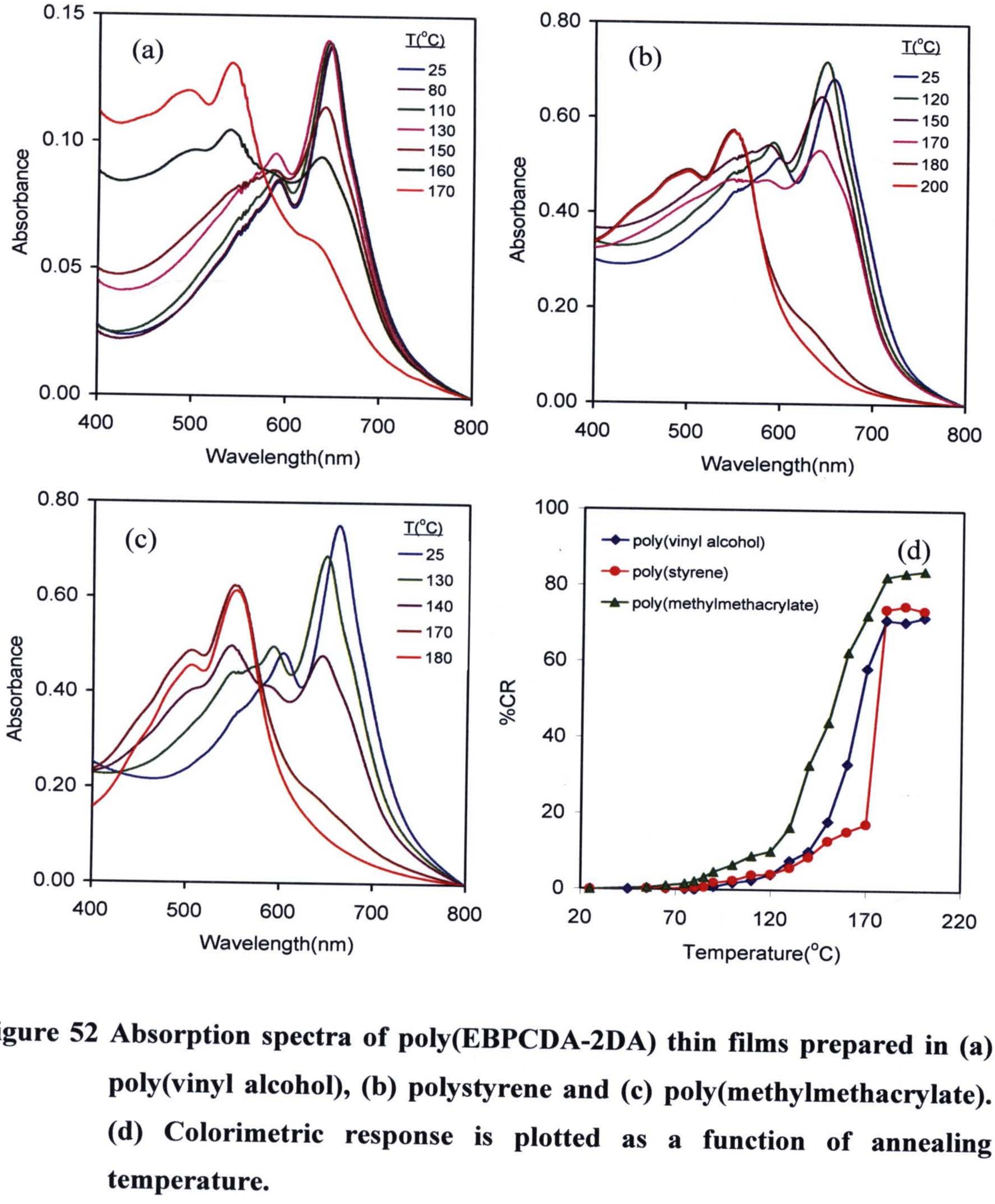


Figure 52 **Absorption spectra of poly(EBPCDA-2DA) thin films prepared in (a) poly(vinyl alcohol), (b) polystyrene and (c) poly(methylmethacrylate). (d) Colorimetric response is plotted as a function of annealing temperature.**

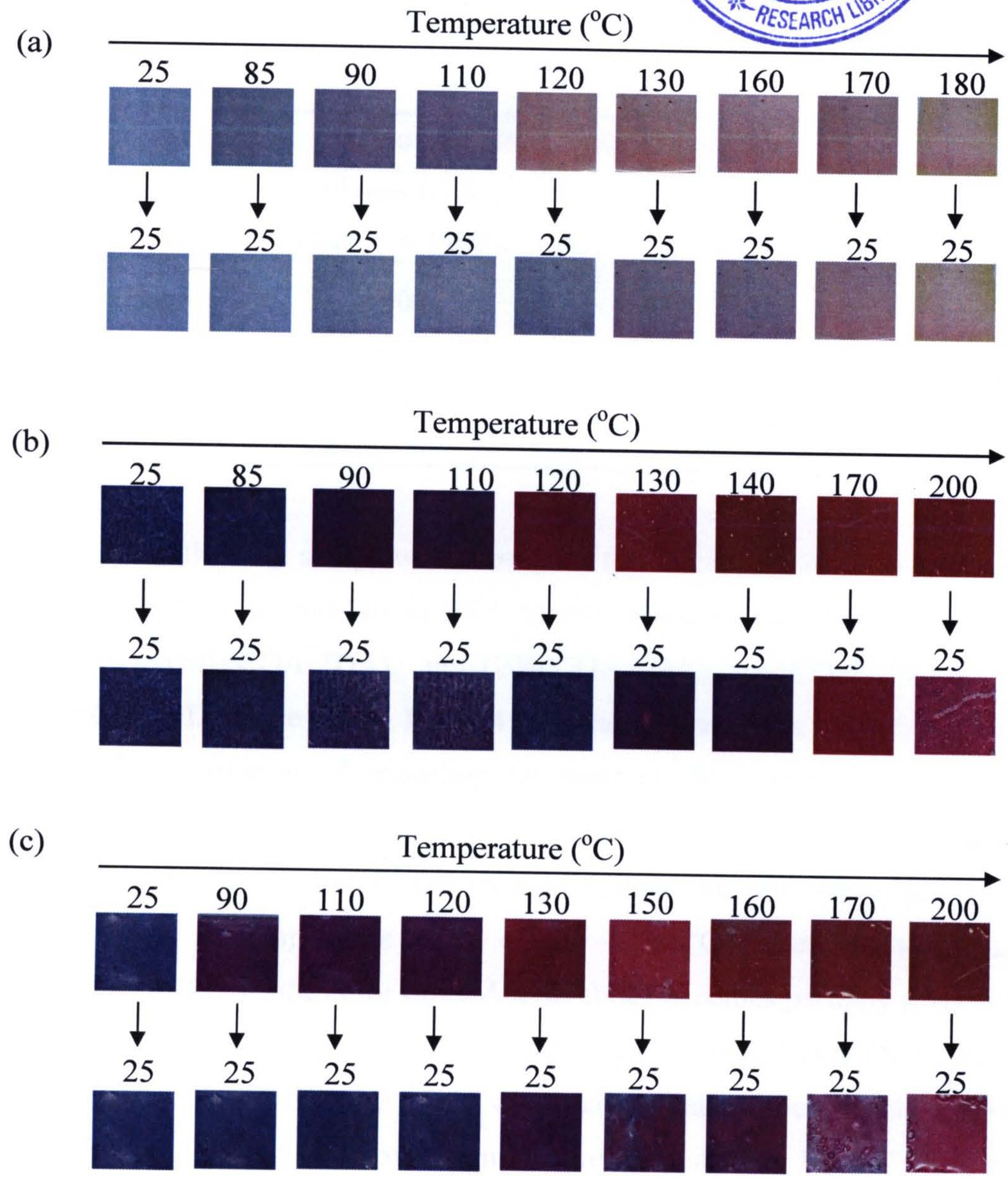


Figure 53 Color photographs of poly(EBPCDA-2DA) thin film prepared in (a) poly(vinyl alcohol), (b) polystyrene and (c) poly(methylmethacrylate) taken upon heating and then cooling to 25°C

Table 16 Color transition temperature and reversibility of the poly(EBPCDA-2DA) thin films prepared by mixing with polymeric media

Polymer matrices	Color transition temperature (°C)		Temperature range for complete reversibility
	1st transition Blue → Purple	2nd transition Red → Orange	
poly(vinyl alcohol)	90	180	25 – 120
poly(styrene)	90	180	25 – 120
poly(methylmethacrylate)	90	180	25 – 120

In the following study, we investigate the color transition temperature and reversibility of PDA assemblies in PVA matrix. However, different types of PDAs including poly(EBPCDA-2DA), poly(BBPCDA-2DA), poly(PBPCDA-2DA) and poly(HBPCDA-2DA) are used. Fig. 54 illustrates absorption spectra of all films measured upon variation of annealing temperature. We observe that all samples exhibit the 1st and 2nd transition temperatures at about 90 and 180 °C. The PDA assemblies with ethyl, butyl and hexyl linkers exhibit complete reversible thermochromism in temperature range of 25 – 120 °C. When the temperature is increased above 120 °C, the color of PDA assemblies becomes partially reversible (see Fig. 55). We also observe that the increasing length of alkyl linker (N=2,4,6) causes the decrease of %CR. For the PDA with pentyl linker, the complete reversible thermochromism is detected at lower temperature range at 25 – 75 °C. Color transition temperature and reversibility of the PDA assemblies in thin films are summarized in Table 17.

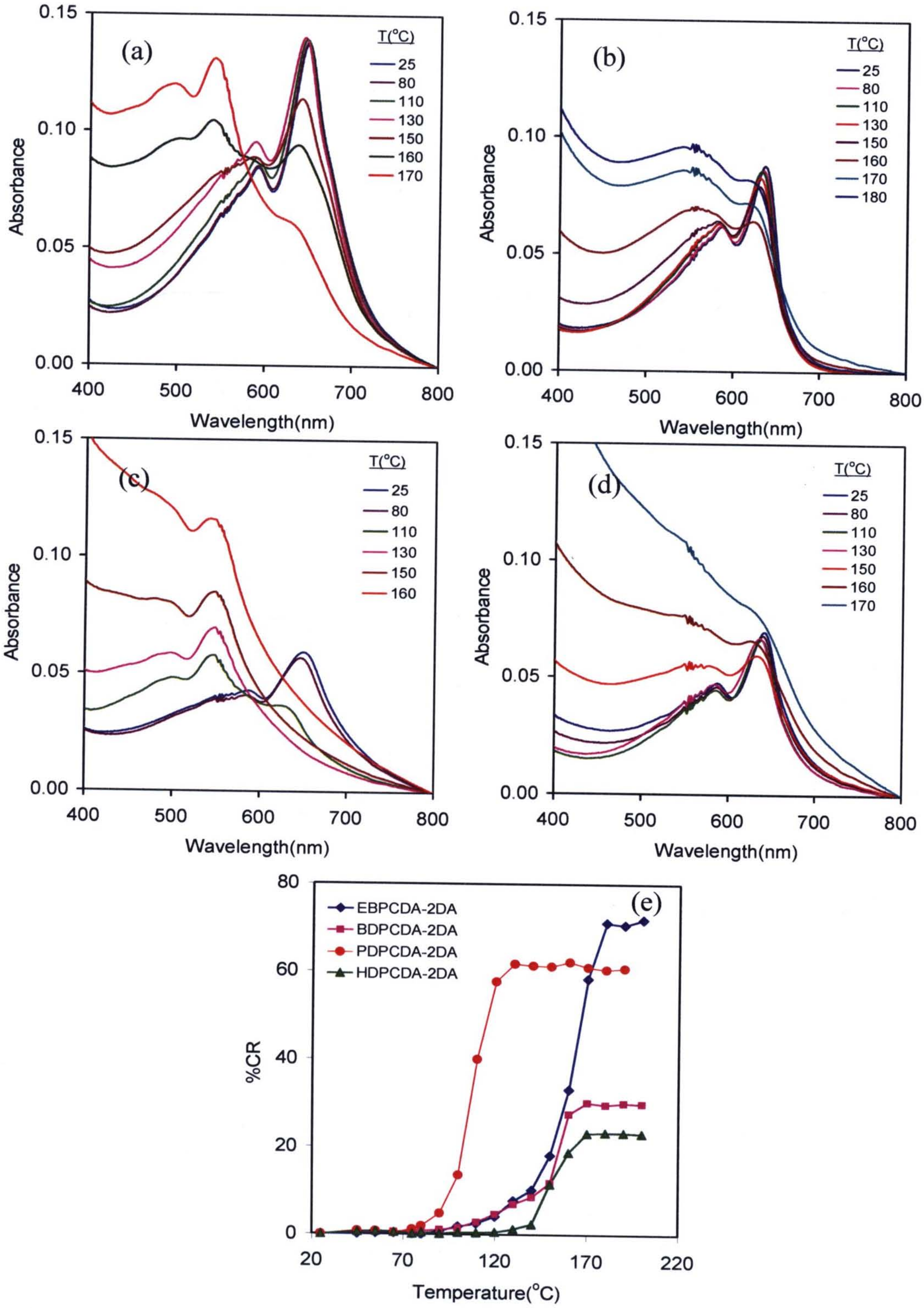


Figure 54 Absorption spectra of (a) poly(EBPCDA-2DA), (b) poly(BBPCDA-2DA), (c) poly(PBPCDA-2DA) and (d) poly(HBPCDA-2DA) thin film prepared in PVA taken at different annealing temperature. (e) Colorimetric response is plotted as a function of temperature.

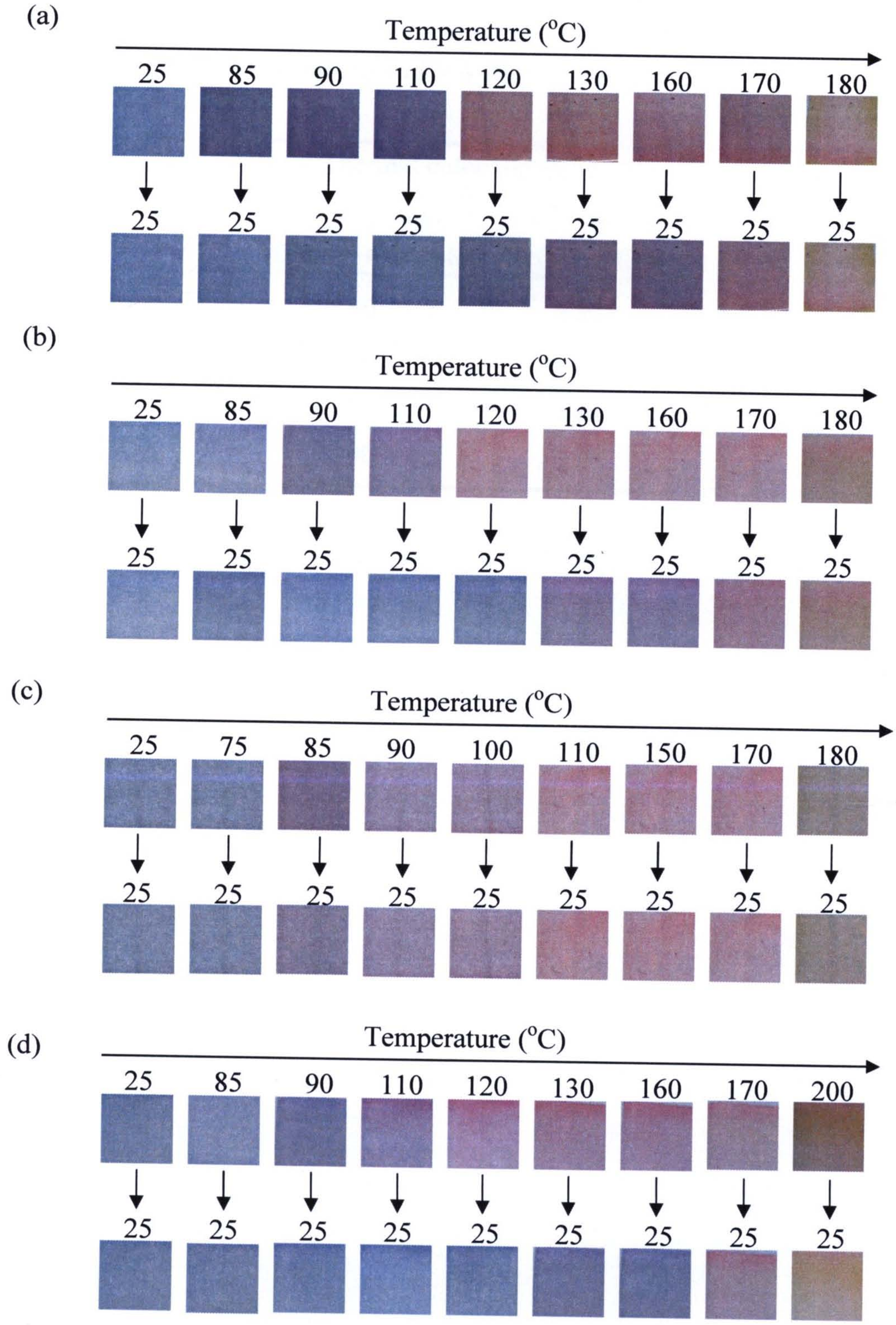


Figure 55 **Color photographs of (a) poly(EBPCDA-2DA), (b) poly(BBPCDA-2DA), (c) poly(PBPCDA-2DA) and (d) poly(HBPCDA-2DA) thin film prepared in PVA taken at various temperature.**

Table 17 Thermal color transition and reversibility of the poly(EBPCDA-2DA) assemblies embedded in PVA film

Monomer	Thermal color transition (°C)		Temperature range for fully reversibility
	1st transition Blue → Purple	2nd transition Red → Orange	
EBPCDA-2DA	90	180	25 – 120
BDPCDA-2DA	90	180	25 – 120
PDPCDA-2DA	85	180	25 – 75
HDPCDA-2DA	90	180	25 – 120

Fluorescence properties of PDA assemblies

In the last section, we investigate the fluorescent properties of the PDA assemblies by using luminescence spectroscopy. It has been known that the PDA assemblies become fluorescent in the red form. In this study, we investigate the effect of structural modification of PDAs on their fluorescent properties. We observe that the reversible color transition from blue to red or purple does not lead to the fluorescent property. The irreversible blue to red color transition, on the other hand, tends to induce the fluorescence. The fluorescent spectra of the poly(PCDA), poly(APOEO-2DA) and poly(p-PA-2DA) assemblies in the red form are illustrated in Fig 56. The fluorescent intensity of all samples is rather weak. The spectra also exhibit different shape, which is probably due to the difference of molecular packing within the assemblies. However, the other PDAs assemblies, poly(PDPCDA-2DA) and irreversible which exhibit irreversible color transition do not show fluorescent properties. Fluorescence properties of PDA assemblies are summarized in Table 18.

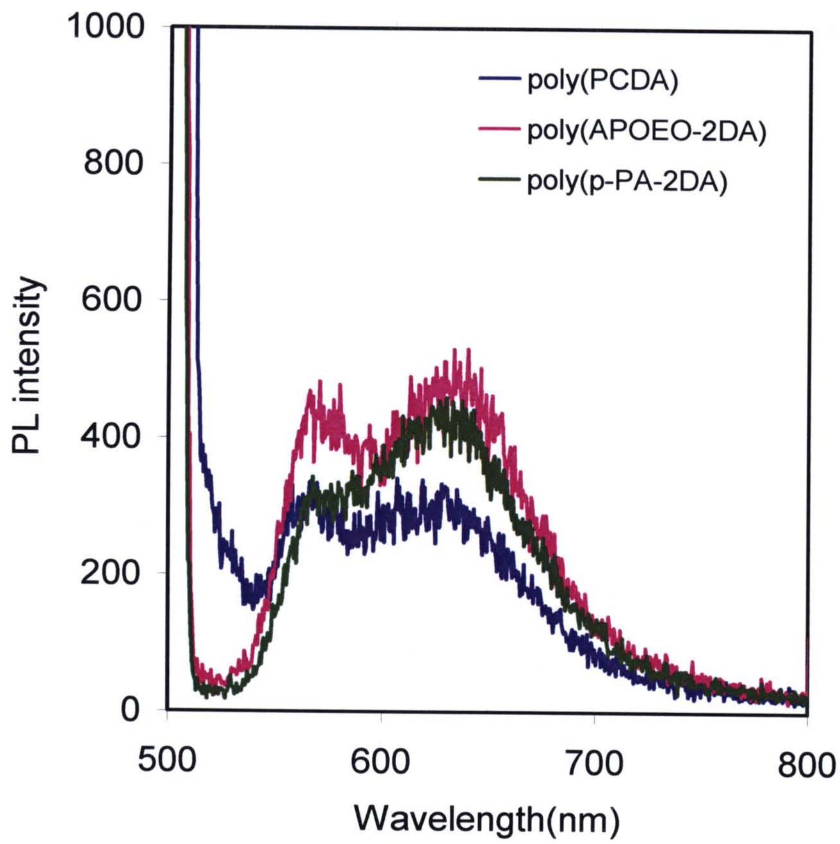


Figure 56 Fluorescent spectra of PDA assemblies in red from in aqueous solution

Table 18 Fluorescent properties of PDA assemblies

PDA assemblies	Reversibility	Fluorescence properties
Poly(PCDA)	irreversible	√
poly(EBPCDA-2DA)	reversible	×
poly(BDPCDA-2DA)	reversible	×
poly(PDPCDA-2DA)	irreversible	×
poly(HDPCDA-2DA)	reversible	×
poly(APOEO-2DA)	irreversible	√
poly(p-PA-2DA)	irreversible	√
poly(m-PA-2DA)	reversible	×
poly(c-CA-2DA)	irreversible	×