

Development of Thermochromic Paints, Plastics, and Rubbers for Rapid Visual Assessment of Temperature

Brett L. Lucht and William B. Euler

University of Rhode Island

June 2009

URITC PROJECT NO. 536152- 536183
(This report is the result of a 2-years grant)

PREPARED FOR
UNIVERSITY OF RHODE ISLAND
TRANSPORTATION CENTER

DISCLAIMER

This report, prepared in cooperation with the University of Rhode Island Transportation Center, does not constitute a standard, specification, or regulation. The contents of this report reflect the views of the author(s) who is (are) responsible for the facts and the accuracy of the data presented herein. This document is disseminated under the sponsorship of the Department of Transportation, University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof.

Technical Report Documentation Page

1. Report No. URITC FY01-02	2. Government Accession No. N/A	3. Recipient's Catalog No. N/A	
4. Title and Subtitle <i>Development of Thermochromic Paints, Plastics, and Rubbers for Rapid Visual Assessment of Temperature</i>		5. Report Date June 2009	
		6. Performing Organization Code	
7. Author(s) Brett L. Lucht and William B. Euler		8. Performing Organization Report No. 536152 - 536183	
9. Performing Organization Name and Address University of Rhode Island Department of Chemistry 51 Lower College Rd. Kingston, RI 02881		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address University of Rhode Island Transportation Center Carlotti Administration Building, 75 Lower College Road Kingston, RI 02881		13. Type of Report and Period Covered	
		14. Sponsoring Agency Code	
15. Supplementary Notes This document is the result of a 2 years-grant. The report summarizes the findings of both grants 536152 and 536183. Findings related to the 536152 grant appear under "3. Results YR 2001," whereas findings related to the 536183 grant appear under: "4. Results YR 2002."			
16. Abstract During our effort to develop novel thermochromic pigments for use in paints plastics and rubbers for the rapid visual assessment of temperature, we discovered an entirely new thermochromic property of these interesting materials. Poly(3-docosylthiophene) was found to have a two-step thermochromic process for samples that are rapidly cooled from the melt. The melt-quenched samples are a red-orange color that changes first to purple and then to yellow upon heating. In contrast, slowly cooled materials are purple and have a single thermochromic transition to yellow, typical of most poly(3-alklythiophene)s. This phase behavior is found in both regioregular and regioirregular samples. The thermal behavior of the polymers were studied using differential scanning calorimetry and visible reflection spectroscopy. The DSC thermograms of slowly cooled samples show two endotherms upon heating and three exotherms upon cooling. In contrast, rapidly cooled samples exhibit three endotherms upon heating and three exotherms upon cooling. Reflection spectra show color changes that correlate with the DSC features. A model is proposed to explain the data that involves trapping of a high temperature mesophase under the rapid cooling conditions.			
17. Key Words		18. Distribution Statement No restriction. This document is available to the Public through the URI Transportation Center, Carlotti Administration Building, 75 Lower College Rd., Kingston, RI 02881	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 19	22. Price N/A

Table of Contents

List of Figures and Tables	iv
1. Introduction	1
2. Experimental	4
2.1. Synthesis	4
2.2. Measurements	4
3. Results YR 2001	6
4. Results YR 2002	10
5. Discussion	14
6. Conclusion	17
7. Acknowledgments	17
8. References	18

List of Tables and Figures

Figure 1. A thin film of RR rapidly cooled with a room temperature metal template	6
Figure 2. DSC thermograms of regioregular poly(3-docosyl-thiophene)	8
Figure 3. DSC thermograms of regiorregular poly(3-docosyl-thiophene)	9
Figure 4. Kubelka-Munck transformed reflection spectra of RR and RIR samples	11
Figure 5. Kubelka-Munck transformed reflection spectra of RR and RIR samples	12
Figure 6. Plots of k/s at 600 nm vs. temperature	13
Table 1. Summary of measured properties	6
Scheme 1. Proposed Mechanism for Novel Thermochromic Properties	16

1. INTRODUCTION

Poly(thiophene)s have been intensely studied for a number of years because they have interesting optical and electronic properties.(1) Doped poly(thiophene)s have good electronic conductivity because of the delocalized π system along the polymer backbone and have been one of the prototype conducting polymer systems.(2) In the reduced state, the poly(thiophene)s possess intense electronic absorptions in the visible region attributed to π - π^* bandgap transitions and in many cases the excited states emit visible light. This combination of properties has led to the use of poly(thiophene)s as organic light emitting diodes.(3-8) The synthetic chemistry to modify the poly(thiophene)s at the 3-position of the thiophene ring is well developed so modulation of the polymer properties can readily be done to increase our understanding of this material.(9-16)

Poly(3-alkylthiophene)s (PATs) are thermochromic and solvatochromic.(17) Both of these properties have been extensively studied to develop a more complete picture of the electronic states of this class of materials.(18-34) In particular, the thermochromism of PATs has led to some puzzling observations. Some derivatives show relatively sharp changes with temperature while others are quite broad. Some PATs are reported to exhibit isosbestic points in the temperature dependent optical spectra and some do not. There is common agreement that the dramatic chromic change is based on a twisting of the poly(thiophene) backbone. At low temperature the thiophene rings along a single polymer chain are all relatively more coplanar, which gives a long delocalization length and low energy electronic transition. At high temperature, the intrachain thiophene rings twist away from the near coplanarity, which reduces the conjugation length, thereby increasing the energy of the electronic transition leading to the observed thermochromism. The role of the alkyl side groups is less well understood. As the temperature is raised, the ordered alkyl side chains melt but without an apparent chromic change. This is observed as a low temperature peak in the DSC thermograms. Further, the twisting between the thiophene monomer units is driven by a steric interaction between the methylene group at the 3-position of the thiophene ring and the adjacent sulfur atom.(17-27) However, the role of the disordered side chains on the main chain twisting has been debated. In particular, the long range interaction of the side chains may have some influence on the thermochromic response in these materials.

Leclerc and coworkers (18-25) have investigated a wide number of poly(thiophene) derivatives and concluded that the thermochromic response is primarily a single chain event and that the substitution pattern on the poly(thiophene) is what drives the thermochromic phase change. In this interpretation crystallization or aggregation effects are less important. Those materials that have

isosbestic points are those that have sufficient local steric interactions to drive a cooperative phase transition. When the local steric interactions are reduced by alternating repeat unit of high and low steric repulsion, the phase transition loses cooperativity and the thermochromic response is gradual as a function of temperature and no isosbestic point is seen.

In contrast, Holdcroft, *et al*, (26,27) proposed that the crystallinity (i.e., long range order) was the key feature to understanding the thermochromism in poly(3-alkylthiophene)s. When the polymer has a short alkyl substituent (less than ten carbons), then there is no side chain order (evidenced by no low temperature peak in the DSC thermograms) so that as the polymer is heated the polymer lattice gradually expands and the thiophene rings progressively twist, leading to a color change but no isosbestic point. For poly(3-alkylthiophene)s with longer chain substituent groups the side chains order into crystallites at low temperature. When the side chains melt, a quasi-ordered phase is formed that melts into a fully disordered phase at the thermochromic transition temperature. If the side chain melting temperature is close enough to the main chain melting, then all three phases can be in equilibrium and no isosbestic point is observed. If the side chain melting occurs at sufficiently low temperature, then the three-phase equilibrium is not observed and an isosbestic point is found. The sharpness of the thermochromic transition for some derivatives was attributed to a cooperative “zipper” effect associated with the alkyl side groups. This work also pointed out that the regioregularity of the polymer has an important influence on the thermochromic properties.

The significance of the crystallinity and long range order was supported by studies reported by Levon and coworkers (28,29) for poly(3-dodecylthiophene). These researchers determined the effect of annealing temperature and time on the growth of the crystalline phases and showed that there are multiple phases that can undergo thermochromism. The predominate red, crystalline phase was formed in a fast kinetic process but a yellow-brown, less-ordered phase could also be trapped when the polymer viscosity was low enough. Each of these phases gave a different melting peak in the DSC thermogram upon transition to the high temperature phase.

Further complicating matters, Winokur and coworkers (30) found that two different low temperature structures could be obtained for poly(3-dodecylthiophene), depending upon the precipitation temperature used to deposit the polymer from solution. The two structures differ by the relative orientation of the alkyl substituent to the thiophene rings. Both structures have the alkyl groups ordered, but in one case the alkyl groups are interdigitated and in the other case they are noninterdigitated.

Finally, theoretical calculations using an atomistic simulation and molecular dynamics by Morton-Blake, *et al.*, (31-33) have suggested that the thermochromism is associated with sliding of the thiophene chain along the polymer axis. In this idea, the nearest neighbor thiophene units of adjacent chains (along the b axis) are in a staggered conformation at low temperature. After the side chains melt, sufficient mobility is imparted so that neighboring chains can slide relative to each other leading to an eclipsed conformation. In the eclipsed conformation, there are steric interactions between the alkyl side chains and the neighboring thiophene rings, which then drives the chain twisting associated with the color change. No experimental results have been reported to support this mechanism.

In this paper, we report the observation that poly(3-docosylthiophene) has a two-step thermochromic response for both regioregular and regioirregular materials. Pristine samples prepared at room temperature are a purple color. Upon slow heating regioirregular samples turn a darker burgundy color followed by the final change to the yellow high temperature color. Under similar slow heating conditions regioregular samples change directly to the high temperature yellow color. When either polymer is cooled slowly to ambient the original purple color is reestablished. However, when either of the polymers is cooled rapidly, the final color is red-orange, distinctly different from the pristine color. The original purple color can be reestablished by heating the red-orange sample to yellow and then slowly cooling. This process can be repeated for tens to hundreds of cycles. A well defined endotherm in the DSC thermogram is found for each process. The red-orange phase is stable at room temperature for long times – we have samples that have retained this phase for more than a year. The existence of a mesophase that can be trapped by liquid nitrogen quenching was previously reported by Bolgnesi, *et al.* (34) These workers reported that poly(3-decylthiophene) had two stable low temperature phases and a metastable (lifetime less than 1 day) mesophase. The colors of the various phases and thermochromic transitions were not reported. The thermochromism in poly(3-docosylthiophene) is similar to that reported for a urethane substituted poly(thiophene) where a high temperature mesophase could be stabilized by rapid quenching of the high temperature state.(35) The presence of an isolatable mesophase by rapid quenching with new thermochromic properties strongly argues that interchain phenomena (aggregation and crystallization) are critical components in understanding the mechanism of thermochromism in poly(3-alkylthiophene)s.

2. EXPERIMENTAL

2.1. Synthesis

Regioregular poly(3-docosylthiophene): 3-docosylthiophene (19.3 g, 49.2 mmol) was dissolved in 100 mL of CHCl_3 . Bromine (15.8 g, 98.4 mmol) was added to the solution over a period of 10 min. The solution was stirred at room temperature for 2 h followed by washing with 5% NaOH solution and water. MgSO_4 was used to dry the solution followed by removal of solvent by evacuation to afford 2,5-dibromo-3-docosylthiophene. The product was used directly for the polymerization without further purification. Under a positive atmosphere of nitrogen, 2,5-dibromo-3-docosylthiophene was dissolved in 250 mL of THF. Methylmagnesium bromide (35 mL, 1.4 M solution in toluene/tetrahydrofuran 75/25) was added and the solution was stirred at reflux for 1 h. $\text{Ni}(\text{dppp})\text{Cl}_2$ (200 mg) was added and the solution was stirred at reflux overnight. After addition of 5 mL of methanol, the solution was concentrated to 100 mL. The polymer was then precipitated by 350 mL methanol and washed with 300 mL warm acetone to afford the title polymer (5.0 g, 26% yield from 3-docosylthiophene).

Regioirregular poly(3-docosylthiophene): Under a positive atmosphere of nitrogen, 3-docosylthiophene (50.0 g, 128 mmol) was dissolved in 400 mL of CH_2Cl_2 . The solution was added to FeCl_3 (46.0 g, 283 mmol) in 500 mL of CH_2Cl_2 at room temperature. The mixture was allowed to stir overnight. The polymer was precipitated in 2000 mL methanol and washed with warm methanol (3×500 mL) to afford the title polymer (42.2 g, 85%).

Bulk samples of rapidly cooled material were prepared by first making a thick film (100 – 500 μm) of the polymer by drip coating a THF solution onto an aluminum foil substrate. The thick film was then heated above the thermochromic transition and rapidly cooled by pouring liquid nitrogen on the aluminum foil. The red-orange sample was then removed from the substrate.

2.2. Measurements

Differential scanning calorimetry (DSC) thermograms were measured on a TA Instruments Q100 instrument in aluminum pans at 10 $^\circ\text{C}/\text{min}$ under a flowing nitrogen atmosphere (50 mL/min). The instrument was calibrated with indium. Reflection spectra were measured with an Ocean Optics S2000 instrument using a cylindrical fiber optic reflection probe containing one source fiber and seven collection fibers. The spectra were referenced against a white standard between 450 and 800 nm and a tungsten-halogen lamp. Variable temperature spectra were measured by drip coating the polymer (saturated in THF) onto a piece of paper and then evaporating the solvent off with a

heat gun. The samples were placed on an aluminum block containing a thermometer and placed on a hot plate, which was used to heat the sample at about 2 °C/min. Removal of the heat source gave a similar cooling rate. The surface temperature at the sample site was calibrated by using the reflection change associated with the melting of biphenyl (69 °C) and naphthalene (80 °C). NMR spectra were measured on a JEOL Eclipse 400 spectrometer at 400 MHz using CDCl₃ as a solvent. Polymer molecular weights were estimated by size exclusion chromatography (Agilent Technology series 1100 HPLC; Detector: Differential Refractometer G1362A; Pump: Isocratic 1310A; Software: Chemstation; Column: Plgel 10³ A using THF as solvent and polystyrene standards).

3. RESULTS YR 2001

Regioregular poly(3-docosylthiophene) (RR) was synthesized using McCullough's method (13) and regioirregular poly(3-docosylthiophene) (RIR) was synthesized using oxidative polymerization of the monomer with anhydrous FeCl₃.(12) Molecular weights, as estimated by GPC, and head-to-tail (HT) content, as estimated by ¹H NMR, are given in Table 1.



FIGURE 1. A thin film of RR rapidly cooled with a room temperature metal template

When preparing thin film samples for spectroscopic analysis a THF solution of the material was dropped onto a substrate and heated to drive off the solvent. We observed that the cooling rate had a significant affect on the nature of the final thin film. Slowly cooled samples (one to tens of degrees per minute) gave thin films that were purple in color. In contrast, rapidly cooled samples (tens to hundreds degrees per second) gave much lighter, red-orange colored films, as demonstrated by the photograph in Figure 1. Both RR and RIR samples exhibited this behavior. The trapped mesophase appears to be indefinitely stable: films stored at room temperature retain the red-orange color for more than one year. This set of unusual properties prompted us to investigate the thermal behavior of poly(3-docosylthiophene) using DSC and visible reflection spectroscopy.

Property	regioirregular		regioregular	
	no mesophase	with mesophase	no mesophase	with mesophase
M _n (GPC)	3.5 × 10 ⁴	–	7.9 × 10 ³	–
M _w (GPC)	6.5 × 10 ⁴	–	2.5 × 10 ⁴	–
% HT content (NMR)	80 %	–	> 95 %	–
DSC Peak 1 heating (°C)	57.3	57.4	53.1	53.3
DSC Peak 2 heating (°C)	76 (sh)	70 (sh)	–	70.6
DSC Peak 3 heating (°C)	96.1	95.2	103.2	103.8
DSC Peak 1 cooling (°C)	50.7	49.7	45.7	45.0
DSC Peak 2 cooling (°C)	–	67 (sh)	53.9	53.9
DSC Peak 3 cooling (°C)	85.6	84.4	73.1	73.1

Reflection Transition 1 heating (°C)	64.3	62.0	–	60.8
Reflection Transition 2 heating (°C)	95.9	96.0	115.8	114.6
Reflection Transition 1 cooling (°C)	66.5	61.3	89.8	87.3

TABLE 1. Summary of measured properties

The DSC traces of RR samples are shown in Figure 2. In slowly cooled samples containing no mesophase (upper thermogram, Figure 2) two endotherms are observed upon heating, typical of poly(3-alkylthiophene)s. The lower temperature endotherm at about 53 °C is assigned to melting of the alkyl side chains and the higher temperature endotherm at about 103 °C is assigned to melting of the poly(thiophene) backbone. The higher temperature transition is associated with the thermochromic color change. Upon cooling, three exotherms are observed at 46, 54, and 73 °C. This result demonstrates the existence of a monotropic mesophase for this polymer. A second heating cycle of the slowly cooled sample is identical to the first cycle. The thermograms of the rapidly cooled sample are shown in the lower graph in Figure 2. The initial heating scan shows three endotherms at 53, 71, and 104 °C. The feature at 71 °C is unique to the rapidly cooled sample. The cooling scan is identical to that of the slowly cooled sample. Upon reheating, the thermogram reverts to that of a slowly cooled sample, with loss of the endotherm at 71 °C. Thus, it appears that rapidly cooled samples freeze out a new monotropic mesophase, which has not been previously observed.

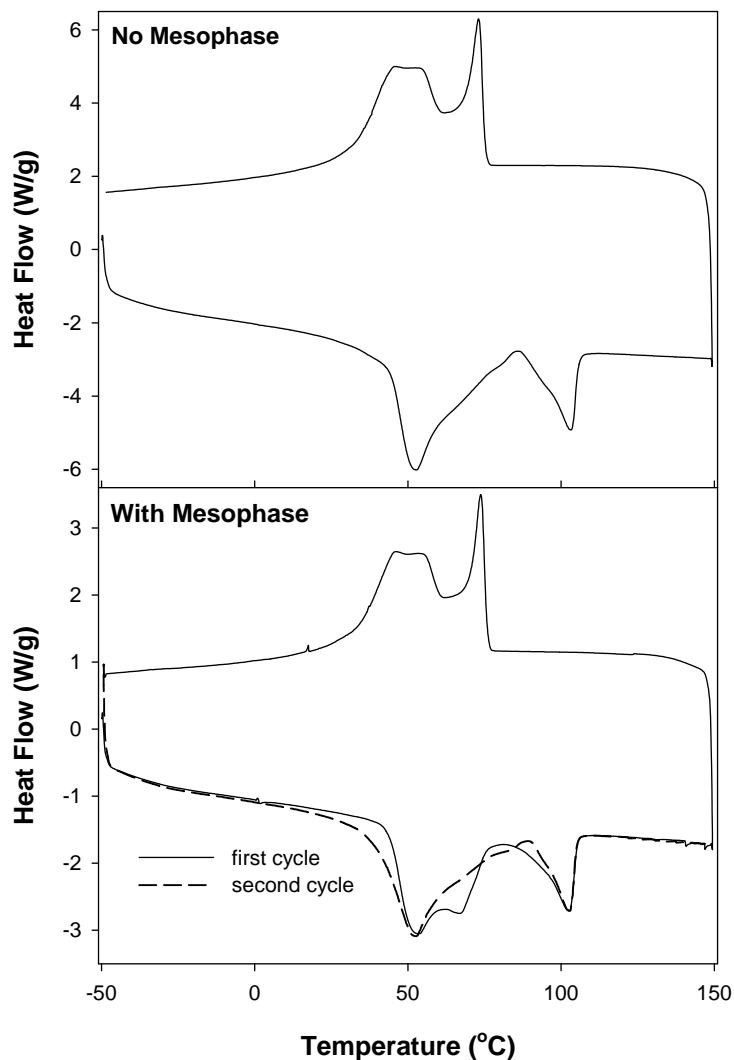


FIGURE 2. DSC thermograms of regioregular poly(3-docosyl-thiophene). Top: slowly cooled sample containing no mesophase. Bottom: rapidly cooled sample containing the trapped mesophase. Endotherms are down and all data were collected at 10 °C/min.

Similar results are found for RIR, as shown in Figure 3. For slowly cooled samples in the heating cycle prominent endotherms are observed at 57 and 96 °C and a small endothermic shoulder is found at 76 °C. Upon cooling, a sharp exotherm at 86 °C and broad exotherm centered at 51 °C are found. For rapidly cooled samples, during the first heating cycle the shoulder at 70 °C is noticeably larger, but still not well defined, and this shoulder disappears during the second heating cycle. The cooling cycle is nearly identical to that of the rapidly cooled sample except that the broad exotherm has a slightly observable shoulder at about 67 °C. For RIR, a small amount of the mesophase is trapped even at slow cooling rates but obtaining large amounts of the mesophase is

more difficult than for RR. All of the peak temperatures for both RR and RIR are listed in Table 1.

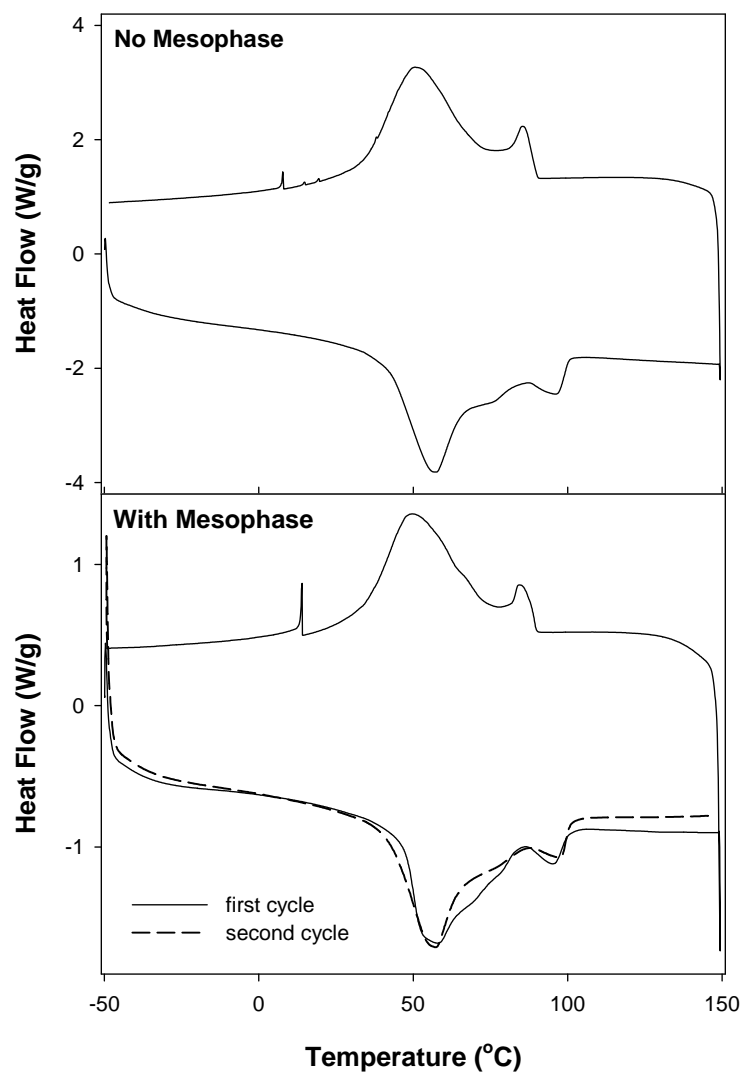


FIGURE 3. DSC thermograms of regioirregular poly(3-docosyl-thiophene). Top: slowly cooled sample containing no mesophase. Bottom: rapidly cooled sample containing the trapped mesophase. Endotherms are down and all data were collected at 10 °C/min.

4. RESULTS YR 2002

The reflection spectra were measured on thin films (on a paper substrate) from room temperature to above the thermochromic transition. The reflection data was transformed using the Kubelka-Munck protocol to give spectra plotted as k/s vs. wavelength. The Kubelka-Munck transform gives a unitless ratio of k/s , where k is the absorption coefficient, and s is the scattering coefficient. The k/s ratio is typically compared to absorption spectra under the assumption of constant scattering but for the samples under discussion here that is not a good assumption. Kubelka-Munck spectra for each of the three phases for both RR and RIR are shown in Figure 4. The change in the baseline (700 -800 nm) where little absorption occurs indicates that the scattering factor is changing with temperature. Visually, this is apparent as a noticeable transparency change between low and high temperatures. The low temperature spectrum is typical for a regioregular poly(3-alkylthiophene) and has a band edge (found by a linear extrapolation of the spectrum to $k/s = 0$) of about 700 nm (1.77 eV). The resulting high temperature spectrum has a band edge of about 600 nm (2.07 eV). For RIR, the room temperature spectrum has a band edge at about 660 nm (1.88 eV), slightly blue-shifted from the RR analogue. The high temperature form of RIR has a band edge of about 600 nm (2.07 eV), similar to RR. The mesophases for both RR and RIR have band edges between the low and high temperature forms.

Spectra for RR at 10 °C intervals are shown at the top of Figure 5. For samples with no mesophase, as the temperature is raised the spectra change little until about 90 °C and then there is a dramatic blue-shift. The thermochromic transition is complete at about 120 °C. There may be an isosbestic point in these spectra at about 500 nm. The lower portion of Figure 5 shows the spectra for RIR at 10 °C intervals. As the temperature is raised the spectra initially red shift upon heating beginning at about 50 °C and ending at 75 °C (band edge at 670 nm, 1.85 eV) and then dramatically blue shift at about 90 °C and there is no isosbestic point. For rapidly cooled samples, both RR and RIR, the spectra red shift from 50 °C to about 75 °C and then blue shift until the high temperature form is attained.

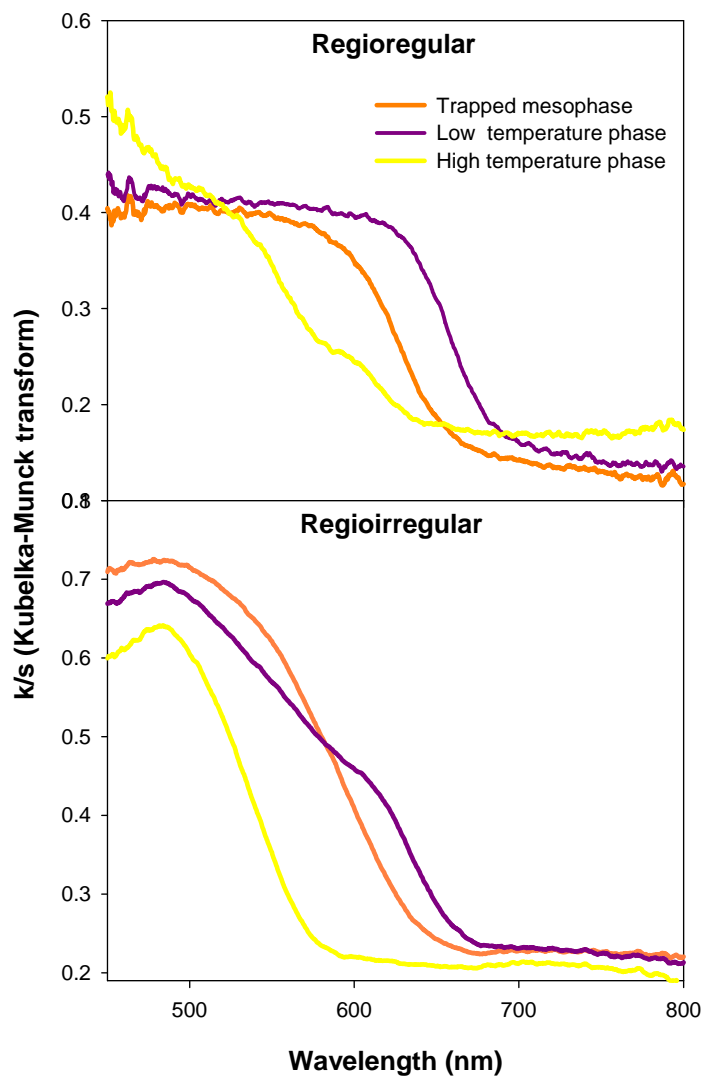


FIGURE 4. Kubelka-Munck transformed reflection spectra of RR (top) and RIR (bottom) samples. The purple lines are for the low temperature phase, the red-orange lines are for the trapped mesophase, and the yellow lines are for the high temperature phase, corresponding to the visual appearance.

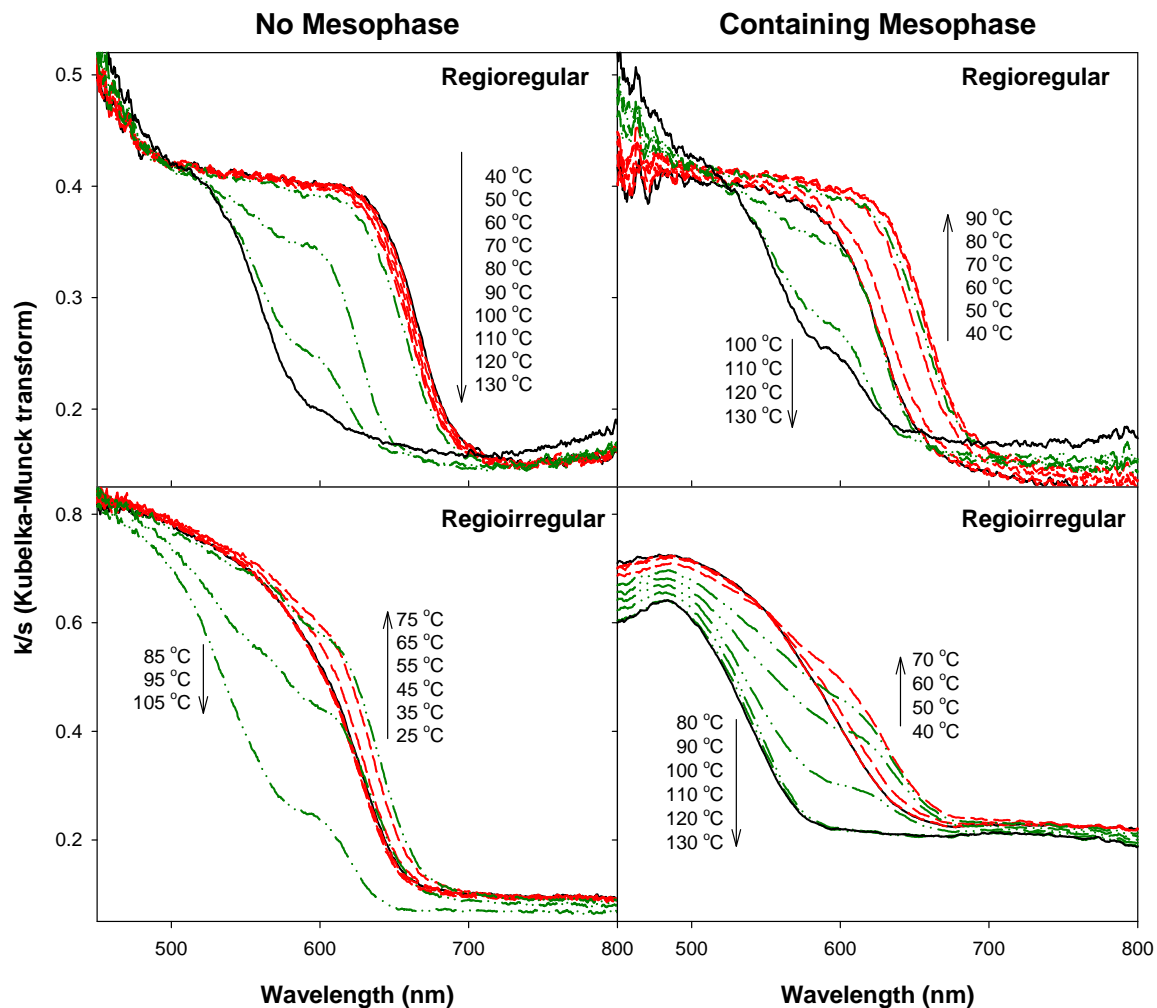


FIGURE 5. Kubelka-Munck transformed reflection spectra of RR (top) and RIR (bottom) samples. Spectra in black are the initial and final spectra collected for each sample. Spectra in red, dashed lines, are from room temperature to the temperature indicated by the increasing arrow, and spectra in green, dash-dotted lines, are from that temperature to the maximum temperature. Spectra on the left are samples that were slowly cooled and spectra on the right are samples that were rapidly cooled.

To assess the temperatures of the chromic changes the k/s values at 600 nm were monitored. This wavelength was selected because it showed the largest changes between high and low temperatures. Plots of the k/s values at 600 nm as a function of temperature are shown in Figure 6. For RR that is slowly cooled, therefore containing no mesophase, the data are fairly constant from room temperature to about 105 °C, a sharp drop occurs over about 15 °C, and then the data levels out again. Upon cooling, k/s returns to near the original room temperature value but there is a marked hysteresis in the temperature of the thermochromic transition. For rapidly cooled RR samples, the k/s values rise between 50 °C and 75 °C, maximize, and then sharply drop around 110 °C. Upon cooling, there is a single rise back to the maximum k/s value.

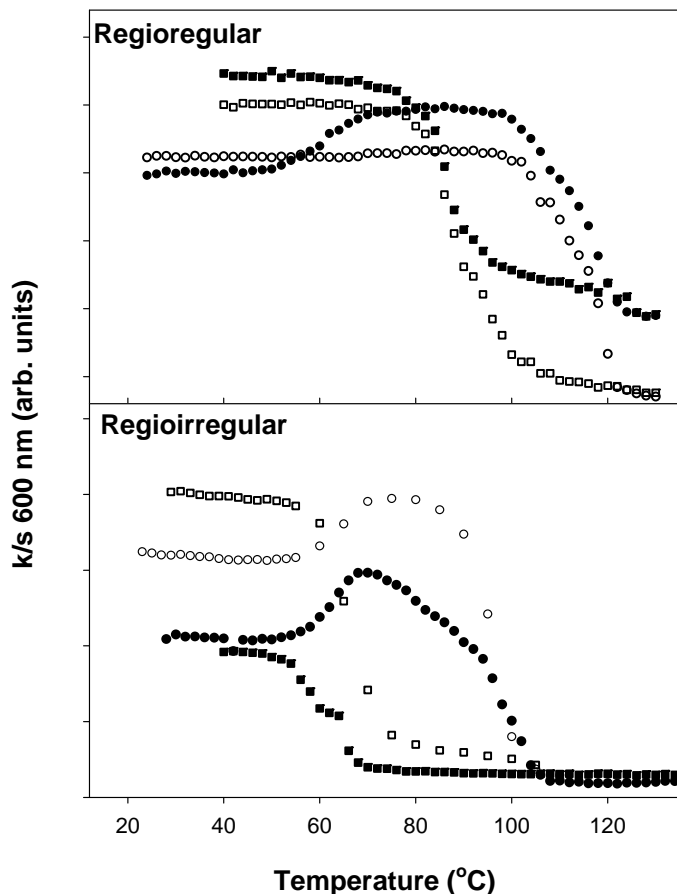


FIGURE 6. Plots of k/s at 600 nm vs. temperature. Top: RR. Bottom: RIR. Symbols: open circles, heating and no mesophase; open squares, cooling and no mesophase; filled circles, heating and containing mesophase.

RIR shows similar behavior with one exception: there is a slight rise between 50 and 70 °C in the slowly cooled sample, indicative of the presence of the mesophase. This is consistent with the DSC results where there is evidence of the mesophase in all samples.

To quantitatively determine the thermochromic transition temperatures from the spectral data an arbitrary sigmoidal function was used, as shown below:

$$(k/s) = y_0 + a/[1+\exp((T-T_0)/\Delta_T)]$$

where the center of the thermochromic transition is denoted by T_0 , the width of the transition is denoted by Δ_T , and y_0 and a are arbitrary parameters. We do not ascribe any particular physical interpretation of the functional form chosen; it merely represents a quantitative and reproducible

method for determining the thermochromic transition temperatures. All the data fit the functional form well with correlation coefficients $r^2 > 0.981$. The transition temperatures found using this technique are given in Table 1.

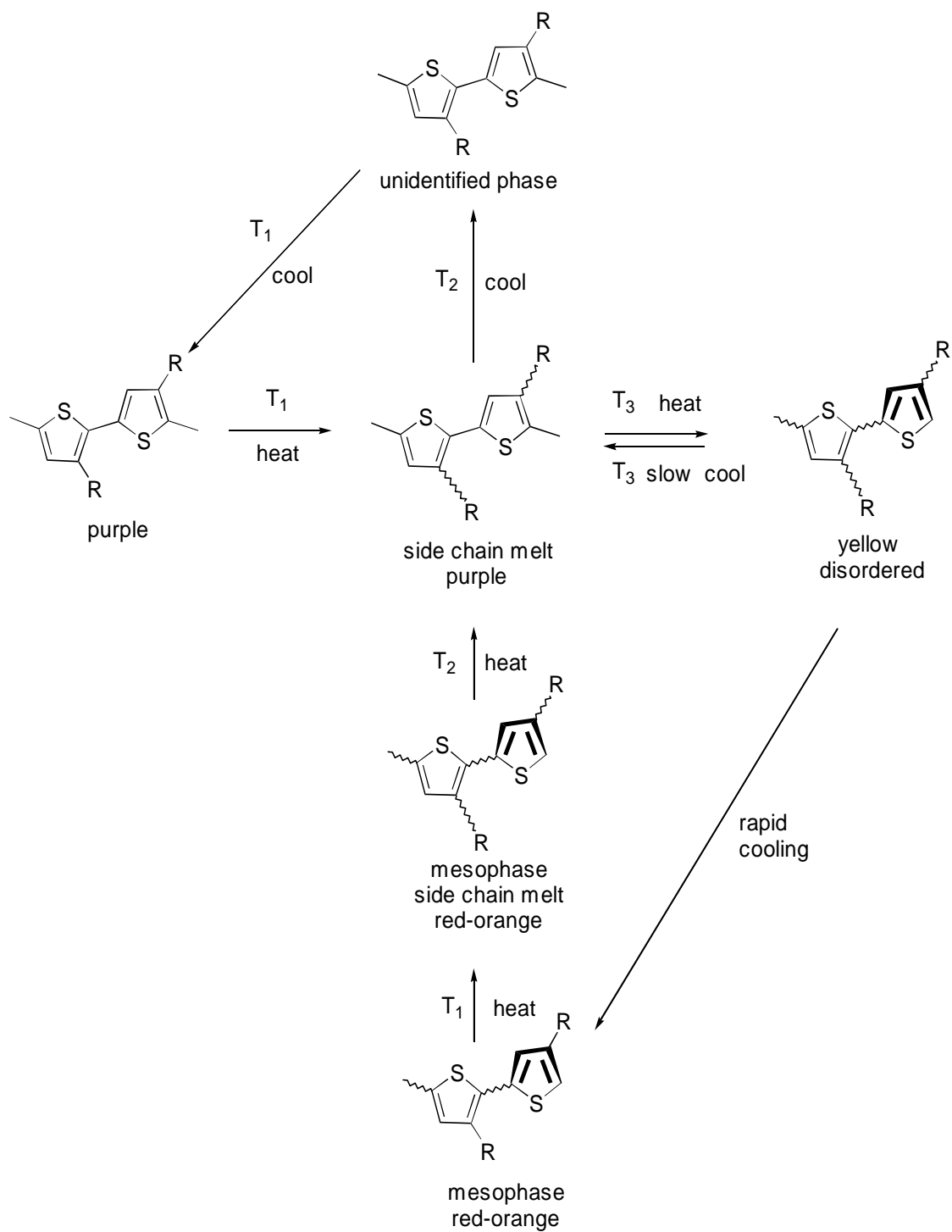
5. DISCUSSION

The reflection spectra of the different samples in the different phases are consistent with most previous reports.(17,18,26) At room temperature, in the slowly cooled samples, the regioregular form has a slightly smaller band gap (~1.8 eV) than the regioirregular form (~1.9 eV), indicating either a longer conjugation length or better three-dimensional dispersion. The high temperature forms have the same band gap for both RR and RIR, about 2.1 eV. For rapidly cooled samples, the room temperature band edges are about 0.1 eV higher in energy than the corresponding slowly cooled samples. The initial thermochromic change in rapidly cooled samples is a red shift giving spectra similar to the room temperature, slowly cooled samples. Thus, the spectroscopy indicates that the red-orange form created by rapid cooling initially changes back to the purple form upon heating, which then transforms to the yellow form at higher temperatures. The origins of the reflection spectra associated with the mesophases are ambiguous. The red-orange mesophase could be a mixture of the low temperature and high temperature forms or the spectrum could arise from an independent phase.

The assignment of the highest temperature endotherm in the DSC thermograms to the thermochromic transition is well supported by the correlation to the changes observed in the reflection spectra. For the regioirregular samples the correlation between the spectroscopically measured transition and the DSC peak is excellent while there is about a 10 °C difference in the regioregular samples. The differences between the two measuring methods can be attributed, at least in part, to the different heating rates (10 °C/min for DSC and 2 °C/min for spectroscopy). This is likely due to the difference in the kinetics of the transitions between and samples with different HT contents. The lowest temperature endotherm is assigned to the side chain melting. Upon cooling, the highest and lowest exotherms correspond to the freezing of the main chain and side chains, respectively. The only unidentified feature is the central exotherm in the cooling cycle. This may be the β -phase identified by Bolognesi, *et al.*(34) or phase II assigned by Prosa, *et al.*(30) The phase behavior for sample with no trapped mesophase is summarized in the top portion of Scheme 1.

For samples containing the trapped mesophase, the lower temperature chromic transition found in the heating cycle correlates reasonably well with the central DSC transition found in the initial

heating cycle. Since the mesophase is always found to some extent in the RIR samples, we postulate that the phase is associated with defect sites along the thiophene backbone. Defect sites are inherent for regio-irregular samples at either head-to-head or tail-to-tail linkages. Head-to-head sites will give substantial twisting between adjacent thiophene units because of steric repulsion. This type of geometry reduces the conjugation length and increases the band gap energy, as measured, and would be observed as a lighter color to the eye. Defect sites also could be formed during rapid cooling: at high temperatures the thiophene chain is completely disordered and the delocalization length is low, indicating twisting between thiophene rings at a high percentage of repeat units. During cooling, the rings replanarize but if the cooling is fast enough the polymer will increase viscosity to an extent that the geometric reorganization becomes too slow to occur. Under these conditions some of the twisted ring sites will remain, leading to a blue shift of the band edge. This hypothesis would also be consistent with a lower melting point for the trapped mesophase, which is observed. Thus, we assign the trapped mesophase to a structure that has the alkyl side chains immobile and ordered while the thiophene backbone contains a fair number of twist defects. With this assignment, interpretation of the DSC thermogram is as follows. The lowest temperature phase transition is still a side chain melt; the transition temperature for side chain melting should be largely independent of the thiophene chain structure for these long alkyl groups. Then, the increased mobility associated with the mobile side chains allows crystallites associated with twisted main chains to melt. This, in turn, allows the thiophene chain to replanarize at the lower temperature thermochromic transition, consistent with the red-shift found in the spectroscopic data. At this temperature all of the mesophase is gone so the sample then undergoes the normal thermochromic transition at the highest temperature. These conclusions are summarized in the lower half of Scheme 1.



SCHEME1. Proposed Mechanism for Novel Thermochromic Properties

6. CONCLUSION

This study has identified an unusual phase behavior in poly(3-docosylthiophene). For samples that are slowly cooled from the melt, the phase behavior is typical of poly(alkylthiophene)s: there is a low temperature endotherm associated with side chain melting and a high temperature endotherm assigned to main chain melting. A distinct thermochromic transition is observed at the higher temperature. In contrast, samples that have been rapidly cooled trap a mesophase that has three endothermic transitions and two thermochromic transitions upon heating. The new endotherm and the new thermochromic transition correlate and are assigned to a mesophase that consists of polymer chains that contain defect sites along the thiophene backbone. This conclusion is supported by the observation that regio-irregular polymers always contain a small amount of the mesophase while regioregular polymers can trap the mesophase only by rapid cooling. Future work to test this hypothesis will include temperature dependent x-ray diffraction, which will provide more structural details.

Understanding the phase behavior in polythiophenes is important because different processing conditions are used for different applications. While the trapping of the mesophase is obvious to the eye in poly(3-docosylthiophene), it is likely that similar behavior occurs in other poly(3-alkylthiophene)s, as well, albeit to a lesser extent. If trapping of defect-containing mesophases is universal to poly(3-alkylthiophene)s, this could have important consequences for materials properties, especially in optical applications such as light emitting diodes.

7. ACKNOWLEDGMENT

We acknowledge KM Scientific, the University of Rhode Island Transportation Center (funded by the U. S. Department of Transportation), the URI Foundation, and the URI Sensors and Surface Technology Partnership for financial support.

8. REFERENCES

1. Fichou, D., Ed.; *Handbook of Oligo- and Polythiophenes*, Wiley: New York, **1999**.
2. Brédas, J.-L.; Silbey, R., Ed.; *Conjugated Polymers: The Novel Science of Technology of Highly Conducting and Nonlinear Optically Active Materials*; Kluwer Academic Publishers: Dordrecht, **1991**.
3. Berggren, M.; Inganäs, O.; Gustafsson, G.; Anderson, M. R.; Hjertberg, T.; Wennerström, O.; *Synth. Met.*, **1995**, *71*, 2185-2186.
4. Osaka, T.; Komaba, S.; Fujihana, K.; Okamoto, N.; Momma, T.; Kaneko, N.; *J. Electrochem. Soc.*, **1997**, *144*, 742-748.
5. Granström, M.; Berggren, M.; Inganäs, O.; Andersson, M. R.; Hjertberg, T.; Wennerström, O.; *Synth. Met.*, **1997**, *85*, 1193-1194.
6. Ahn, S.-H.; Czae, M.; Kim, E.-R.; Lee, H.; Han, S.-H.; Noh, J.; Hara, M.; *Macromolecules*, **2001**, *34*, 2522-2527.
7. Endo, T.; Rikukawa, M.; Sanui, K.; *Synth. Met.*, **2001**, *119*, 191-192.
8. Bolognesi, A.; Giacometti Schieroni, A.; Botta, C.; Marinelli, M.; Mendichi, R.; Rolandi, R.; Relini, A.; Inganäs, O.; Theandher, M.; *Synth. Met.*, **2003**, *139*, 303-310.
9. Chen, T.-A.; Rieke, R. D.; *J. Am. Chem. Soc.*, **1992**, *114*, 10087-10088.
10. McCullough, R. D.; Williams, S. P.; *J. Am. Chem. Soc.*, **1993**, *115*, 11608-1169.
11. Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233-244.
12. Amou, S.; Haba, O.; Shirato, K.; Hayakawa, T.; Ueda, M.; Takeuchi, K.; Asai, M. *J. Poly. Sci. A: Poly. Chem.* **1999**, *37*, 1943-1948.
13. Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D.; *Adv. Mater.*, **1999**, *11*, 250-253.
14. Laird, D. W.; Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R.; *Polym. Prepr.*, **2001**, *42*, 556-557.
15. Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R.; *Macromolecules*, **2001**, *34*, 4324-4333.
16. Yamamoto, T.; *J. Organomet. Chem.*, **2002**, *653*, 195-199.
17. Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F.; *J. Polym. Sci.: Part B: Polym. Phys.*, **1987**, *25*, 1071-1078.
18. Roux, C.; Bergeron, J.-Y.; Leclerc, M.; *Makromol. Chem.*; **1993**, *194*, 869-877.
19. Roux, C.; Leclerc, M.; *Chem. Mater.*, **1994**, *6*, 620-624.
20. Faïd, K.; Fréchet, M.; Ranger, M.; Mazerolle, L.; Lévesque, I.; Leclerc, M.; Chen, T.-A.; Rieke, R. D.; *Chem. Mater.*, **1995**, *7*, 1390-1396.

21. DiCésare, N.; Belletête, M.; Durocher, G.; Leclerc, M.; *Chem. Phys. Lett.*, **1997**, *275*, 533-539.
22. DiCésare, N.; Belletête, M.; Leclerc, M.; Durocher, G.; *Chem. Phys. Lett.*, **1998**, *291*, 487-495.
23. DiCésare, N.; Belletête, M.; Marrano, C.; Leclerc, M.; Durocher, G.; *J. Phys. Chem. A*, **1999**, *103*, 795-802.
24. DiCésare, N.; Belletête, M.; Garcia, E. R.; Leclerc, M.; Durocher, G.; *J. Phys. Chem. A*, **1999**, *103*, 3864-3875.
25. Garreau, S.; Leclerc, M.; Errien, N.; Louarn, G.; *Macromolecules*, **2003**, *36*, 692-697.
26. Yang, C.; Orfino, F. P.; Holdcroft, S.; *Macromolecules*, **1996**, *29*, 6510-6517.
27. Yang, C.; Holdcroft, S.; *Synth. Met.*, **1997**, *84*, 563-564.
28. Hsu, W.-P.; Kevon, K.; Ho, K.-S.; Myerson, A. S.; Kwei, T. K.; *Macromolecules*, **1993**, *26*, 1318-1323.
29. Park, K. C.; Levon, K.; *Macromolecules*, **1997**, *30*, 3175-3183.
30. T. J. Prosa, M. J. Winokur, R. D. McCullough, *Macromolecules*, **1996**, *29*, 3654-3656.
31. Xie, H.; Corish, J.; Morton-Blake, D. A.; *Synth. Met.*, **2000**, *113*, 65-72.
32. Xie, H.; O'Dwyer, S.; Corish, J.; Morton-Blake, D. A.; *Synth. Met.*, **2001**, *122*, 287-296.
33. O'Dwyer, S.; Xie, H.; Corish, J.; Morton-Blake, D. A.; *J. Phys.: Condens. Matter*, **2001**, *13*, 2395-2410.
34. Bolognesi, A.; Porzio, W.; Provasoli, F.; Ezquerra, T.; *Makromol. Chem.*, **1993**, *194*, 817-827.
35. Tachibana, H.; Hosaka, N.; Tokura, Y.; *Macromolecules*, **2001**, *34*, 1823-1827.