On the structural origins of solid-state urethane polydiacetylene thermochromism: thermal and structural properties of IPUDO monomer and polymer

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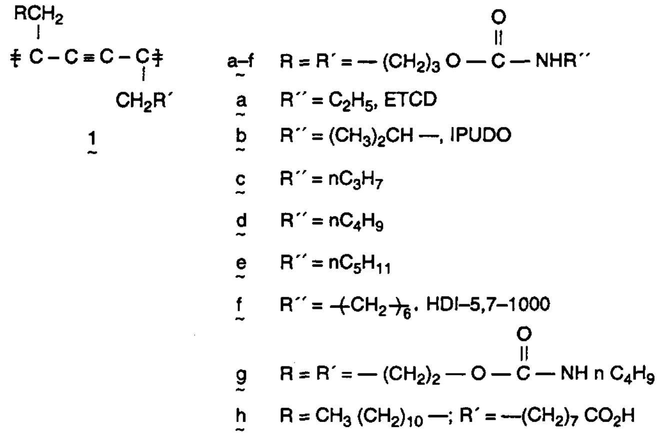
Calorimetric studies of the diacetylene monomer bis-isopropylurethane of 5,7-dodecadiyn-1,12-diol, synthesized by a new method, and the polydiacetylene (PDA) from this monomer (PDA-IPUDO) rule out the possibility that monomer melting plays a significant role in the thermochromic phase transition of this polymer. X-ray powder diffraction studies at room temperature and 150 ± 5°C reveal that the structural changes which occur in the course of the endothermic thermochromic phase transition are analogous to those of a related PDA.

(Keywords: polydiacetylene; thermochromic transition; thermal analysis; X-ray diffraction)

While solid-state thermochromism has been observed in polydiacetylenes (PDA, **1**, see *Scheme 1*) with various side chain substitution patterns and in other classes of polymers as well[1,2], the study of thermochromism in the urethane-substituted PDA ETCD (**1a**) and IPUDO (**1b**) is particularly important because of the high degree of compositional and crystallographic definition attained in these systems. As these PDAs are heated to temperatures above 120°C, structural changes take place, and the electronic spectrum shifts to higher energy. From X-ray diffraction studies of poly(ETCD)[3,4], the unit cell volume expands by ~3.7% on heating from room temperature to 135°C, a temperature above the thermochromic transition. Thermal mechanical analysis[5] of poly(ETCD) fibres indicates abrupt elongation at the thermochromic phase transition. Additionally, the X-ray studies[3,4] revealed a chain direction lattice constant in the range 4.8–4.9 Å both at room temperature and above the thermochromic transition. This observation indicates that the conjugated chain does not undergo a significant planar–non-planar transition in the course of the thermochromic transition, as suggested earlier[6]. *FT*i.r. studies[7] revealed that the hydrogen bonding in poly(ETCD) is preserved on heating to temperatures above the thermochromic transition, but below the polymer melting point of 223°C. The possibility that thermochromism in poly(ETCD) involves a change in backbone bond representation from acetylenic to butatrienic[8] was ruled out by theoretical studies[9] and by ^{13}C CP/MAS n.m.r. studies[10], as the latter revealed the usual acetylenic bonding above and below the thermochromic transition. Changes in the conformer populations of the side chain methylene groups are revealed in both *FT*i.r.[7] and ^{13}C CP/MAS n.m.r.[10,11] studies, and the possible involvement of mechanical strains on the backbone related to thermochromism has been discussed[1,5,11].



Scheme 1

Another possible aspect of PDA solid-state thermochromism is revealed in *Table 1*. For the examples in *Table 1;* which include urethanes as well as other types of side groups, the temperature of the thermochromic phase transition is close to that of the monomer melting point or other monomer phase transition[12]. A priori, the melting of unpolymerized monomer in a PDA sample would lead to a volume expansion which might modify a mechanical strain and conceivably could be responsible for many of the experimental observations associated with thermochromism. For the thermochromic poly(3-alkylthiophene)s, we note that the thermochromic phase transitions occur roughly in the same temperature region where melting occurs[13]. Since polymerization of ETCD does not proceed to completion[14], we chose to perform the experiments herein with crystals of the related poly(IPUDO) which are reported[15] to contain >99% polymer.

In view of the known side reactions which occur when urethane-substituted diacetylenes are synthesized by reaction of a diol with isocyanates[16], we have synthesized IPUDO monomer by the previously reported[16] method

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Table 1 Monomer melting points and thermochromic phase transition temperatures of assorted PDA materials

PDA	Monomer m.p. (°C)	Thermochromic phase transition temperature (°C)
1a	121[a]	120[b]
1b	138[c]	133[d]
1c	123[e]	127[e]
1d	117[e]	115[e]
1e	115[e]	137[e]
1f	112[f]	110[g]
1g	106[e]	127[e]
1h	61[h], 62.3[i]	60[i]
Phosphatidylcholine PDA	64[j]	>50[j]
A lipid bilayer PDA	35, 85[k]	<50[k]

[a] Ref. 14
[b] Ref. 8
[c] Ref. 15
[d] Ref. 5
[e] Ref. 21
[f] Ref. 22
[g] Ref. 23
[h] Ref. 24
[i] Ref. 25
[j] Ref. 26
[k] Ref. 27. This monomer exhibits thermotropic liquid crystalline behaviour

as follows:

$HC{\equiv}C{-}(CH_2)_4{-}OH + (CH_3)_2CH{-}NCO$
$\rightarrow HC{\equiv}C{-}(CH_2)_4{-}O(CO)NH{-}CH(CH_3)_2$
↓
IPUDO monomer

5-Hexyn-1-ol and 2-isocyanatopropane react exothermically to give the desired monoacetylene (b.p. 78–80°C at 10 μm) with an i.r. triple bond stretching frequency of 2120 cm^{-1}. The monoacetylene was oxidatively coupled in acetone solution at room temperature for 4 h. Crystallization of the product from ethyl acetate gave IPUDO monomer in 45–50% yield (m.p. 138–139°C) in agreement with a previous report[15]. IPUDO monomer exhibited the expected molecular ion in its mass spectrum at *m/e* 364 and was polymerized with ^{60}Co γ radiation (at least 50 Mrad during 42 days). Soxhlet extraction of the polymer crystals with ethyl acetate resulted in no measurable weight loss. The ambient temperature X-ray powder diffraction pattern of the polymer crystals was consistent with the reported[15] crystallographic data.

To further establish the relationship between poly(ETCD) and poly(IPUDO), we carried out X-ray diffraction studies of the latter material as a function of temperature. From the powder data at 25°C, $a = 10.70$ Å, $b = 4.89$ Å and $c = 38.98$ Å, in agreement with a previous report[15]. At 150°C, the observed lattice constants are $a = 11.05$ Å, $b = 4.89$ Å and $c = 39.27$ Å. *Figure 1* exhibits primarily the [0 0 l], $l = 2, 4, 6$ reflections at 25 and 150 ± 5°C; note that all reflections move to smaller angle as the temperature increases, indicating unit cell expansion. The powder pattern at 100°C is very similar to the 25°C data, and cooling of a sample from 150 to 25°C gives an unchanged room temperature pattern. Hence, the crystallographic data for poly(ETCD)[3,4] and poly(IPUDO) as a function of temperature are similar.

From d.s.c., the heat of fusion for IPUDO *monomer* is 140.4 J g^{-1}. D.s.c. and thermogravimetry of poly(IPUDO) are displayed in *Figure 2*. From *Figure 2*, the heat of the initial scan of the thermochromic phase transition is 21.9 J g^{-1}. Thermogravimetry reveals that there is no detectable weight loss in this polymer below the melting point near 220°C. If all of the heat associated with the thermochromic phase transition was associated with monomer melting, it would be associated with the presence of ~15% monomer, an amount which is most definitely not present. The presence of trace monomer in a material such as poly(IPUDO) cannot be rigorously excluded. The observed heat of the endothermic thermochromic transition represents an upper limit, since some contribution to this heat from traces of monomer is possible. The heat of the thermochromic transition for poly(IPUDO) is close to that reported[17] for the related **1c**.

While it has long been recognized that thermochromism in urethane-substituted PDA is not strictly reversible[18], it is often discussed as a reversible phenomenon[17]. When samples of poly(ETCD) are heated and cooled between 25°C and 160°C for 10 cycles, the temperature of the endothermic phase transition decreases by ~20°C and the shape of the transition broadens, consistent with an earlier[18] report. As shown in *Figure 3*, heating of poly(IPUDO) in the same manner causes similar, but somewhat less drastic, changes. The first endotherm is observed at 143°C and the tenth at 129°C, a 14°C difference. All of the endotherms subsequent to the first are broader and of less intensity than that first transition. After 30 heating cycles, the transition has shifted to 125°C. Results analogous to those shown in *Figure 3* have been previously mentioned[5], but only in qualitative terms. The hysteresis observed in the d.s.c. study of poly(IPUDO) is also found in Raman spectra[19]. For the d.s.c. experiments, change in heating rate from 5 to 0.5°C min^{-1} did not have a significant effect on the transition.

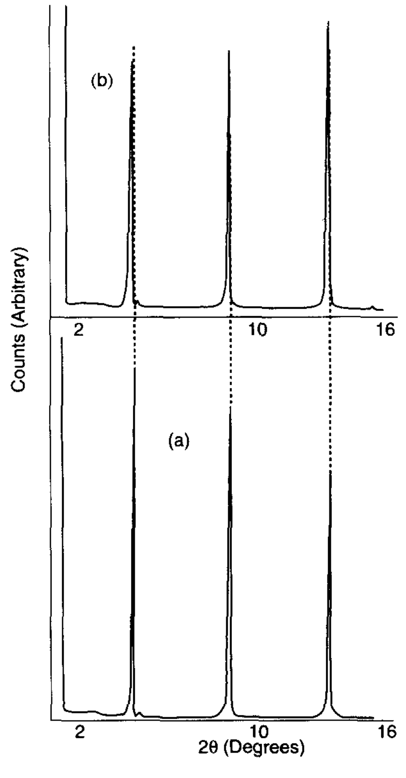

Figure 1 X-ray powder diffractogram revealing primarily the [0 0 l], $l = 2, 4, 6$ reflections of poly(IPUDO) at (a) 25°C and (b) 150 ± 5°C. The vertical broken line is for a visual guide only

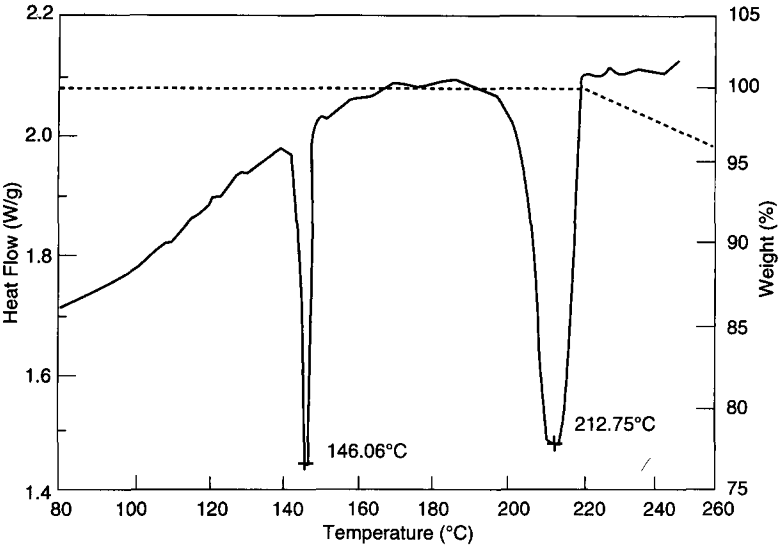

Figure 2 D.s.c. thermogram (——) for a previously untreated sample of poly(IPUDO) (0.932 mg) obtained from 80 to 160°C at 5°C min^{-1} under 40 cm^3 min^{-1} argon purge. Thermogravimetric thermogram (– – –) for poly(IPUDO) obtained from 20 to 300°C at 10°C min^{-1} under 100 cm^3 min^{-1} argon purge. The differential scanning calorimeter and thermogravimetric analyser are DuPont (now TA Instruments) 2910 and 2950 modules, respectively, with a 2100 controller

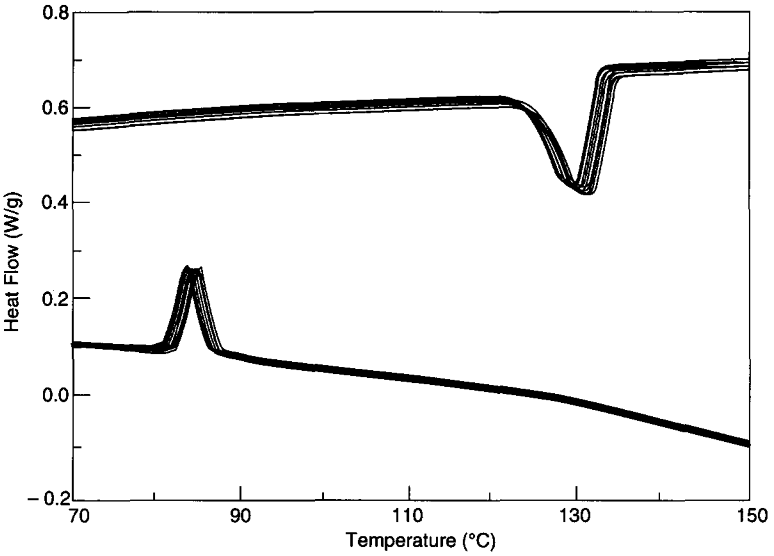

Figure 3 D.s.c. thermogram obtained for 10 heat/cool cycles of a previously heat-treated sample of poly(IPUDO). The furnace was programmed from 20 to 160°C at 0.5°C min^{-1} under 40 cm^3 min^{-1} argon purge

In summary, our thermal and crystallographic studies reveal that thermochromism in poly(IPUDO) is generally analogous to that in poly(ETCD). More specifically, these studies rigorously rule out the possibility that monomer melting plays a significant role in the phase transition. Increased conformational freedom in the $(CH_2)_4$ side groups is the most likely structural change which occurs in the course of the thermochromic transition. The details of these changes would be best observed in high precision crystal structures of an appropriate urethane-PDA at temperatures above and below the transition[20]. The question of whether thermochromism is a single chain phenomenon or if a larger domain is required remains open.

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