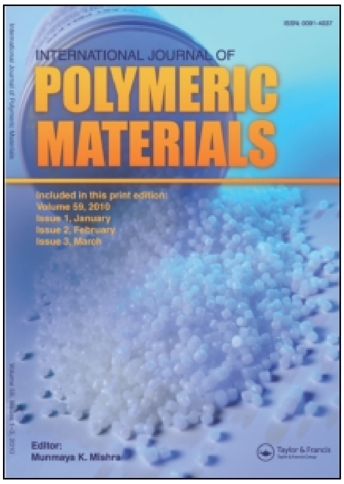


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polydiacetylenes Produced from the Liquid Crystal State

C. Campbell[a]; G. H. Milburn[a]; A. J. Shand[a]; A. R. Werninck[a]; J. Wright[a]
[a] Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh, Scotland

To cite this Article Campbell, C. , Milburn, G. H. , Shand, A. J. , Werninck, A. R. and Wright, J.(1993) 'Polydiacetylenes Produced from the Liquid Crystal State', International Journal of Polymeric Materials, 22: 1, 85 — 90

To link to this Article: DOI: 10.1080/00914039308012061

URL: http://dx.doi.org/10.1080/00914039308012061

Intern. J. Polymeric Mater., 1993, Vol. 22, pp. 85–90
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Polydiacetylenes Produced from the Liquid Crystal State

C. CAMPBELL, G. H. MILBURN, A. J. SHAND, A. R. WERNINCK, and J. WRIGHT

Department of Applied Chemical and Physical Sciences, Napier University, 10 Colinton Road, Edinburgh EH10 5DT, Scotland

The preparation and characterization by standard methods of eleven diphenyldiacetylenes is discussed. All of these materials are liquid crystalline with phase transitions ranging from 90°C to 205°C. The liquid crystal behavior is studied using differential scanning calorimetry and polarized light microscopy. All the materials undergo irreversible polymerization from a liquid crystal state, possibly nematic, at over 210°C. The polymers are red and glassy. Some monomers give promising nonlinear optical results, the polymers are currently being tested. Both monomers and polymers are currently being tested in guest-host systems.

KEY WORDS Diphenyldiacetylene, polydiacetylene, liquid crystal, nonlinear optics, conjugated diacetylene, unsymmetrical diacetylene.

INTRODUCTION

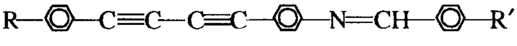
Serious interest in diacetylenes (dienes) and polydiacetylenes (polydienes) commenced with work by Wegner and co-workers in 1971.[1] The solid state polymerization therein utilized dienes with side chains containing flexible spacers next to the diene unit. Dienes and their polymers are of particular interest in studies in nonlinear optics partly because of substantial conjugation in the polymer chain.[2] However, solid state polymerization occurs with relatively few dienes which have particular crystal structures[3] and suitable levels of conjugation may well be obtained by utilizing dienes with side chains directly conjugated to the main chain and resulting in the formation of oligomers rather than high polymers which in any case are often intractable.[4,5] Dienes with conjugated side chains do not tend to polymerize in the solid state though efforts to achieve this have been made.[6] For third order nonlinear optical effects (see Equation (1)) to be manifested formation of high polymer is not necessary as conjugation does not require to be so extensive.

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l, \tag{1}$$

where P_i is a nonlinear polarization, E_j, E_k, E_l are electric intensity components, $\chi^{(n)}$ is n-th order nonlinearity coefficient.

The crystal structure of the material does not need to be noncentrosymmetric as is the case for second order nonlinear materials. However, for maximum values of $\chi^{(3)}$ some orientation is necessary[2] and our group has thus concentrated on producing liquid crystalline dienes with conjugated side chains.[7] Investigations into the polymerization of these materials both in the liquid crystalline state and in the isotropic liquid state has been pursued.[8] The optical clarity of the glassy polymers formed in the isotropic liquid state renders them suitable for nonlinear applications.[9] Currently our concern is with producing dienes and polydienes with good nonlinear optical properties, with lowering the transition temperatures of the phase changes and with investigating the nature of the polymer formed from the liquid crystalline phases.

This paper therefore reports recent work on dienes of the general structure:

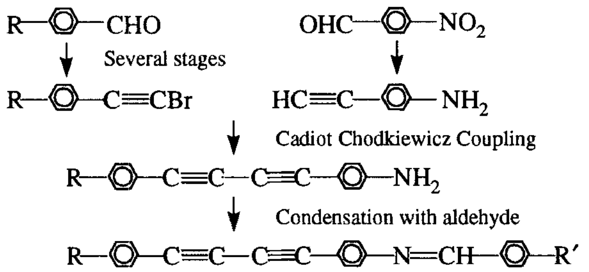


where R = CF_3, H, $PhCH_2O$ and R′ = OC_nH_{2n+1} (n = 3–10, 12).

RESULTS AND DISCUSSION

The general synthesis of these families of compounds is shown in Scheme 1. It is described more fully in a previous paper.[7]

Scheme 1



The structures of all materials produced were confirmed by the standard methods of elemental analysis, infrared and ultraviolet spectroscopy and by nuclear magnetic resonance. Liquid crystal studies were performed by differential scanning calorimetry (DSC) (Perkin–Elmer DSC7) and polarized light microscopy (Nikon Optiphot Pol). Thermogravimetric (TG) analysis (Stanton Redcroft STA780) was also utilized to determine the temperatures at which degradation occurs. A typical DSC plot is shown in Figure 1. Information from plots such as these was used to compile the data in Tables I, II, and III and in Figure 2.

The DSC studies shown in Table I and microscopy studies of different phases as revealed on the DSC traces showed that compounds with R = CF_3 and R′ = OC_nH_{2n+1} all displayed smectic phases. There is general trend to phase transitions at lower temperatures with increasing values of n. The photomicrograph (Figure 3) shows the focal conic texture typical of smectic phases. A more detailed analysis of the results indicates that the transitions for $n \leq 8$ are:

$$K \rightarrow S_A \rightarrow N \rightarrow \text{Polymer},$$

whereas for $n \geq 10$,

$$K \rightarrow S_B \rightarrow S_A \rightarrow N \rightarrow \text{Polymer}.$$

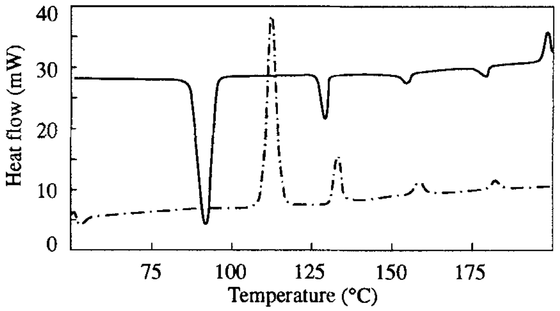


FIGURE 1 DSC heating/cooling cycle for R = H, R′ = $OC_{12}H_{25}$. Sample weight is 5.9 mg, heating velocity is 20°C min^{-1}.

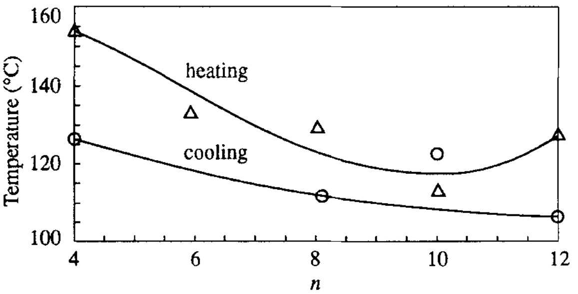


FIGURE 2 Onset heating/cooling temperatures for the main melting/crystallization peak for R = 4-$PhCH_2O$ and R′ = OC_nH_{2n+1}.

TABLE I
R = CF_3, R′ = OC_nH_{2n+1}

	Heating		Cooling	
n	Peak onset (°C)	Δ H (kJ mol^{-1})	Peak onset (°C)	Δ H (kJ mol^{-1})
3	152.1	16.6	161.0	− 11.4
5	117.0	14.9	154.0	− 2.63
	152.0	2.29	71.0	− 3.70
6	142.0	3.10	162.9	− 3.33
	113.0		154.5	
8	90.7	13.3	143.5	− 1.88
	107.0	2.38		
	144.0	3.36		
9	91.0	24.0	145.5	− 3.09
	147.0	3.86		
10	105.0	29.5	146.0	− 3.38
	144.0	4.02		
12	95.0	22.1	146.0	− 2.61
	142.0			

The compounds R = H and R′ = OC_nH_{2n+1} for some of which the DSC results are shown in Table II were further examined by DSC using a series of heating and cooling cycles with each compound; the results for n = 12 are shown in Table III.

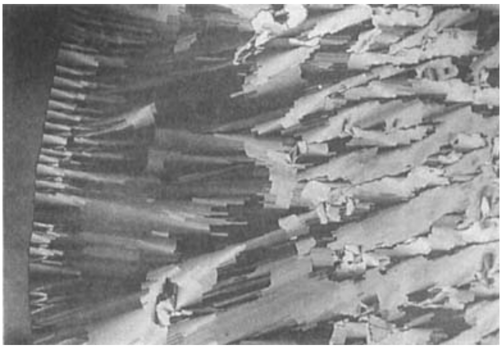


FIGURE 3 Photomicrograph showing smectic character.

TABLE II
$R = H, R' = OC_nH_{2n+1}$

n	Heating: Peak onset (°C)	Heating: Δ H (kJ mol^{-1})	Cooling: Peak onset (°C)	Cooling: Δ H (kJ mol^{-1})
8	109.5	1.40	127.0	− 2.14
	133.0	32.1	120.0	− 18.6
	147.0	0.91	101.0	− 0.74
	202.0	1.02		
9	116.0	32.3	125.5	− 2.47
	130.0	4.51	103.0	− 24.8
	151.0	1.15		
	195.0	1.08		
10	91.0	1.27	121.0	− 2.23
	116.0	25.9	92.0	− 19.3
	125.0	2.96		
	145.0	1.37		
	189.0	0.95		
12	95.0	1.73	150.0	− 0.64
	111.0	31.1	129.5	− 3.06
	132.0	5.06	96.5	− 23.6
	157.0	1.68		
	180.0	1.23		

TABLE III
Values of onset temperature (°C) and of ΔH (kJ mol^{-1}) for $R = H, R' = OC_{12}H_{25}$

	Cycle number											
	1H		1C		2H		2C		3H		3C	
Peak number	OT	ΔH	OT	ΔH	OT	ΔH	OT	ΔH	OT	ΔH	OT	ΔH
1	111	31.0	96	− 29.0	111	−29.0	96	− 29.0	110	29.0	96	− 29.0
2	134	5.0	132	− 4.7	132	4.8	132	− 4.5	132	4.7	131	− 4.4
3	159	1.9	159	− 1.7	158	1.6	159	− 1.6	156	1.3	157	− 1.0
4	182	1.4	182	− 1.1	182	1.1	182	− 1.1	181	0.9	181	− 0.8

Here OT, H, and C denote the onset temperature, heating, and cooling, respectively.

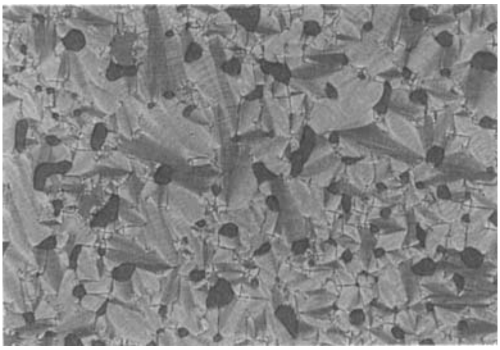


FIGURE 4 Photomicrograph showing $S_A \leftrightarrow S_B$ effects.

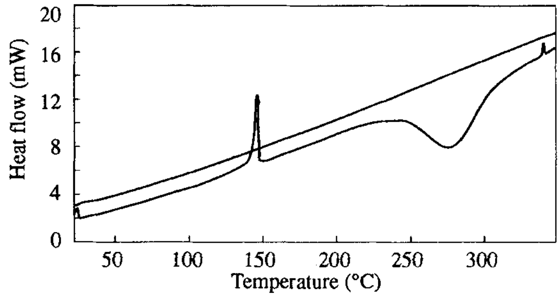


FIGURE 5 DSC illustrating irreversible polymerization.

The behavior of this compound on heating is similar to the other higher members of this family and is of more interest than that of lower ones. The consistency of the results shown over three cycles of heating and cooling is striking. This consistency held for four or more cycles also. Microscopy studies taken with these results again show the possible sequence of changes on heating to be

$$K \rightarrow S_B \rightarrow S_A \rightarrow N \rightarrow \text{Polymer}.$$

The appearance of bars across focal conics in photomicrographs is considered by Gray and Goodby[10] to be a consequence of S_B to S_A transitions. An example of this is shown in Figure 4.

The general downward trend in transition temperatures is shown in Figure 2 for the family of compounds with the structure R = $PhCH_2O$ and $R' = OC_nH_{2n+1}$. Detailed DSC studies were performed on the family member with $n = 12$ and again revealed consistency over all the cycles. Microscopy studies on this family of compounds showed that all are liquid crystalline though this is not evident from DSC studies alone.

The specific compound mentioned above showed more complex behavior on heating than other members of the family. The tentative conclusion to date for this compound is that the sequence of melting behavior is:

$$K \rightarrow S_? \rightarrow S_F \rightarrow S_C \rightarrow N \rightarrow \text{Polymer}.$$

In all the materials described above, polymerization seems to occur from the nematic liquid crystal state and the polymers formed have a red and glassy appearance. This is similar

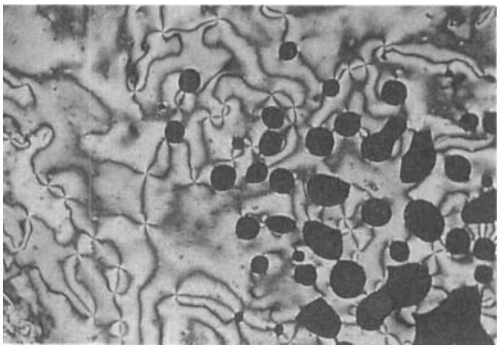


FIGURE 6 Photomicrograph showing red polymer forming in a liquid crystal phase.

to results discussed in the work of Schen.[9] The polymerization peak on the DSC trace is shown in Figure 5 and a photomicrograph showing red polymer forming from a liquid crystal phase in Figure 6. The polymer itself is clearly not liquid crystalline.

This work is being extended to other conjugated diene families and studies of the nonlinear optical properties of monomers, polymers and guest-host systems based on these will be reported shortly.

References

1. G. Wegner, *Makromol. Chem.*, **145,** 85 (1971).
   G. Wegner, *Makromol. Chem.*, **154,** 35 (1972).
2. P. N. Prasad, *Polymer,* **32,** 1746 (1991).
3. D. Bloor, *Mol. Cryst. Liq. Cryst.*, **93,** 183 (1983).
4. S. Okada, M. Ohsugi, A. Masaki, H. Matsuda, S. Takanagi, and H. Nakanishi, *Mol. Cryst. Liq. Cryst.*, **183,** 81 (1990).
5. J. Tsibouklis, A. R. Werninck, A. J. Shand, and G. H. W. Milburn, *Chemotronics,* **3,** 211 (1988).
6. H. Matsuda, H. Nakanishi, N. Minami, and M. Kato, *Mol. Cryst. Liq. Cryst.*, **160,** 241 (1988).
7. G. H. W. Milburn, C. Campbell, A. J. Shand, and A. R. Werninck, *Liquid Crystals,* **8,** 623 (1990).
8. J. Tsibouklis, C. Campbell, A. R. Werninck, A. J. Shand, and G. H. W. Milburn, *Polym. Bull.*, in press.
9. M. A. Schen, K. Kotowski, and J. Cline, *Polymer,* **32,** 1843 (1991).
10. G. W. Gray and J. W. G. Goodby, *Smectic Liquid Crystals: Textures and Structures,* (Leonard Hill, Glasgow, 1984).