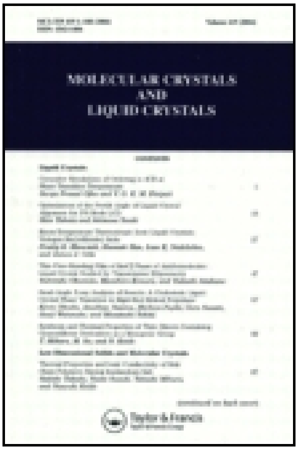

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Mesomorphic Properties of Copolymers Containing Diacetylenic and Siloxane Units in the Flexible Spacers

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Copolymers containing bis-carboxypropyltetramethyl disiloxane, 10,12-docosadiyne-1,22 dioic acid and various mesogenic diols were synthesized and investigated. Particular attention was paid to the system containing the biphenyl mesogen. Interestingly most of the copolymers displayed crystallinity at room temperature in spite of large differences in the structure and length of the repeating unit. In some cases smectic mesophases of higher order were displayed. The copolymer system containing the biphenyl mesogen displays at low compositions of diacetylenic spacer (high compositions of tetramethyldisiloxane spacer) a smectic mesophase of lower order (S_A or S_C) while at higher compositions of diacetylenic spacer high order smectics (S_H) were displayed. No nematic mesophases were found.

INTRODUCTION

In the preceding paper we have reported the synthesis of homopolymers and model dimeric compounds based on bis-carboxypropyltetramethyldisiloxane spacer.[1] Here we report the results of the synthesis and study of copolymers containing disiloxane and diacetylenic moieties.

The rationale for synthesis of copolymers containing siloxane and diacetylene units in the flexible spacer of a liquid crystalline main chain thermotropic polyester is to obtain liquid crystalline diacetylenic compounds with mesophase transition temperatures low enough to prevent the diacetylenic bond from spontaneously reacting in the liquid crystalline mesophase. In addition such polymer systems are of interest because of the possibility of introducing potential for lateral reinforcement via crosslinking through diacetylene bonds. Last but not least, it is interesting to explore copolymers of structurally differing flexible moieties such as those containing incorporated siloxane and diacetylenic bonds.

In the preceding paper we have studied siloxane containing homopolymers and model-dimeric compounds.[1] We have also previously studied homopolymers con-

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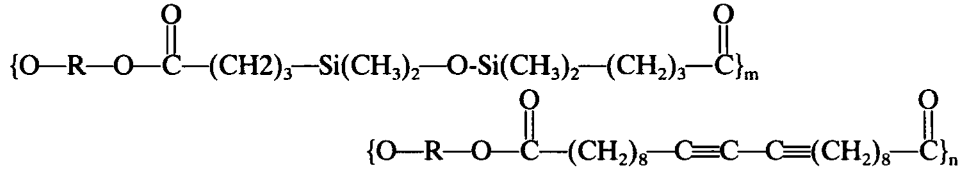
taining a diacetylenic spacer: 10,12-docosadiyne-1,22-dioic acid.[2] Out of five different diacetylenic polyesters synthesized by us, only two (one containing a biphenyl, the other an α-Methyl stilbene mesogenic moiety) have shown a liquid crystalline phase which was characterized as a smectic mesophase of higher order consistent with a smectic H assignment. All homopolymers were strongly crystalline.[2]

For the present study, the following copolymers were synthesized:

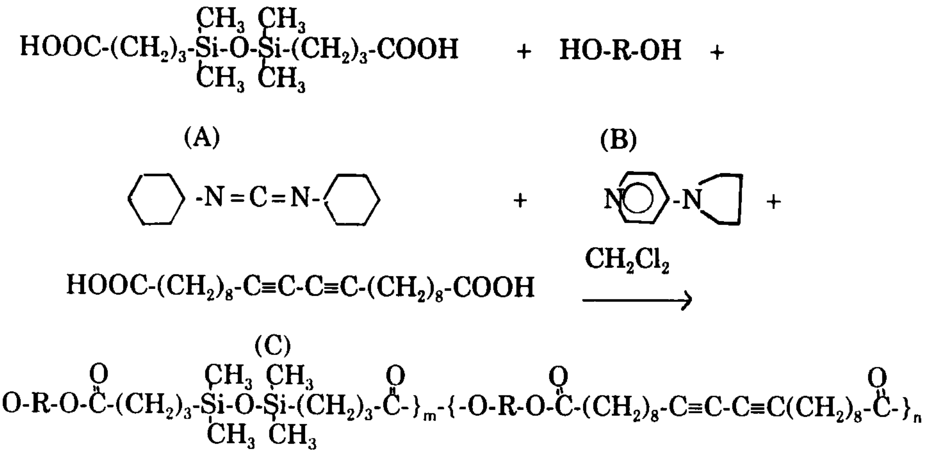


$$\{O-R-O-\overset{O}{\overset{\|}{C}}-(CH2)_3-Si(CH_3)_2-O\text{-}Si(CH_3)_2-(CH_2)_3-\overset{O}{\overset{\|}{C}}\}_m \quad \{O-R-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-C\equiv C-C\equiv(CH_2)_8-\overset{O}{\overset{\|}{C}}\}_n$$

with R representing the mesogen. Most systems reported here were studied for m/n = 1. In addition copolymer with R: biphenyl was studied for various m/n compositions.

EXPERIMENTAL

The copolymers were synthesized following the general scheme:



$$-\{-O\text{-}R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}(CH_2)_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\}_m\text{-}\{\text{-}O\text{-}R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_8\text{-}C\equiv C\text{-}C\equiv C(CH_2)_8\text{-}\overset{O}{\overset{\|}{C}}\text{-}\}_n$$

Bis-carboxypropyltetramethyldisiloxane (A) Farchan Labs) was purchased and recrystallized from ethanol-water mixture. The 4,4′-dihydroxy- 2,2′-dimethylazoxybenzene[3,4] and the 4,4′-dihydroxyphenylbenzoate,[5] 1,4-bishydroxyhexylbenzoate[6] were prepared according to the references given above. 10,12-Docosadiyne-1,22 dioic acid (C) was synthesized according to the procedure given in Reference 2.

Synthesis of copolymers

For the synthesis of copolymers with n/m = 50/50, 0.0025 mole of 1,3-bis(3-carboxypropyl) tetramethyldisiloxane, 0.005 mole of mesogenic diol, 0.0025 mole of

10,12-docosadiyne-1,22 dioic acid, 0.01 mole of *N,N'*-dicyclohexylcarbodiimide and 0.001 mole of *N*-pyrrolidino-4-pyridine were mixed in 30 ml dry dichloromethane for five days at room temperature. The white precipitate of *N,N'*-dicyclohexylurea was filtered. The filtrate was washed successively with water, 5% acetic acid, water and dried over anhydrous magnesium sulfate. The copolymer was precipitated in methanol. The feed ratio n/m of compound (A) and (C) was 1/1 with the exception of copolymer I_c (see Table I) for which the proportions were varied from 0/1 to 1/0 while the total was kept in correct stoichiometry with the mesogenic diol (B).

The polymeric products were purified by dissolving the sample in chloroform and adding ethanol dropwise until the appearance of turbidity. The cloudy solution was left to stand overnight and the precipitate formed was filtered off to remove oligomers and low molecular mass products. Column chromatography, using Woelm SiO_2 and chloroform as eluent was also used to purify the polymeric products from low molecular contaminants. Combination of both purification techniques gave the best results. The effectiveness of the purification process is illustrated in Figure 1 which shows GPC chromatograms of copolymers I_c of various compositions after extensive purification. Most samples display a, relatively narrow peak suggesting a homogeneous compositional distribution of the copolymer.

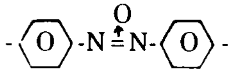
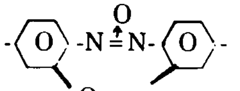
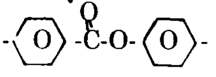
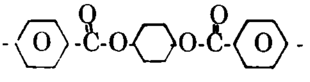
Standard characterization of copolymers included gel permeation chromatography, elemental analysis, DSC and X-ray scattering. Reduced viscosities η_{red} were

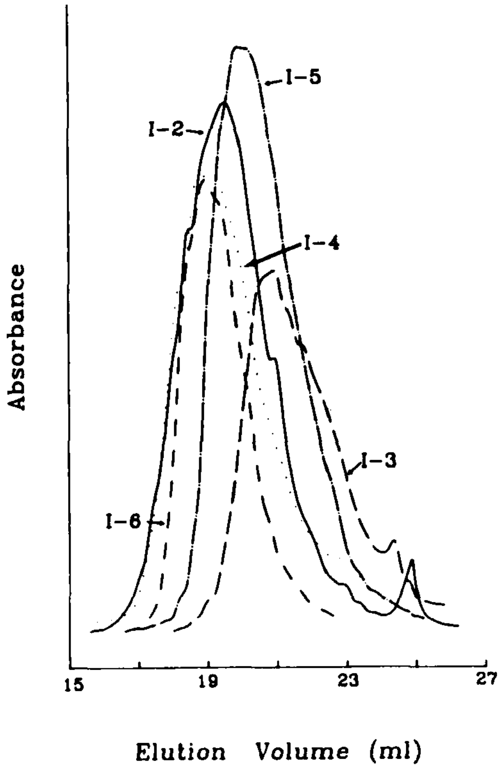
TABLE I

Elemental Analysis of Copolymers (50/50)

$$\text{-\{-O-R-O-CO-(CH}_2)_3\text{-Si(CH}_3)_2\text{-O-Si(CH}_3)_2\text{-(CH}_2)_3\text{-CO-\}}_{0.5}\text{-}$$

$$\text{-\{-O-R-O-CO-(CH}_2)_8\text{-C}\equiv\text{C-C}\equiv\text{C-(CH}_2)_8\text{-CO-\}}_{0.5}\text{.}$$

DIESTER	R	Calculated (%) C	H	N	Found (%) C	H	N
I_c		71.89	7.49	-	71.53	7.57	-
II_c		65.88	6.86	5.30	59.34	6.59	5.77
III_c		66.88	7.24	5.03	67.50	7.41	5.25
IV_c		68.15	6.84	-	68.58	7.20	-
V_c		68.07	6.79	-	67.83	7.52	-



GPC Chromatograms of Copolymers; I-2, I-3, I-4, I-5 and I-6 (see Table II)

FIGURE 1 GPC chromatograms of the diacetylene-siloxane-biphenyl copolymer system after purification (see Table V).

obtained for a concentration of 0.5 g/dl in sym-tetrachloroethane at 30°C. The procedures used for DSC and X-ray scattering were briefly described in the preceding publication.[1] Table I gives the results of elemental analysis for siloxane-diacetylene copolymers 50/50. Table II gives the results of elemental analysis for the siloxane-diacetylene-biphenol copolymer system after purification as described above.

It is apparent from Tables I and II that for most copolymer systems the calculated values of atomic composition agree well with the calculated values with the exception of copolymer II_c (Table I) for which the values of carbon found are significantly below the calculated values for the expected composition of the copolymer. Copolymers I, III and IV gave single uniform and relative narrow GPC peaks and one can therefore reasonably assume that the original feed composition led to the expected copolymer formation. This assumption is questionable in the case of copolymers II and V for which a series of additional peaks for low degrees of polymerization suggest contamination of the copolymer with oligomeric species.

TABLE II

Elemental Analysis of Siloxane-Diacetylene-Biphenol Copolymer System

$$\text{-\{-O-R-O-CO-(CH}_2\text{)}_3\text{-Si(CH}_3\text{)}_2\text{-O-Si(CH}_3\text{)}_2\text{-(CH}_2\text{)}_3\text{-CO-\}}_m$$

$$\text{-\{-O-R-O-CO-(CH}_2\text{)}_8\text{-C}\equiv\text{C-C}\equiv\text{C-(CH}_2\text{)}_8\text{-CO\}}_n\text{-}$$

R:


POLYMER	n/m	Calculated (%) C	Calculated (%) H	Found (%) C	Found (%) H
I-1	0/100	63.14	7.02	63.44	7.16
I-2	10/90	64.92	7.10	64.86	7.23
I-3	25/75	67.74	7.23	67.70	7.51
I-4	35/65	69.37	7.32	69.51	5.50
I-5	50/50	71.89	7.49	71.53	7.57
I-6	75/25	75.90	7.63	75.46	7.77
I-7	100/0	79.64	7.88	79.49	7.88

RESULTS AND DISCUSSION

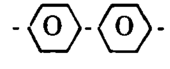
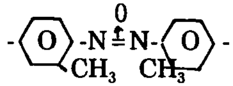
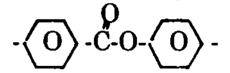
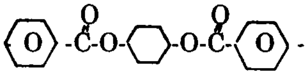
1. Copolymer systems at fixed molecular composition of n/m = 50/50.

Table III gives the mesomorphic properties of various copolymers with the exception of copolymer II_c for which the ratio n/m was found to be approximately 10/90. Not surprisingly the properties of copolymer II_c were found to closely resemble that of homopolymer II_p described in the preceding paper.[1] On cooling under microscope a biphase was replaced at 82°C by a "Schlieren" texture. This texture could be supercooled to room temperature. The smectic nature of this copolymer was established by x-ray diffraction, which displayed a single strong ring at 24.4 Å and a broad halo around 4–4.5 Å.

Copolymer IV_c showed on heating two very broad overlapping peaks followed by two well defined broad peaks at 104° and 115°c. (See Figure 2). Under micro-

TABLE III

Properties of Copolymers

COPOLYMER m/n = 50	R	VISCOSITY[a] $\eta_{red.}^{30°}$ dl/g	TRANSITION TEMP.°C[b]	M_d
1_c		0.25	$C115S_H132I$ $I120S_H102C_283C_1$	4900
III_c		0.31	(Tg3)40I I25C	8900
IV_c		0.23	$C104S^{(c)}115I$	4400
V_c		0.22	C135I I100C	4000

[a] 0.5 g/dl in tetrachloroethane at 30°C.
[b] From DSC second heating and cooling (20°/min).
[c] Smectic of higher order.
[d] From GPC.

scope a birefringent melt was observed above 104° which on cooling transformed into a glass without changing its appearance. Copolymer IV_c displayed an intense ring at wide angles, accompanied by two much weaker rings persistent up to approximately 100°C. A broad ring of medium intensity was present at low angles. The low angle ring at 31.1 Å persisted at 110°C while the weaker wide angle rings disappeared. A diffuse halo appeared and superimposed on the intense wide angle ring indicating the appearance of an isotropic phase (see Figure 3). This was confirmed by microscopy. This copolymer is smectic between 90° and 110°. The diffuseness of the low angle ring and the strong intensity and sharp definition of the wide angle ring makes the system unusual indicating possible irregular stacking of layers.

Table IV gives the spacings for copolymers II_c, IV_c and V_c. One may note that the low angle spacing of IV_c of 34.4 ± 0.5 Å is approximately half of the "all-trans" length of the repeating unit of 64.2 Å.

Unlike the copolymer IV_c which quenched easily to a glassy state (no crystallization was detected on cooling), copolymers Ic, II_c, and V_c displayed a crystal phase either on slow cooling or after annealing. This is most interesting in view of the structural disparity of the diacetylenic and siloxane spacers differing not only by their length (26.75 Å for an "all-trans" diacetylenic spacer as compared to 13.75 Å for the siloxane spacer) but also by their chemical constitution (conjugated —C≡C— bonds vs. siloxane groups).

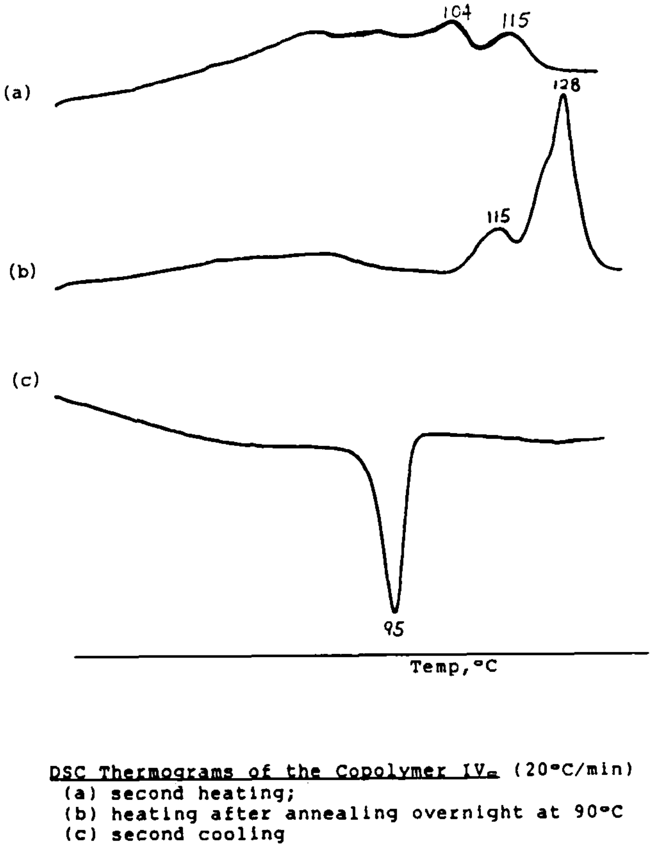


FIGURE 2 Thermograms of copolymer IV$_c$ (a) 2nd heating; (b) after extensive annealing at 90°C and (c) 2nd cooling.

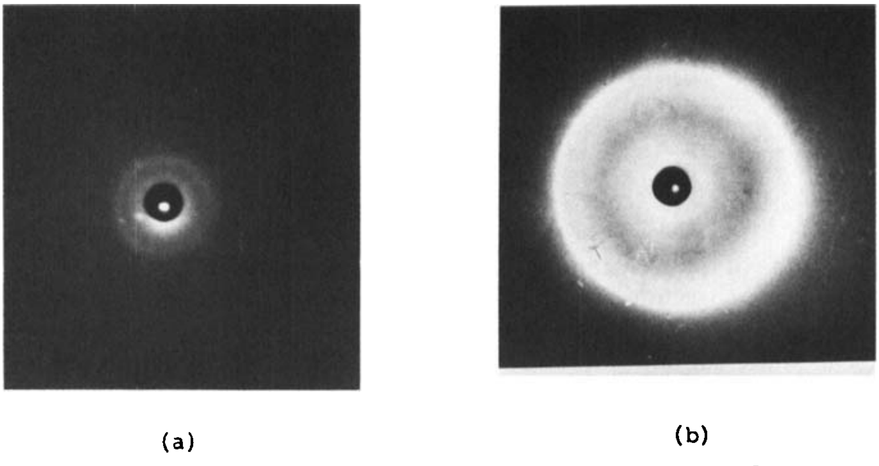

(a) (b)

FIGURE 3 (a) SAXS and (b) WAXS diffraction patterns of IV$_c$ at 90°C.

TABLE IV

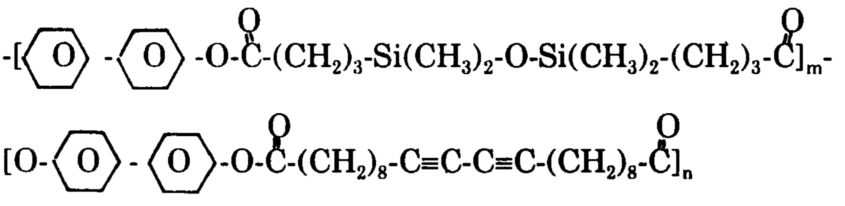
X-ray Diffraction Spacings of Copolymers

n/m	Polymer	Room Temperature	d = Spacings in Å
10/90	II_c	2.9(vw), 3.1(vw), 3.9(m) 4.4(s), 5.3(vw), 6.1(m) 6.8(w), 7.7(vw), 15.2(vw)	85^0C = 24.4(s)
50/50	IV_c	4.1(s), 28.9(m)	90^0C = 4.3(s), 9.6(vw) 10.5(vw). 34.4(m) 110^0C = 4.3(s), 31.1(m)
50/50	V_c	3.1(vw), 3.9(s), 4.2(s) 4.6(m), 5.0(m), 6.0(vw)	101^0C = 3.2(vw), 3.9(m) 4.1(w), 4.4(m) 4.7(m), 5.1(m) 6.0(w) 121^0C = 3.3(vw), 3.9(m) 4.1(s), 4.6(s) 5.1(s), 6.2(vw)

vs: very strong; s: strong; m: medium; w: weak; vs: very weak.

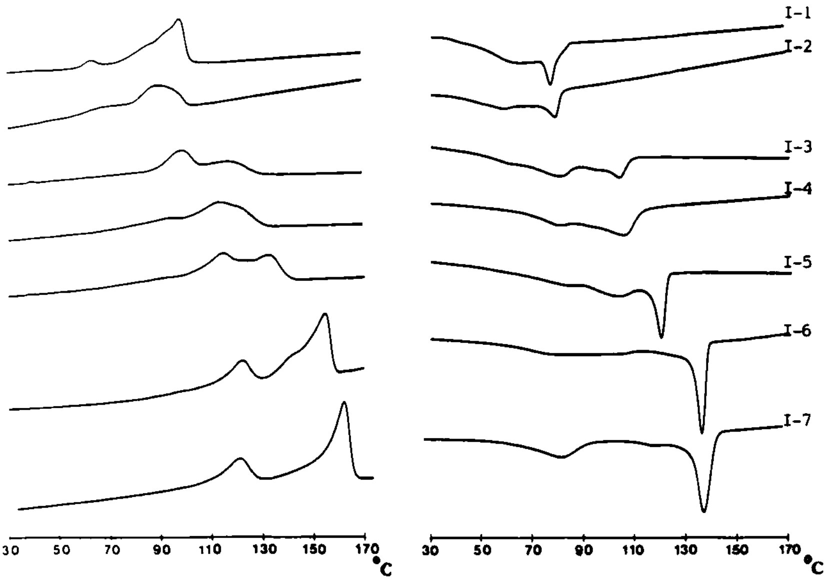
Copolymer I_c changed from white to blue in daylight and dark blue on exposure to x-rays especially in its mesomorphic state at high temperatures. The dark blue copolymer was only partially soluble in chloroform. This may be due to partial crosslinking. In contradistinction to copolymer I_c none of copolymers II_c–V_c displayed color changes in daylight or on exposure to X-rays suggesting that the packing requirements for reactivity of diacetylenic groups have not been met neither in the crystals nor in the smectic phases displayed by these copolymers.

2. Copolymer System Siloxane-Diacetylene-Biphenol:



The results of the elemental analysis of the copolymer are given in Table II in the experimental section. From Table II it can be seen that the copolymer composition agrees well with the composition of the feed. In addition, GPC peaks after purification are single, sharp and symmetrical. This indicates that the copolymer samples investigated are compositionally homogeneous.

Figure 4 gives the DSC thermograms of the copolymer system on heating and cooling (see also Table V). Peaks corresponding to crystal melting were very broad with substantial overlap between peaks. The transition temperatures corresponding



(a) (b)

FIGURE 4 Thermograms of the copolymer I system (see Table V) (a) heating (b) cooling.

TABLE V

Properties of Biphenol-Siloxane-Diacetylenic Copolymer System

Polymer	n/m	Viscosity[a] dl/g 30°η inh	Transition Heating	Temp.°C[b] Cooling	−ΔH Kcal/g, deg. Cooling	−ΔS cal/g, deg. Cooling
I-1	0/100	0.21	C_161C_2 C_298I	$(S_C)63C_1$ $I76(S_C)$	4.3 1.1	12.9 3.15
I-2	10/90	0.20	$C67S_C$ S_C88I	S_C58C $I78S_C$	3.6 1.4	10.9 4.0
I-3	25/75	0.19	C99S* S117I	S79C I103S	3.2 2.0	9.1 5.3
I-4	35/65	0.24	$C94S_H$ S_H116I	S_H81C $I104S_H$	2.8 2.9	7.9 7.6
I-5	50/50	0.24	$C115S_H$ S_H132I	S_H102C $I120S_H$	3.9 3.0	10.4 7.6
I-6	75/25	0.32	S_H155I	$I1380S_H$	4.0	9.7
I-7	100/0	0.41	$C122S_H$ S_H161I	$S_H\ 84C$ $I144S_H$	1.40 3.4	3.9 8.2

(a) 0.5 g/dl in 1,1-2,2tetrachloroethane, (b) second heating and cooling at 20°c/min.
*S = possibly (S_c + S_H).

to crystal transformation reported in Table V are therefore midpoints of broad ranges extending after 10–15°C on both sides of the reported value. In contradistinction to crystal transformation peaks, the smectic to isotropic transition peaks were sharp but still overlapping substantially with the broad crystal to smectic transition peaks. Since cooling decreased the overlap between the isotropic to smectic and smectic to crystal transition peaks the value of ΔH estimated by peak deconvolution were more reliable from cooling than from heating thermograms. They are reported together with the mid transition ranges in Table V.

As we know from previous work[1] the homopolymer of biphenol-10,12-bis-carboxypropyl-tetramethyl disiloxane was not liquid crystalline and gave only one phase transition C→I. On the other end of compositions the homopolymer of biphenol and the docosadiyne-1,22-dioic acid displays a mesophase of a higher order consistent with a S_H assignment.[2]

The mesophase assignments corresponding to peaks on thermograms of Figure 4 are given in Table V. The assignments were made on the basis of X-ray diffraction data given in Table VI. Some of the X-ray patterns are given in Figure 5.

It is interesting to observe the way in which the liquid crystalline phase changes with the increase of the diacetylene spacer content. The homopolymer I-1 (described in the previous paper)[1] is a monotropic smectic; the lowering of the melting point by copolymerization of 10 mole percent of diacetylenic spacer induces the formation of an enantiotropic smectic mesophase. This can be clearly seen from

TABLE VI

X-ray Spacings of Siloxane-Diacetylenic Biphenol Copolymer System

Polymer		(Spacings dA)	
		Room Temperature	Higher Temperature
I-1	0/100	4.2(s), 4.7(w), 5.3(w) 6.3(w), 10.7(vw),14.3(vw) 21.0(s)	90^{0}C = 4.3(vs), 4.8(s) 5.3(s), 6.2(s) 6.9(vw), 10.3(s)
I-2	10/90	4.0(s), 4.6(w), 5.2(w) 6.0(w), 9.4(vw), 17.6(s)	83^{0}C = 21.6(s)
I-3	25/75	3.6(w), 3.9(m), 4.3(vs) 7.2(w), 14.0(s)	106^{0}C = 4.1(w), 4.3(vw) 27.3(m)
I-4	35/65	3.5(vw), 4.1(w), 4.4(s) 15.1(w)	96^{0}C = 4.1(m), 4.3(vw) 25.0(m)
I-5	50/50	4.3(s), 14.8(vw)	119^{0}C = 4.2(s), 4.6(w) 24.5(m)
I-6	75/25	3.6(w), 3.8(s), 4,3(vs) 6.9(vw), 15.O(w)	126^{0}C = 4.1(s) 24.5(s)
I-7	100/0	3.1(w), 3.6(s), 3.9(s) 4.2(s), 4.8(w), 14.7(m)	140^{0}C = 4.2(s), 4.8(w) 24.9(s)

vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

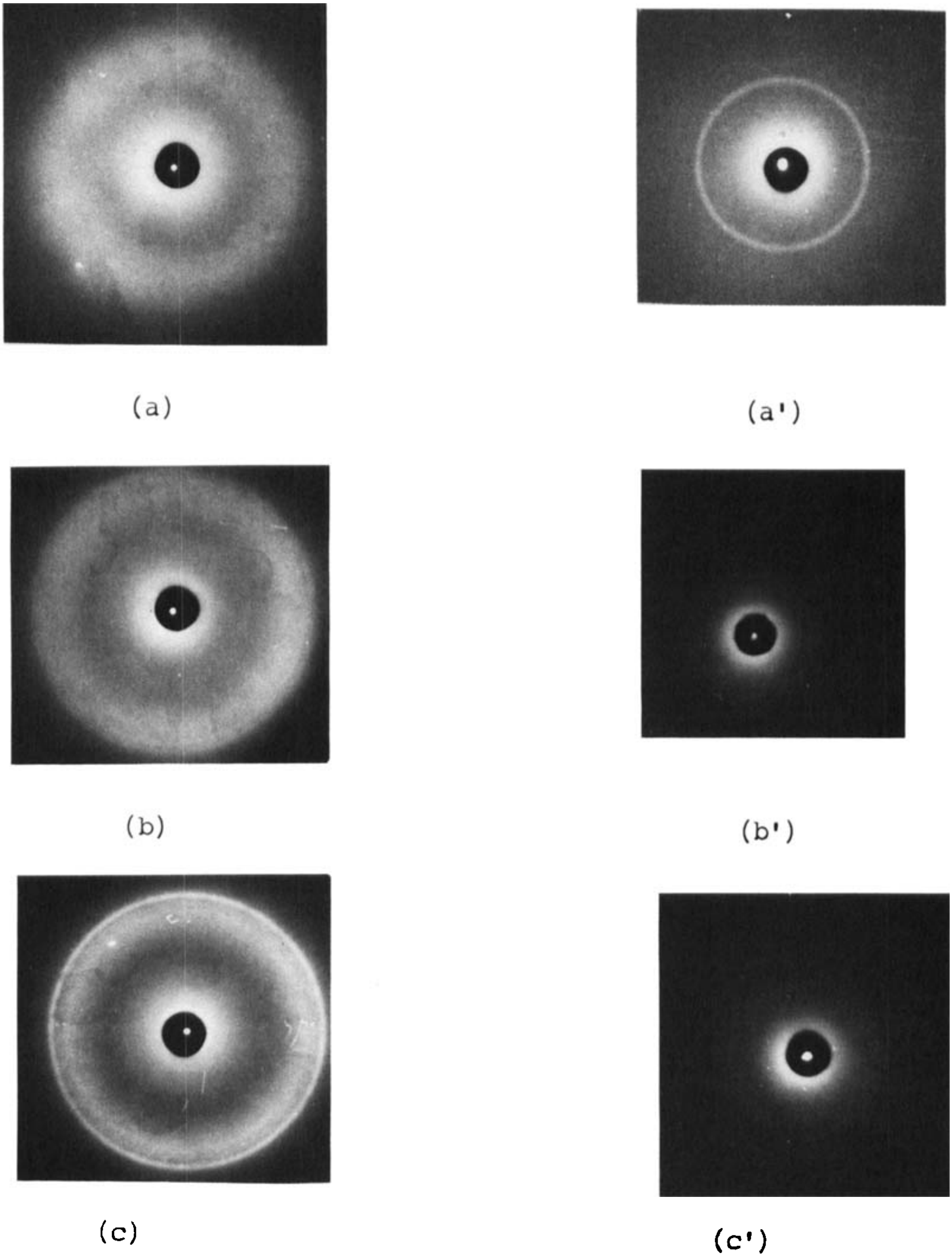


FIGURE 5 X-ray diffraction patterns of the copolymer I system (a) WAXS and (a') SAXS pattern of I-2 at 83°C, (b) WAXS and (b') SAXS pattern of I-3 at 116°C, (c) WAXS and (c') SAXS pattern of I-5 at 119°C, (d) WAXS and (d') SAXS pattern of I-6 at 126°C.

(d)

(d')

FIGURE 5 (continued)

the sharp SAX ring at 21.6 Å. The low order of this mesophase is shown by the halo at wide angles.

Increasing the diacetylene content to 25 mole percent changes the X-ray diffraction pattern as a sharp ring becomes visible at 4.1 Å (on a diffuse background.) The low angle spacing becomes less intense and increases its spacing to 27 Å. It is clear that an important change in the nature of the mesophase is taking place from the lower to a higher order smectic mesophase at about 20–30 mole percent of diacetylene spacer content. This change is also apparent from the sudden emergence of a new DSC transition peak centered for the I-3 copolymer at 117°C on heating and at 103°C on cooling (see Figure 4). It is possible in view of the superposition of the wide angle halo and a sharp diffraction line at 4.1 Å that a bi-phase of both types of mesophases is present. This ambiguity disappears for higher diacetylene contents which give at higher temperature patterns similar to the pattern of the pure diacetylenic homopolymer with a strong low angle and strong wide angle reflection preceded by a weak external line, a pattern which we thought to be consistent with a S_H assignment.[2] These results make it possible to draw the phase diagram given in Figure 6.

It is possible to see from Figure 6 and Table V that the copolymer crystallizes (albeit reluctantly) over almost the whole range of compositions with an eutectic in the vicinity of 10–15 mole percent of diacetylenic spacer (n/m is .1 to .15). For compositions rich in siloxane (n/m is 0–.2) the data suggests the formation of an imperfect crystalline lattice as the T_m decreases abruptly when n/m passes from 0 to 0.1 and the $-\Delta S_{S/C}$ values decrease. It is possible that both repeating units enter the lattice. On the other side of compositions T_m does not significantly vary with the composition suggesting a lattice dominated by the repeating units containing the diacetylenic spacer, and the exclusion of units containing the siloxane spacer.

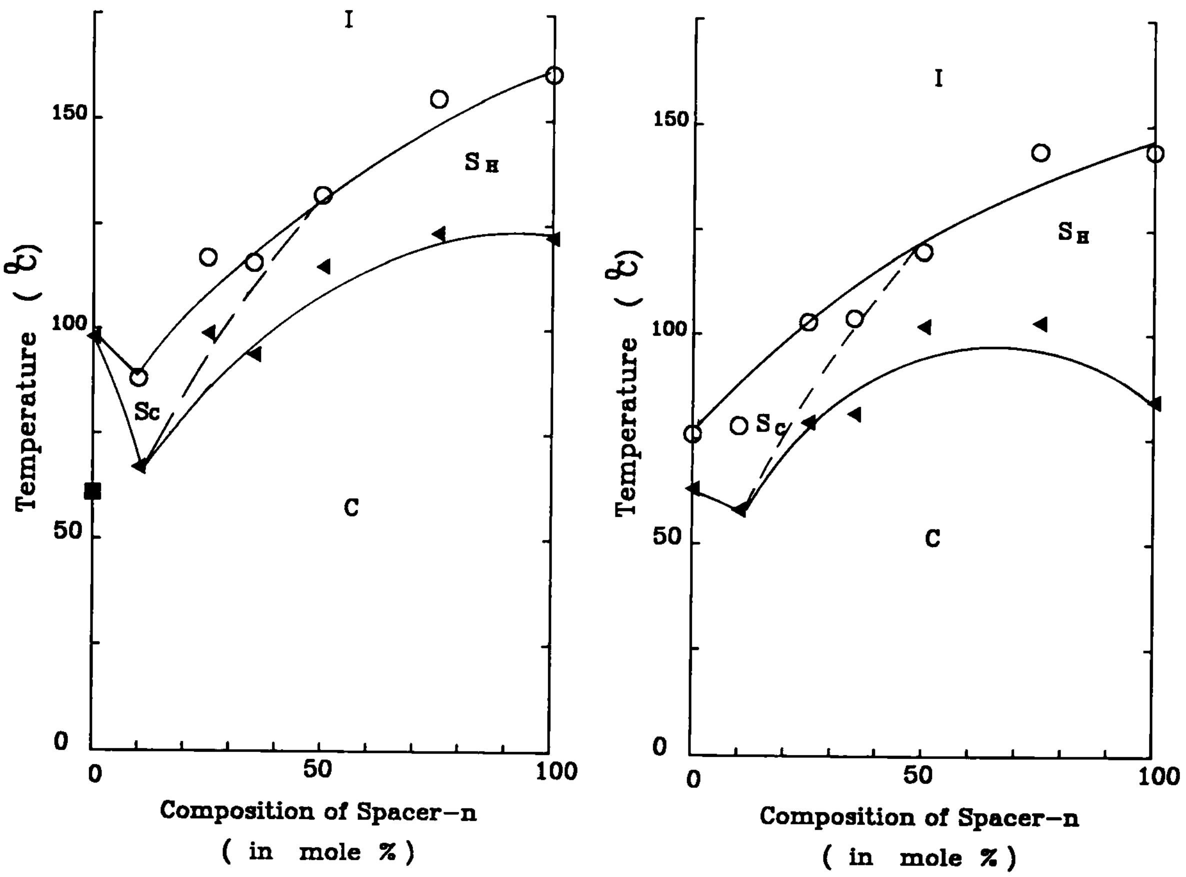


FIGURE 6 Phase diagram of (a) heating and (b) cooling for the I copolymer system.
■ ——Crystal/Crystal
▲ ——Crystal/Liquid Crystal
○ ——Liquid Crystal/Isotropic Liquid

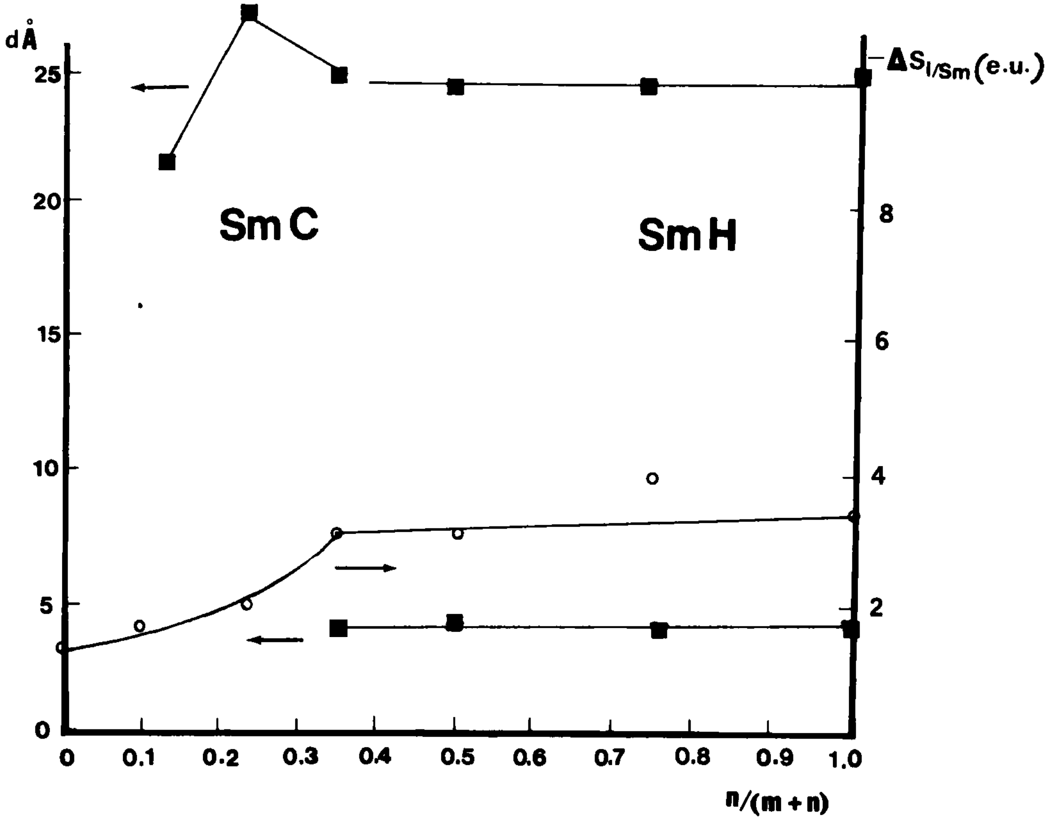


FIGURE 7 Evolution of I/Sm transition entropy and of the SAXS and WAXS spacings for the diacetylenic-siloxane biphenyl copolymer system.

In the liquid crystalline state obtained by heating the collapse of the lattice rich in siloxane generates a lower order smectic such as smectic C. It is interesting to observe that while the homopolymer I-1 is a monotropic smectic C, the addition of small amounts of diacetylene spacer units transforms it into an enantiotropic smectic C. As the diacetylene spacer content increases a higher order smectic (smectic H) appears and dominates from then on the structure of the mesophase. This can clearly be seen from Figure 7 in which the evolution of $-\Delta S_{I/Sm}$ and of the SAXS and WAXS peak position is juxtaposed. The $-\Delta S_{I/Sm}$ increases almost linearly until n/m is .3–.35 then stabilizes while the x-ray pattern changes at first and then remains the same. It appears from Figure 7 that the smectic mesophase unlike the crystalline phase has a certain tolerance for the siloxane component of the copolymer.

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