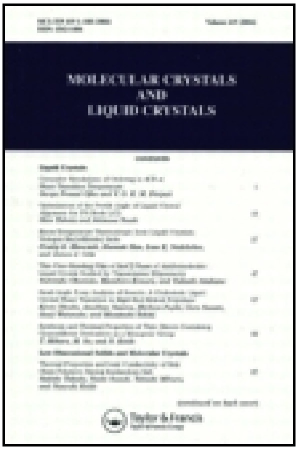

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of New Stilbene-Based Polycarbonates

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To cite this article: A. L. Bluhm , P. Cebe , H. L. Schreuder-gibson , J. T. Stapler & W. Yeomans (1994): Synthesis of New Stilbene-Based Polycarbonates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 239:1, 123-140

To link to this article: http://dx.doi.org/10.1080/10587259408047177

Mol. Cryst. Liq. Cryst., 1994, Vol. 239, pp. 123–140
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Printed in the United States of America

Synthesis of New Stilbene-Based Polycarbonates

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(Received May 11, 1993; in final form May 21, 1993)

A series of polycarbonates with stilbene mesogens has been prepared and characterized, expanding upon past work with stilbene-based polyesters and polyethers. It has been found that the stilbene mesogen, mono- or di-substituted with methyl or ethyl groups, significantly affects polymer morphology. Polycarbonates containing stilbene mesogens have been studied by differential calorimetry, polarized microscopy and X-ray diffraction. Methyl substituted stilbenes are semicrystalline and appear to be liquid crystalline, whereas ethyl substituted stilbenes are amorphous. Disubstitution lowers the transition temperatures from those values observed for monosubstituted stilbenes.

Keywords: stilbene, liquid crystal, polymer, thermotropic, amorphous, diethyl stilbestrol, x-ray diffraction, DSC, substituents

INTRODUCTION

During the last decade, extensive synthesis and characterization of stilbene-containing polymers has led to the identification of a large number of promising thermotropic liquid crystalline polymers. Jackson's[1] stilbene (SD) polyesters were first reported in the 1980's as high melting thermotropic liquid crystalline materials. Reasonably high strength fibers and injection molded plaques were produced from them. Polyesters[2,3] of α-methyl stilbene (HMS) were found to melt at temperatures similar to the Jackson polyesters and were also liquid crystalline. Percec's[4] α-methyl stilbene polyethers were reported to be lower melting liquid crystalline polymers of stilbene. However, Sato[5] recently reported α,β-diethyl stilbene (DES) polyesters that exhibit melting ranges closer to those of Percec's polyether; this indicates that the substituents on the stilbene mesogen influence the thermal behavior of the polymers as well. Figure 1 and Table I summarize the reported thermal transitions of the past research efforts. Shown in these data are two temperatures, T_m, the lower temperature of crystal melting and T_i, the higher temperature of isotropization to liquid melt.

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Earlier, we reported on a series of stilbene polycarbonates using one stilbene mesogen and varying lengths of alkyl spacer groups.[6] In the present work, the goal is to identify high yield, low cost synthetic approaches to thermotropic liquid crystalline polymers by evaluating stilbene mesogens that are potentially low cost starting materials because of their past commercial history as synthetic hormones and cattle growth steroids. Utilizing synthetic procedures[7-12] developed for the stilbene class of compounds (except DES which was obtained commercially), the following monomers listed in Table II have been synthesized for this study of thermotropic liquid crystallinity.

From these monomers, alkyl carbonate-linked polymers, listed in Table III, have been prepared and characterized with regard to their thermal properties and morphology in an effort to screen them as thermotropic liquid crystalline materials that have useful fiber forming properties (i.e. nematic order and rapid crystallization kinetics).

EXPERIMENTAL

Materials

Reagents for monomer and polymer synthesis (used as received): phosphorous tribromide, 99.99+% (Aldrich Chemical Co.); ethylmagnesium bromide, 1N solution in THF (Aldrich); deoxyanisoin, 97% (Pfaltz and Bauer); ethanethiol, 97% (Aldrich); calcium hydride, 40 mesh (Aldrich); sodium hydride, 60% dispersion in mineral oil (Aldrich); 4,4'-dimethoxystilbene, 97% (Janssen Chimica, AS 4705-34-4); phenylchloroformate 98% (Pfaltz and Bauer); 1,7-heptanediol (Aldrich). Additionally, phenol (Aldrich) was distilled[13] before use; chloroacetone and 3-chloro-2-butanone (Aldrich) were vacuum distilled and stored over $CaCO_3$ stabilizer; diethylstilbestrol (Aldrich) was recrystallized from ethanol.

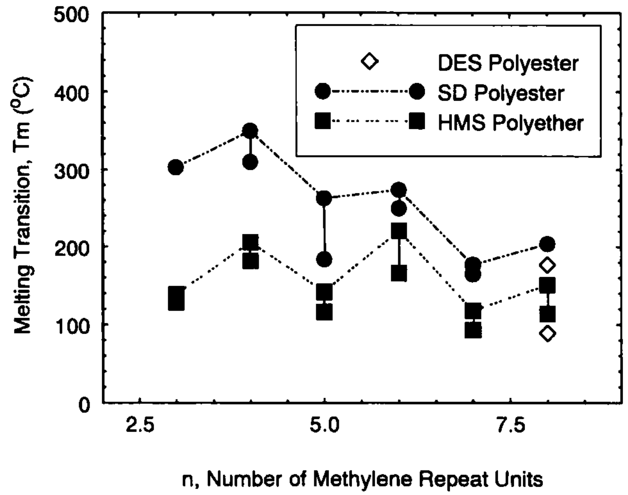
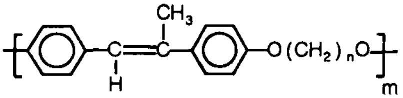
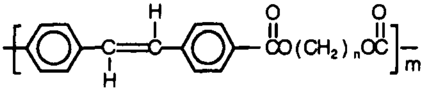
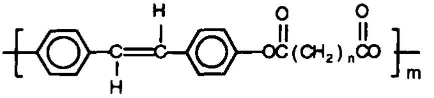
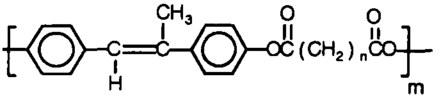
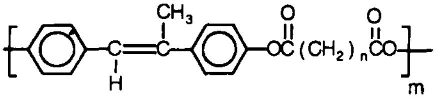
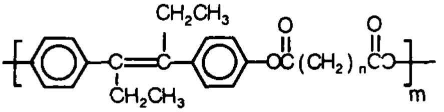


FIGURE 1 Thermal transitions for stilbene-based polymers of varying alkyl chain length, —$(CH_2)_n$—.

TABLE I

Melting transitions of reported stilbene polymers

Type/Structure	n	T_m (°C)	T_i (°C)	(Ref.)
Polyethers				
	3	128	139	(4)
	4	79	97	(4)
	5	91	106	(4)
	6	182	206	(4)
	7	116	221	(4)
	8	166	221	(4)
	9	—	118	(4)
	10	—	151	(4)
Polyesters				
	3	—	303	(1)
	4	310	350	(1)
	5	184	263	(1)
	6	250	274	(1)
	7	165	177	(1)
	8	—	204	(1)
	8	—	203	(5)
	6	197	247 & 287	(3)
	8	162	202 & 242	(3)
	8	211	255	(5)
	8	89	177	(5)

Techniques

Monomers were characterized by high pressure liquid chromatography (HPLC) with a reversed phase C-18 column and methanol/water (8/2) carrier solvent, thin layer chromatography (TLC) with C-18 plates and methanol/water (8/2) carrier solvent, and by melting point determination. Polymer molecular weight was measured by size exclusion chromatography with a Waters 590 Programmable Solvent Delivery System, Waters 410 Differential Refractometer, and a column combination of Ultrastyragel-10^4 and linear Ultrastyragel with chloroform at 1 mL/min, 40°C. Molecular weight calibration was established with polystyrene standards.

Polymer structure was verified by infrared spectroscopy using a Nicolet SX20 FTIR with samples prepared as films deposited onto NaCl plates from chloroform

TABLE II

Stilbene monomers

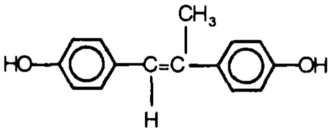
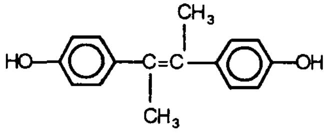
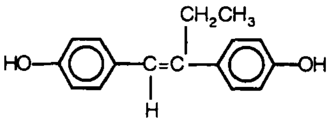
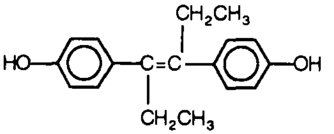
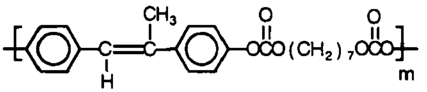
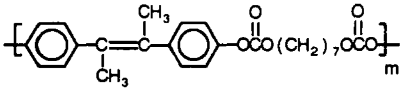
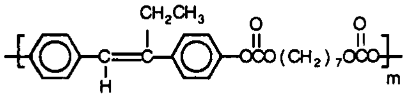
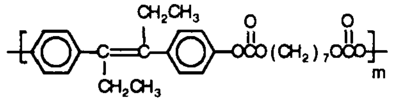
4,4'-dihydroxy α-methyl stilbene (HMS)	
4,4'-dihydroxy α,β-dimethyl stilbene (DMS)	
4,4'-dihydroxy α-ethyl stilbene (HES)	
4,4'-dihydroxy α,β-diethyl stilbene (DES)	

TABLE III

Stilbene-based polycarbonates

	HMS-7
	DMS-7
	HES-7
	DES-7

or prepared in KBr pellet form. Elemental analysis was performed by Midwest Microlab of Indiana.

Thermal properties of the polymer samples were measured with a Perkin Elmer DSC-7 differential scanning calorimeter (DSC) with a CCA7 liquid nitrogen cooling unit. The DSC was equilibrated to a block temperature of – 150°C and calibrated with indium and cyclohexane. DSC information was verified by hot-stage polarized microscopy optically to observe thermal transitions. A Mettler FP-82 hot stage with an FP800 controller was used with a Nikon Optiphot2-pol microscope, outfitted with a 40× strain free objective, 10× in-line magnification, daylight filter and 90° crossed polars.

X-ray data were obtained with a Rigaku RU-300 rotating anode generator in reflection mode using Copper Kα radiation. Polymer film was cast onto quartz plates from chloroform, dried, inserted into a Mettler hot stage, heated to 200°C and slowly cooled to room temperature. Measurements were taken on the polymer film at room temperature after removal from the hot stage.

Synthesis and Characterization of Monomers

Heptane diphenyl carbonate was prepared according to the method of Sato *et al.*[14] In summary, to an ice bath mixture of 0.05 mol of diol in 20 mL of chloroform and 10 mL of pyridine was added 0.10 mole phenyl chloroformate in 10 mL chloroform dropwise with stirring over 30 minutes. Stirring was continued for an additional 30 minutes in the ice bath. After warming the solution to room temperature the crystals of pyridinium chloride were separated on a Buchner filter. The filtrate was washed in a separatory funnel twice with an equal volume of 1 N HCl and once with water. The resulting solution was taken to dryness in a rotary evaporator. The crude yield of solid product was usually 90% or greater. The diphenyl carbonate was recrystallized from methanol, m.p. 34–35°C.

The mesogenic monomers, stilbenes, were obtained in a variety of ways. Diethylstilbestrol was used after recrystallization from methanol. Others were prepared as described.

HMS and DMS were synthesized by a procedure analogous to that of Zaheer *et al.*[11] This acid catalyzed addition of phenol to the chloroketone gave fair yields of 50–60% crude HMS, but poor yields of 5% crude DMS. HMS was recrystallized from ethanol-water, extracted with benzene and washed with petroleum ether to yield 10–15% monomer of m.p. 183.5–184.5°C (lit. 182–183°D).[11]

Synthesis of HMS by the Zaheer method was modified to improve yield as follows: 1) the reagents were carefully distilled before use; 2) the amount of sulfuric acid was reduced by half; 3) the reaction was maintained at −10°C at all times; 4) the water wash layer was worked up to give a significant amount of monomer; and 5) the organic layer was worked up after raising the pH of the mixture and maintaining a cold temperature at all times to prevent acidic degradation of the product.

Similar steps were followed in the preparation of DMS by the Zaheer method. The significant difference was that the HMS reaction proceeded for six hours, while the DMS reaction required 20 hours at a temperature 20 degrees lower than used for HMS. In both cases, reaction was considered complete when the viscous product could no longer be stirred. For the DMS synthesis, a 1 L resin kettle was charged with freshly distilled phenol, 0.6 mol, 3-chloro-2-butanone, 0.3 mol, and assembled with stirrer and drying tube to exclude air. With continuous stirring, the kettle was inserted into a cooling bath (GTE heat exchanger, model 750 with methanol/water circulating coils at −30°C). The temperature was maintained at −15°C as sulfuric acid, 0.3 mol, was added dropwise over a period of 18 hours (six hour reaction times were found to produce poor yields of DMS). Ice cold methanol (50 mL) was added to the viscous mixture, followed by 500 mL ice water. The precipitate was stirred for two hours, collected and washed ten times with 500 mL cold water per wash. No DMS was recovered from the aqueous filtrate, but the precipitate was worked up in the following way. Ethanol/water and methanol/water recrystallizations failed, due to the presence of an oily impurity. Vacuum oven dried precipitate was extracted with benzene overnight; decanting the benzene from a crusty impurity yielded 36% crude DMS after a 24 hour recrystallization. Successive recrystallizations from methanol/water yielded less than 5% product, melting at 192–194°C (lit. 194–196°C).[15]

Preparation of HES by Dodds' method[7] involved three steps: alkylation by Grignard reaction, dehydration of the resulting carbinol, and demethylation of the resulting dimethoxy product to dihydroxy stilbene. To a 250 mL round bottom (RB) flask, fitted with a condenser topped with a drying tube, a nitrogen inlet, a glass stopper, and magnetic stirrer bar, 40 mL (0.12 mol) EtMgBr solution and 60 mL dry ether were added. While stirring, deoxyanisoin (0.047 mol) was added as a solid through the sideneck, portionwise over a period of 45 minutes. The solution was refluxed over a water bath for 2.5 hr, chilled and poured into an ice and water mixture. This was acidified with dilute sulfuric acid; then the mixture was extracted with ethyl ether and washed with water. The ether extract was dried with magnesium sulfate, filtered, and distilled to remove the ether. The residual liquor which solidified, weighed 11.9 g and melted at 61–62°C (1,2-dianisylbutan-2-ol, lit. m.p. 61–62°C).[15] In 250 mL RB flask fitted with air condenser topped with drying tube, 26 mL $CHCl_3$ and 0.041 mol 1,2-dianisylbutan-2-ol were combined while stirred and chilled in ice-water bath; a chilled solution of PBr_3, 0.047 mol, in 13 mL $CHCl_3$ was added. This was removed from ice bath after 30 min and stirred at room temperature overnight. The solution was chilled and poured into 25 mL cold ethanol, followed by addition of 75 mL water. The product was extracted with $CHCl_3$, washed with water, dried over magnesium sulfate, filtered, and rotovapped to remove solvent. White crystals formed and methanol was added; the cold mixture was filtered to yield 29% product of m.p. 77–79°C. A recrystallization raised the m.p. to 80–81°C (lit. 84°C).[15] Additional product crystallized from the original filtrate and was used in the demethylation reaction described below.

Several methods for the demethylation of stilbene methyl ethers have been cited in the literature. Dodds *et al.*[7] reported the demethylation using alcoholic KOH at high temperatures in a sealed tube. Another method baked the methoxy materials with methyl Grignard agent.[16] Other procedures utilized pyridine-HCl[16] or boron tribromide.[17] We found the high temperature sealed combustion technique ineffective. Baking ethyl grignard reagent with the dimethoxy compound indicated a small conversion to the dihydroxy stilbene. A preliminary experiment indicated that the use of pyridine-HCl is a viable procedure for this demethylation. In addition to these demethylation techniques, other procedures were investigated. These included the use of KOH in ethylene glycol at reflux, boron tribromide in $CHCl_3$ at various temperatures, pyridine hydrochloride at 215°C, hydrobromic acid in glacial acetic acid at reflux, and boron tribromide-methyl sulfide complex in methylene chloride at reflux. Although demethylation did occur in all of these procedures, the mixture of products and small yield of desired product was discouraging. A more feasible procedure utilized ethanethiol-sodium hydride complex.

For the preparation of 4,4'-dihydroxy-α-ethylstilbene, the demethylation of the previously made dimethoxy-α-ethylstilbene was carried out according to a procedure as described by Feutrill and Mirrington.[12] The apparatus consisted of a 500 mL RB flask with magnetic stirrer bar, and fitted with a Claisen adapter to which was connected a water condenser, and addition funnel; provision was made for flushing with nitrogen. All components of apparatus were dried in an oven. Dimethylformamide, dried over calcium hydride, was filtered into the reaction flask (to 75 mL) and addition funnel (to 120 mL) under a nitrogen atmosphere. Sodium hydride, 12.8 g (60% dispersion in mineral oil) equivalent to 0.32 mol was added directly to the reaction flask. Ethanethiol, 5.9 mL, 0.08 mol, was added to the addition funnel. To the stirred and ice water-cooled reaction flask the solution from the addition funnel was added. After stirring for an additional 15 minutes, 2.0 g 4,4'-dimethoxy-α-ethylstilbene, 0.007 mol, was added directly to the reaction flask. The mixture was then heated under reflux for 3 hours at which time there was a very dark mixture. To the cooled reaction mixture, water and then 5 g sodium hydrosulfite were added. Acidification with diluted HCl yielded an off-white colored solid. This was filtered, washed with water, and air dried. After several recrystallizations from ethanol, the first with decolorizing charcoal, 0.5 g (30% yield) of fine white needles were obtained, m.p. 129.5–131°C, (lit. m.p. 128–129°C).[15] The product showed only one spot on TLC, and the mass and infrared spectra were in agreement with the structure.

Synthesis and Characterization of Polymers

A polymerization method described by Sato *et al.*[14] was used. The reactions were run in a side-arm test tube (23 mm O.D. by 20 cm) which had a nitrogen inlet tube at the top for flushing while heating the reactants at atmospheric pressure, at which time the side-arm was vented through a water bubbler. In a typical reaction equimolar (0.002 mol) proportions of the heptane diphenyldicarbonate and a stilbene were combined with 20 mg zinc acetate, and the reaction tube and contents placed in a Woods metal bath at 100°C under nitrogen for 1–2 hours. The mixture was then heated to 190°C for 2.5 hours, then house vacuum applied and heating continued at 200°C for 2 hours, with a final heating at high vacuum to 210°C for 1 hour. The cooled reaction mixture was stirred with chloroform. The chloroform solution was filtered and methanol was added to the filtrate, which caused the polymer to separate. Yields were generally in the range of 50%.

The four polymers were characterized with respect to elemental composition and molecular weight in Table IV. All exhibited reasonably high molecular weights with distributions (Mw/Mn) close to 2, which is expected for this type of condensation reaction. The degrees of polymerization were 53 for HMS-7, 36 for DMS-7, 51 for HES-7 and 38 for DES-7.

Chemical structures of the polymers were verified by FTIR. Shown in Figures 2 and 3, the spectra for the diethyl stilbene polymer contains the characteristic double peak at 3000 cm^{-1}, indicating the C—H stretching of both methylene and methyl groups of the ethyl substituents. This feature is not present in the dimethyl

TABLE IV

Elemental analysis and molecular weight of polymers

		%C	%H	%O	Mn (amu)	Mw (amu)	Mw/Mn
HMS-7	calc	70.23	6.38	23.39	21,494	54,862	2.6
	found	69.98	6.37	23.29			
DMS-7	calc	70.73	6.65	22.61	15,360	32,769	2.1
	found	70.30	6.75	23.13			
HES-7	calc	70.74	6.65	22.61	15,298	35.368	2.3
	found	70.76	6.68	22.51			
DES-7	calc	71.66	7.13	21.21	8,326	17,450	2.2
	found	72.66	7.19	19.88			

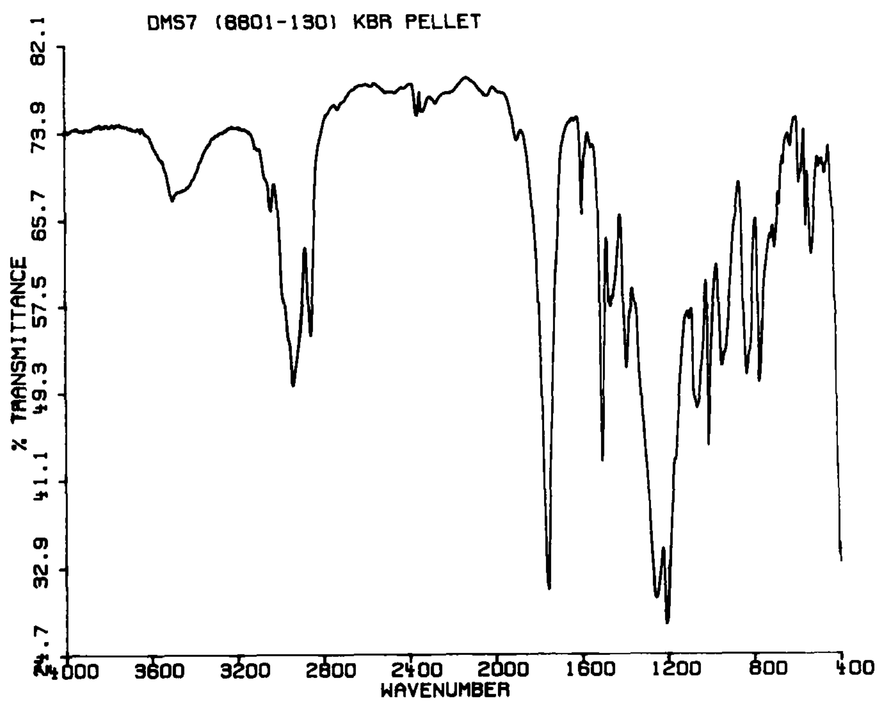


FIGURE 2 FTIR scan of DMS-7 in KBr pellet.

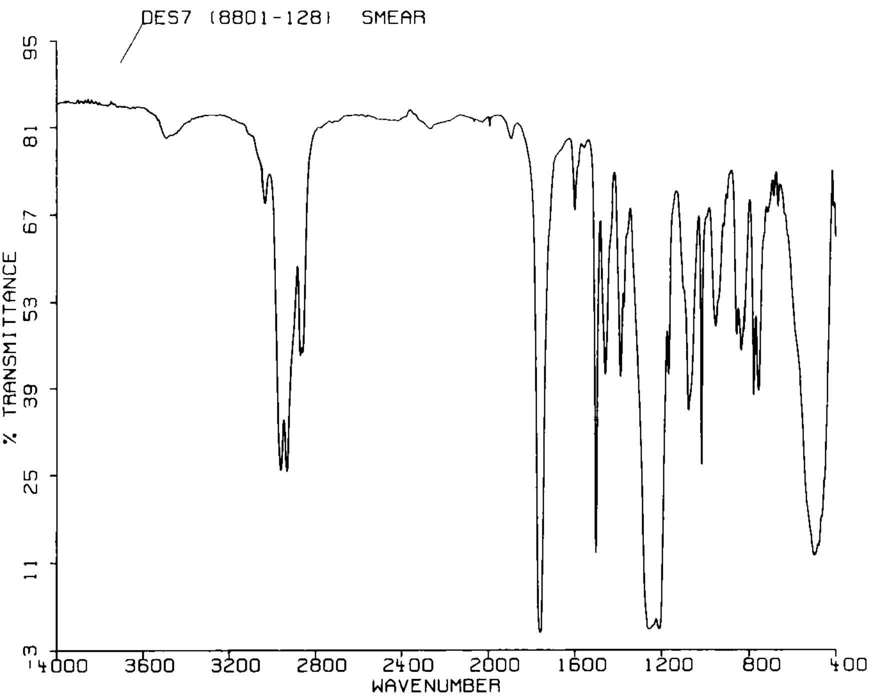


FIGURE 3 FTIR scan of DES-7 film on NaCl plate.

stilbene polymer, DMS-7. Similar features were seen in the infrared spectra of the mono-substituted stilbene polymers, HMS-7 and HES-7. All polymer products exhibited the —OH stretch at 3600 cm^{-1} associated with the expected hydroxyl end groups.

RESULTS AND DISCUSSION

Four polymers have been compared to determine mesogen structure effects on liquid crystallinity. The substituent on the stilbene unit has been varied to examine the effect of the stilbene "cross section" on solid state properties in Figure 4. Molecular dimensions of the stilbene monomers show that the diethyl stilbene (DES) unit is the bulkiest, at 10 Å across. Dimethyl stilbenes (DMS) are also large, at 8.6 Å. These examples are compared to ethyl (7.6 Å) and methyl (6.5 Å) monosubstituted stilbenes and 5.3 Å for an unsubstituted stilbene. The most efficient crystal packing might be achieved with the stilbene with the largest axial ratio. However, the effect of symmetry in the stilbene (mono vs disubstituted monomers) is difficult to predict. Both features are considered in this study of stilbene-based polymers.

HMS polymers have been extensively studied by Percec,[4,18] Jackson,[1] Blumstein[2] and Sato.[5] In a homologous series of HMS polyethers where the size of the alkyl flexible spacer group is varied from C3 to C10, liquid crystallinity is reported for C3 through C8,[4] as shown by the dual melting behavior in Figure 1 and Table I.

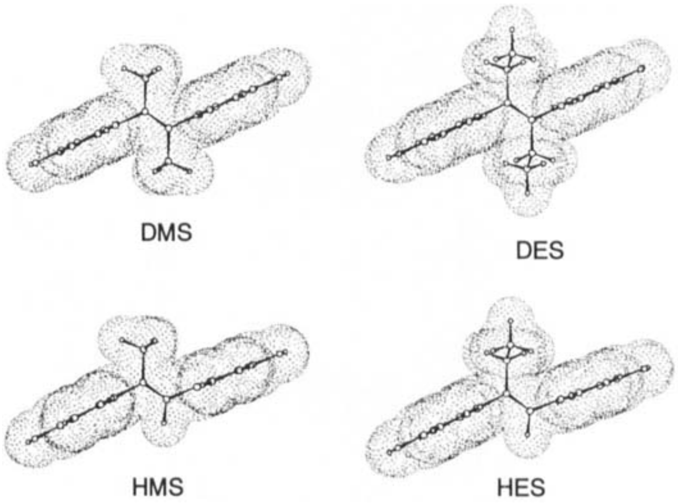


FIGURE 4 Minimized structures of stilbene monomers.

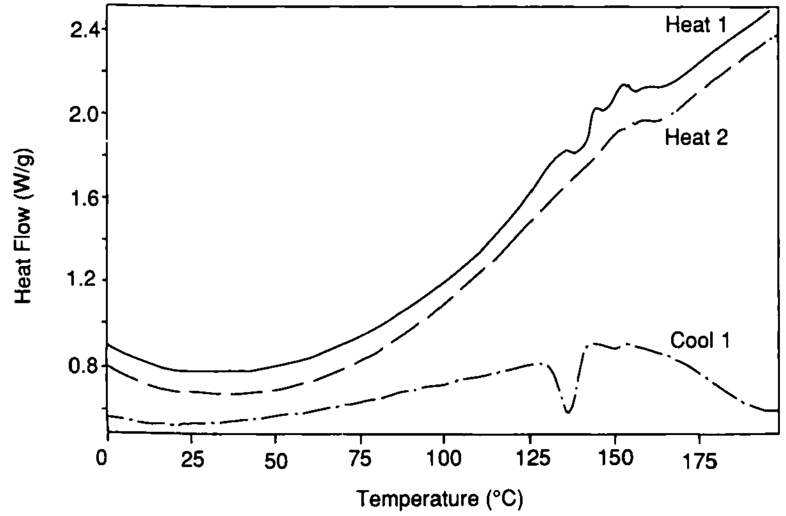


FIGURE 5 DSC scans at 10°C/min for HMS-7. Heating after 2 hours (140°C) isothermal hold (Heat 1), followed by cooling (Cool 1) and second heating (Heat 2).

Polyesters possess enantiotropic liquid crystallinity in C6 and C8.[3] We are currently working on a homologous series of HMS polycarbonates that exhibit liquid crystalline nematic (Schlieren) textures for C4 through C12, and enantiotropic thermal transitions for C5 through C9. The present study concentrates solely on HMS-7 and its comparison to similarly spaced derivative stilbene polycarbonates, DMS-7, HES-7, and DES-7.

Thermal transitions of the four polymers were measured by DSC in Figures 5–8. Data were not used from the initial melting of the samples; the powdery white polymers of HMS-7 and DMS-7 were preheated and cooled prior to use for thermal

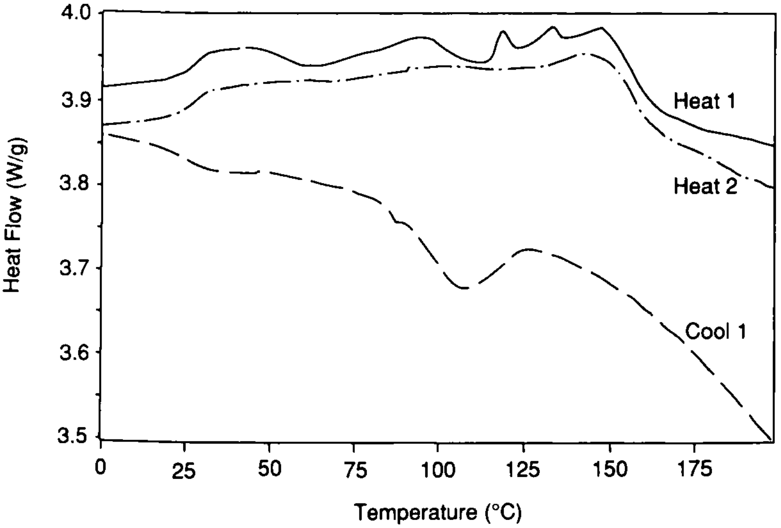
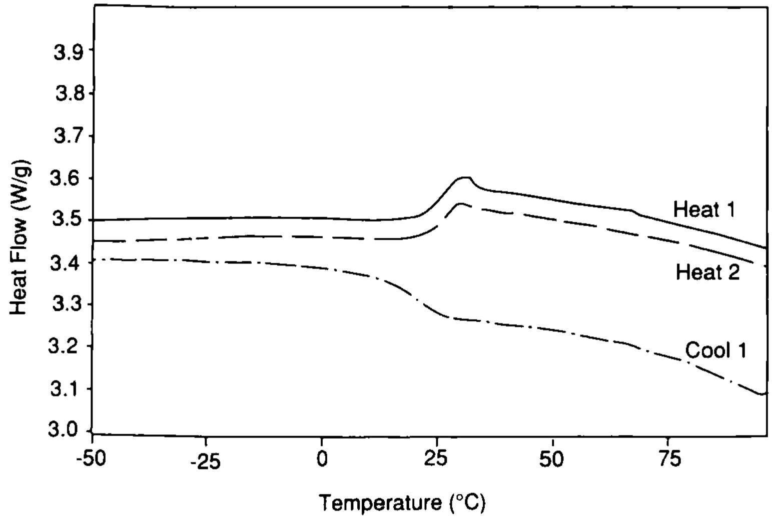


FIGURE 6 DSC scans at 10°C/min for DMS-7. Heating after 2 hours (110°C) isothermal hold (Heat 1), followed by cooling (Cool 1) and second heating (Heat 2).



.FIGURE 7 Glass transition temperatures of HES-7 polymer after isothermal hold, followed by −150°C/min quench to −100°C and heat at 20°C/min to 100°C.

scanning. HMS-7 was heated to 200°C, well beyond isotropization, cooled at 10°C/min to 140°C where crystallization just started, and held for two hours under a helium purge. Quenching then proceeded at −150°C/min to −50°C, followed by a heating scan at 10°C/min (Figure 5, Heat 1). A subsequent cooling (Cool 1 curve) and reheating at 10°C/min enabled comparison of the isothermal holding conditions and a normal heating scan (Heat 2). For HMS-7, a glass transition temperature could not be detected in this experiment, but was seen in subsequent runs and is reported in Table V. The isothermal hold at 140°C produced three

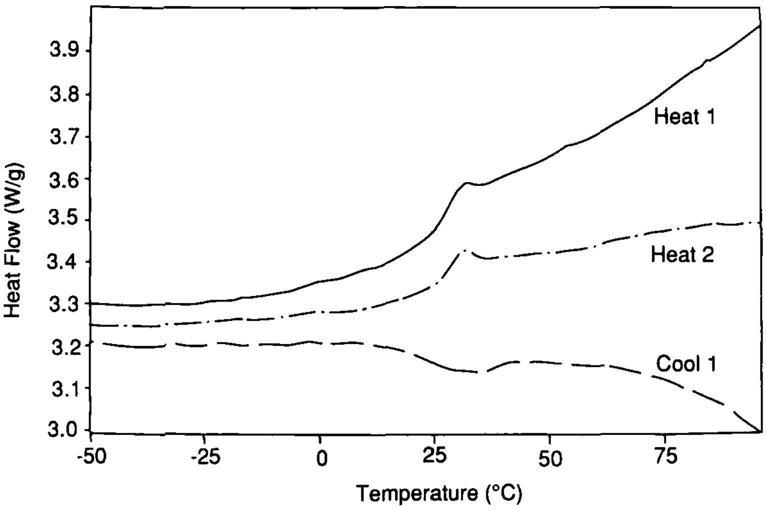


FIGURE 8 Glass transition temperatures of DES-7 polymer, treated as HES-7, above.

TABLE V

DSC thermal transitions for stilbene-based polycarbonates

					Melting Transition					Crystallization		
	Rate (°C/m)	Tg (°C)	$T_{(K-N)}$ (°C)	$\Delta H_{(K-N)}$ (J/g)	$T_{(N-I)}$ (°C)	$\Delta H_{(N-I)}$ (J/g)	$T_{(N-I)}$ (°C)	$\Delta H_{(N-I)}$ (J/g)	$T_{(I-N)}$ (°C)	$\Delta H_{(I-N)}$ (J/g)	$T_{(N-K)}$ (°C)	$\Delta H_{(N-K)}$ (J/g)
HMS-7	10	24	133	5.0	144	1.5	153	3.6	150	0.6	136	10.0
DMS-7	10	28	93	4.3	118	0.7	133	0.5	107	7.1	87	0.1
HES-7	20	25										
	10	18										
DES-7	20	27										
	10	25										

melting transitions in the Heat 1 scan: one below and two above the hold temperature. Crystallization processes that occurred normally below 140°C were allowed time to produce the lower temperature crystal population during the holding period. Above the hold temperature, two more melting transitions suggested the melting of two distinct crystal types. Tentatively, one could assign the lower of the two transitions to the melting of crystals to form the liquid crystal phase; the high temperature transition could be the clearing of the liquid crystal to the isotropic liquid phase. A simple heating scan with no isothermal holding exhibited only one broad transition over the temperature region corresponding to the highest melting transitions of the treated sample. Upon cooling, two crystallization exotherms were apparent; the high temperature exotherm could have been due to the formation of the liquid crystalline phase.

DMS-7 was treated and scanned in the same manner as HMS-7, except the

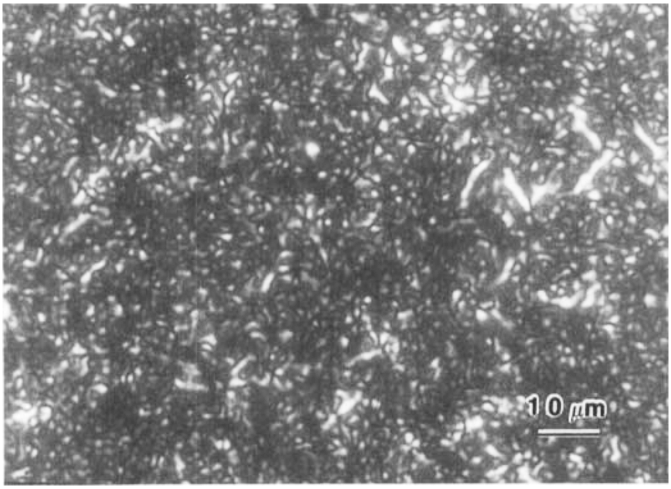


FIGURE 9 Polarized optical micrograph of HMS-7, taken at room temperature after 10°C/min cooldown from 200°C. During cooling, nematic texture developed at 142°C and remained to lower temperatures.

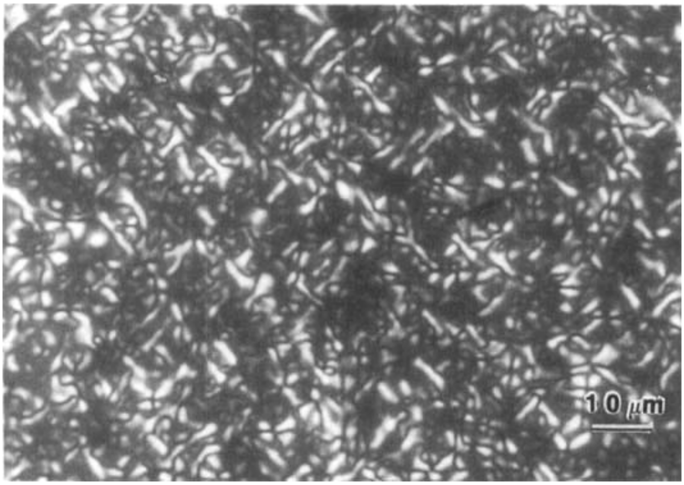


FIGURE 10 Polarized optical micrograph of DMS-7, taken at room temperature after 10°C/min cooldown from 200°C. During cooling, nematic texture developed at 121°C and remained to lower temperatures.

isothermal hold was conducted at 110°C. Again, three distinct populations of crystals were seen to melt in the Heat 1 scan: one below and two above the holding temperature. In this case, a glass transition was apparent at 28°C. Although a slight broad exotherm is apparent around 60°C during the Heat 1 scan of DMS-7 after the hold/quench treatment, this feature is not reproduced in the Heat 2 scan and is probably not a normal cold crystallization event for this sample. Two crystallization exotherms are apparent in the Cool 1 curve: the major exotherm is the higher temperature transition, while the lower temperature transition is barely detectable. This is unusual, as the lower temperature exotherm should be the larger

TABLE VI

d-Spacing values (Å) from X-ray scans

HMS-7	DMS-7	HES-7	DES-7
5.82	4.57	9.01	10.4
4.41	4.35	4.50	5.15
3.90			
3.61			

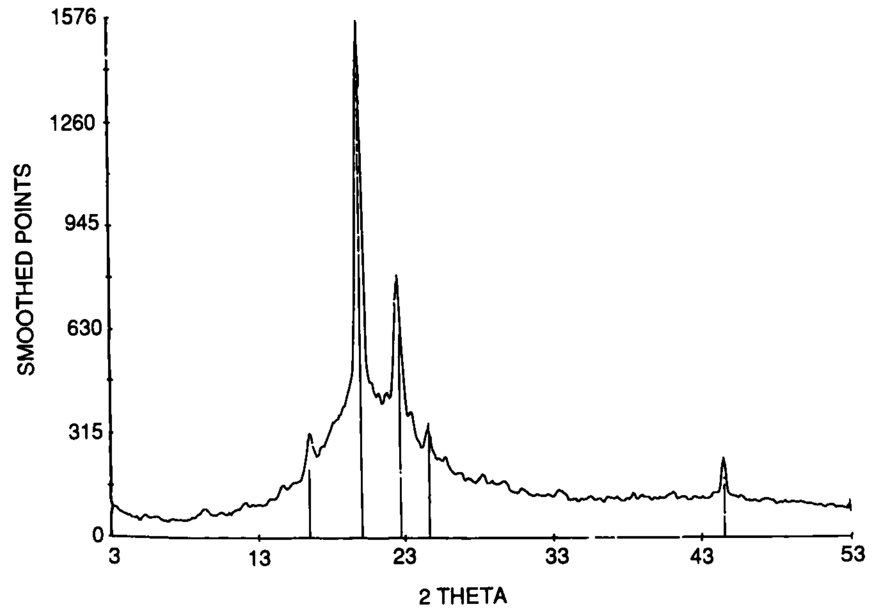


FIGURE 11 X-ray scan of HMS-7.

transition due to the formation of the crystalline phase, while the higher temperature transition should be lower in energy due to the formation of the liquid crystalline phase. This lower temperature exotherm may be an aberration and not a true transition.

Table V summarizes thermal transitions observed by DSC. Upon heating, HMS-7 and DMS-7 exhibited melting temperatures and enthalpies for transitions assigned to the crystal to nematic liquid crystal melt $T_{(\mathrm{K\text{-}N})}$ and $\Delta H_{(\mathrm{K\text{-}N})}$ and to the nematic to isotropic melt $T_{(\mathrm{N\text{-}I})}$ and $\Delta H_{(\mathrm{N\text{-}I})}$. The N-I transition was assigned to endotherms observed above the crystal melt, thus two $T_{(\mathrm{N\text{-}I})}$ and two $\Delta H_{(\mathrm{N\text{-}I})}$ values are listed for both polymers. Cooling produced crystallization temperatures and enthalpies for two transitions: the isotropic to nematic liquid crystallization process $T_{(\mathrm{I\text{-}N})}$ and $\Delta H_{(\mathrm{I\text{-}N})}$ and the liquid crystal to crystal transformation $T_{(\mathrm{N\text{-}K})}$ and $\Delta H_{(\mathrm{N\text{-}K})}$. For both HMS-7 and DMS-7, isothermal holding enabled the development of distinct crys-

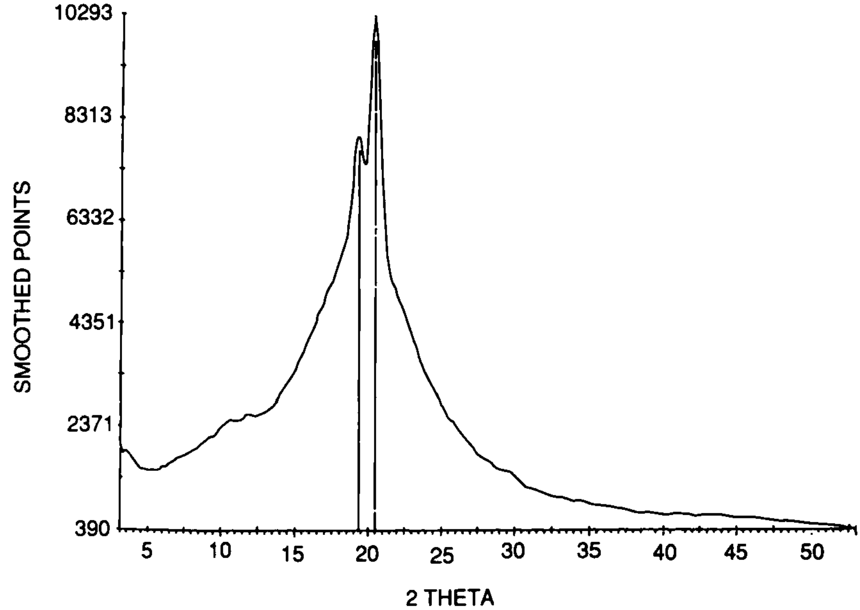


FIGURE 12 X-ray scan of DMS-7 after slow cool from 200°C.

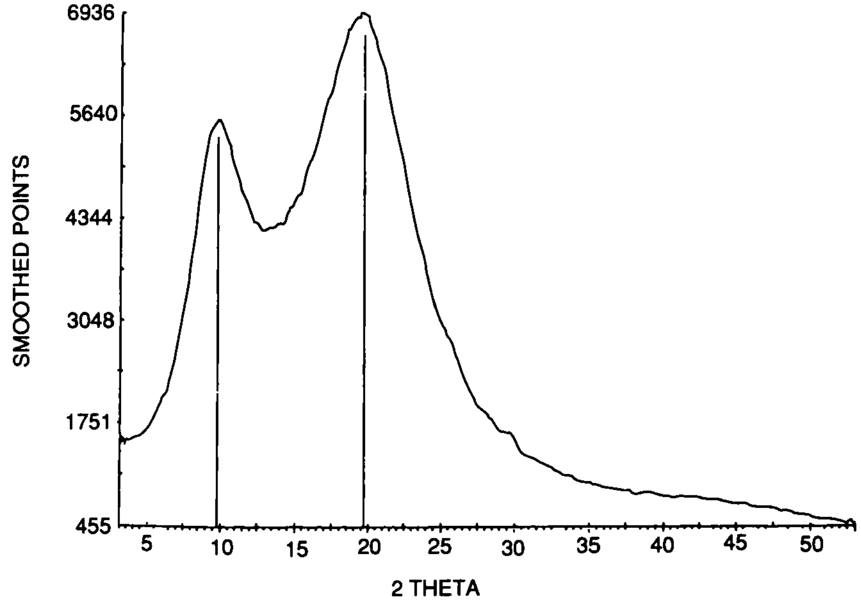


FIGURE 13 X-ray scan of HES-7 after slow cool from 200°C.

talline phases and enantiotropic liquid crystallinity became apparent after this thermal treatment.

Glass transition temperatures were measured for the HES-7 and DES-7 polymers in the following manner. After holding at 40°C for over 200 hours, the samples

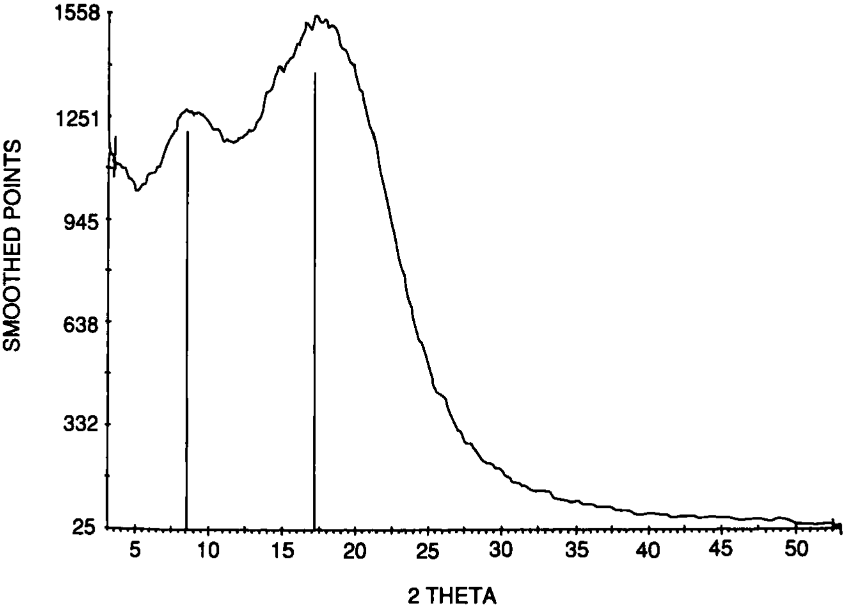


FIGURE 14 X-ray scan of DES-7 after slow cool from 200°C.

were cooled at −150°C/min to −100°C, heated at 20°C/min to −100°C, cooled at −20°C/min to −100°C and heated a second time to 100°C. Under these conditions, glass transition temperatures of 25°C for HES-7 and 27°C for DES-7 were found. Isothermal holding of these ethyl stilbene polymers produced only a hint of crystalline melting in Heat 1 of Figures 7 and 8. Enthalpic relaxation of excess free volume present in the polymers is observed near the glass transition for each sample, due to the entrapment of free volume upon quenching at cooling rates of −150 and −20°C/min.

Polarized optical microscopy was used to confirm the DSC transitions and identify possible liquid crystalline textures. Glass microscope slides were treated with 5% KOH/ethanol, 5%H_2SO_4, distilled water and acetone before a 10% (wt/vol) solution of polymer in chloroform was applied to the surface of the dried slide. After warming to 200°C, the thin film was cooled at a rate of 10°C/min. Shown in Figures 9 and 10, typical nematic liquid crystalline textures were observed for HMS-7 and DMS-7. However, HES-7 and DES-7 remained isotropic throughout the temperature range of 200° down to 50°C, thus confirming the amorphous behavior of HES-7 and DES-7 in DSC scans. Observation of the melting and crystallization transitions under polarized light corresponded well with the transitions measured by DSC and listed in Table V. At the 10°C/min cooling rate of the hot stage, HMS crystallized between 142–130°C, while DMS crystallized between 121–115°C. Upon warming at 10°C/min, HMS-7 melted and cleared at 152–160°C and DMS-7 melted to clarity at 145–155°C.

X-ray scans of the four polymers indicate that the methyl substituted stilbene polymers, HMS-7 and DMS-7 were the most highly ordered crystalline polymers with two sharp reflections. HES-7 and DES-7 were amorphous, each showing two broad reflections. Table VI lists the d-spacing calculated for reflections shown in Figures 11–14. HMS-7 was measured early in the study and treated differently than described in the Techniques section; it was melted onto a teflon substrate, air cooled, removed from the substrate and affixed onto an Al frame with minimum Duco cement. Thus, an Al reflection at 2θ equals 44.5 can be seen in Figure 11. We also see two reflections in HMS-7 that are not apparent in the other polymers. However, the d-spacings of 4.41 and 3.90 Å of the major HMS-7 reflections correspond to the major reflections seen in DMS-7, and it is possible that they are the result of interchain packings distanced by the unsymmetrical cross-section of the stilbene mesogens. The ethyl substituted stilbenes produce chain packings that are highly unsymmetrical; d-spacings of 9.01 and 4.50 for HES-7 and 10.4 and 5.15 for DES-7 suggest an elliptical cross-section for these polymers that might arise from the substituents on the mesogen stilbenes.

CONCLUSION

Preliminary characterization of stilbene-containing polycarbonates indicates that although there are a variety of stilbene structures available for use as mesogens, bulky substituents interrupt chain ordering, preventing the formation of liquid crystalline, or even crystalline phases, as shown in the case of ethyl substituted stilbenes. Methyl substituted stilbenes are liquid crystalline, exhibiting nematic textures and interchain spacings of approximately 4 Å. Ethyl substituted stilbenes produce polymer chains that pack in a manner that suggests an elliptical cross-section with interchain spacings of approximately 10 and 5 Å. Disubstitution lowers the crystal to liquid crystal to isotropic liquid thermal transitions twenty degrees or more below the transitions of the corresponding monosubstituted stilbene polymer. Based on the results of this study, we would expect that the unsubstituted stilbene would be an excellent mesogen for a highly ordered stilbene polycarbonate. Synthesis of the stilbenediol mesogen is in progress.

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