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Novel Thermotropic Main-Chain Polyhydrocarbons and Block Copoly(hydrocarbon-azomethines)

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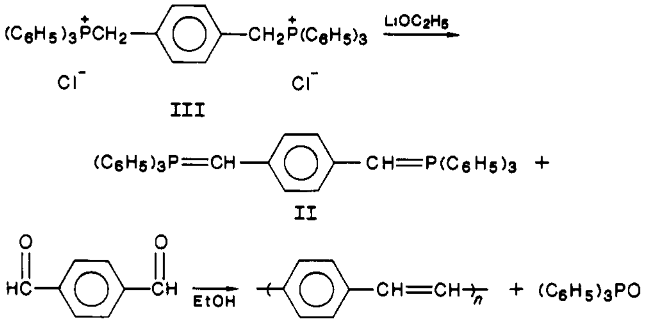
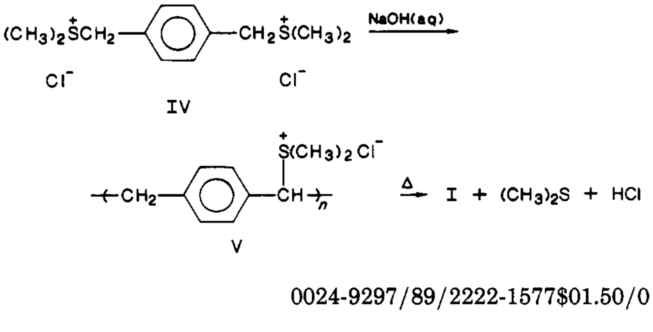
ABSTRACT: Liquid crystalline main-chain polyhydrocarbons have been prepared for the first time. These polymers are derivatives of the much studied "intractable" poly(1,4-phenylene-1,2-ethenediyl), also termed poly(*p*-phenylenevinylene), and were synthesized via the Wittig reaction. Specifically, by use of the concepts of lateral substitution to reduce the melt temperature without overly affecting chain stiffness and copolymerization, a thermotropic polyhydrocarbon, poly[(chloro-1,4-phenylene)-1,2-ethenediyl-1,4-phenylene-1,2-ethanediyl-1,4-phenylene-1,2-ethenediyl], was prepared. The work was extended to the synthesis of several other thermotropic melt forming systems which include in their main chain 9,10-anthracenediyl, 1,5-napthalenediyl, and 2,6-naphthalenediyl. A composition, poly[(phenyl-1,4-phenylene)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl], containing a larger lateral substituent (phenyl) failed to give a thermotropic melt but instead gave one which exhibited a high degree of shear anisotropy. The lack of thermotropism here may be explained by a fairly high *cis*-1,2-ethenediyl content which when coupled to the large lateral group effect prevent proper chain alignment. Fibers were spun from these new polymers and their properties were found to be a function of the degree of order in the polymer melts. In addition, thermotropic aldehyde-ended (chloro-1,4-phenylene)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl oligomers were coupled with aromatic diamines to form high molecular weight thermotropic melt forming polymers containing blocks of rigid hydrocarbons linked by azomethine groups. These polymers yielded fibers with high strength and modulus.

Introduction

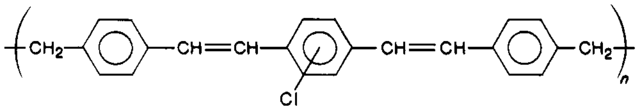
Poly(*p*-phenylenevinylene) (I) was first synthesized by McDonald and Campbell[1] via a condensation polymerization based on the principle of the Wittig reaction involving reaction of bis(triphenyl phosphorane) (II) and terephthalaldehyde. The phosphorane II was formed in situ from treatment of the bis(triphenylphosphonium) salt III with lithium ethylate in ethanol. The poly(*p*-phenylenevinylene) via this scheme had low molecular weight (DP $\sim$ 10). Several other methods for the direct synthesis of polymer, summarized in papers by Hoerhold and Opfermann[2] and Hoerhold and Bergmann,[3] failed to give high molecular weight. This is believed due to the low solubility of poly(*p*-phenylenevinylene) in all polymerization solvents tried thus far. A novel polymerization leading to a soluble precursor of poly(*p*-phenylenevinylene) has been described in a patient by Wessling and Zimmerman.[4] Their procedure involved treatment of a bis(sulfonium salt) (IV) of *p*-xylylene dichloride with aqueous NaOH to give a soluble poly(*p*-xylylene sulfonium salt) (V).





Solutions of V yielded films via dry casting, and upon heating, the films were converted to poly(*p*-phenylenevinylene) with elimination of dimethyl sulfide and HCl. Lenz, Karasz, and co-workers applied this procedure for the preparation of high molecular weight I and its copolymers with substituents at the 2,5-positions of the *p*-phenylene ring[5] and obtained high molecular weight films which after drawing become highly oriented. These films when doped with iodine have, in the case of the 2,5-dialkoxy-substituted copolymers, metallike conductivity, e.g., 428 S/cm in a copolymer with only 13 mol % 2,5-dimethoxy-*p*-phenylene subunit. Wessling and Zimmerman's procedure thus provides a method for synthesizing and fabricating intractable poly(*p*-phenylenevinylene) and its copolymer via a soluble precursor.

The copolymers and derivatives of poly(*p*-phenylenevinylene) prepared in this investigation are believed to represent the first examples of liquid crystalline main-chain polyhydrocarbons. These are in contrast to the many examples of olefinic polyhydrocarbons which are liquid crystalline by virtue of inclusion of mesogenic side chains.[6] In retrospect, from observations by Campbell and McDonald that a number of 1,4-bis(4-substituted-styryl)benzenes exhibit liquid crystallinity,[7] it is not all that surprising that phenylenevinylene units, appropriately substituted and arranged in an all polyhydrocarbon backbone, should lead to liquid crystallinity. The composition which has received most of our attention in this investigation is poly[(chloro-1,4-phenylene)-1,2-ethenediyl-1,4-phenylene-1,2-ethanediyl-1,4-phenylene)-1,2-ethenediyl] (VI), whose structural similarity to the 1,4-bis(4-substituted-styryl)benzenes is quite apparent. Characterization, with respect to melt structure and conditions for processing this polymer and related copolymers containing other aromatic units, with and without the ethanediyl connecting link in their backbone, will be described. Also investigated was the coupling of aldehyde



VI

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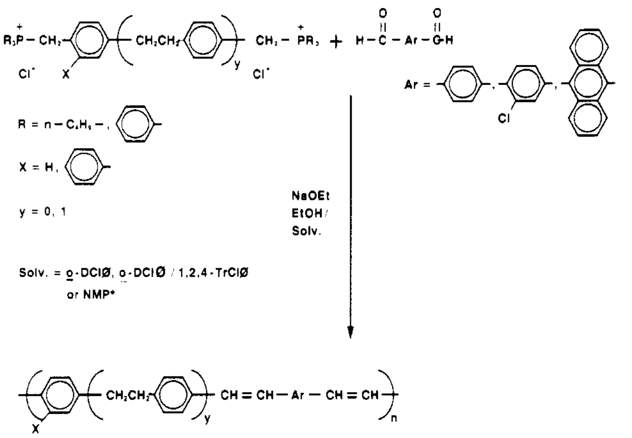
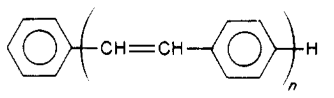
Scheme I
Preparation of Polyhydrocarbons



*N-Methyl-2-pyrrolidone.

ended, liquid crystalline, oligomeric (chloro-1,4-phenylene)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl blocks with aromatic diamines. The resulting high molecular weight polymers containing azomethine connecting links were thermotropic and melt processible to fibers. It is worth noting that well-defined unsubstituted 1,4-phenylene-1,2-ethenediyl oligomers (VII) with n = 1–7 have been reported,[8] without mention of liquid crystallinity, although the materials with n up to 3 melted (352 °C for n = 3) without decomposition. (When n was 4 or higher, the oligomers melted with decomposition: 368–374, 395–400, 415–430, and 425 °C for n = 4, 5, 6, and 7, respectively.)



VII

Results and Discussion

Preparation and Characterization of Polyhydrocarbons. Polymerization. For the preparation of polyhydrocarbons (polymers A–E-2, Table I) investigated in this work, the Wittig reaction was chosen because it affords high yields and allowed the use of intermediates which were available commercially or were relatively easy to prepare and purify. Scheme I shows the general conditions used to prepare these polymers. The key elements to the successful preparation of relatively high molecular weight polymers were (1) placement of lateral groups on one or both intermediates to increase the solubility and therefore delay precipitation of the polymers during their formation, (2) copolymerization, and (3) use of bis(tributylphosphonium) rather than bis(triphenylphosphonium) salt intermediates. In all cases, the polymers precipitated during their formation, at a point determined by the degree and kind of lateral substitution and arylene content of the polymer backbone. This limits chain growth to moderately high levels since polymerization in the solid state is virtually nil. (See discussion below for a way to chain-extend aldehyde-ended hydrocarbon oligomers with diamines to very high molecular weight polymers having a low azomethine content.[9])

As an illustration of the lateral group effect, polymer E-1 (Table I) was easily formed in relatively high molecular weight (fiber and film forming) in contrast with its unsubstituted analogue (I) with a DP of only 10, described previously.[1] Further, in the current work polymer A, with a chloro ring substitutent, has been prepared in relatively high molecular weight and is fusible whereas its parent polymer was found to be infusible and undoubtedly of low molecular weight since its rate of precipitation was extremely rapid, much like poly(1,4-phenylene-1,2-ethenediyl). The effect of copolymerization on formation of relatively high molecular weight polymer may also be illustrated by comparison of polymer E-1 with its parent polymer, but the lateral group effect is primarily responsible in allowing sufficient solubility for appreciable chain growth before polymer precipitation occurs. Finally the effect of the use of bis(tributyl- versus bis(triphenylphosphonium) salt may be illustrated by comparison of the η_{inh} achieved for polymer A. The highest η_{inh} achieved with the triphenyl system was only 0.14 versus 0.35 for the tributyl. This difference is significant and shows up in polymer properties discussed below. The better results with the tributyl salt may be related to its higher solubility which allows better initial mixing before polymer precipitation sets in. In addition, the higher solubility of oligomers containing flexible tributylphosphorane end groups would promote chain growth.

Infrared and ^{1}H NMR Characterization. All of the polymers show the characteristic absorption at 960 cm^{-1} (Figure 1A) due to CH out-of-plane vibration of trans-1,2-ethenediyl.[10] They also exhibit absorption at 885 cm^{-1} which can be attributed to CH vibration of *cis*-1,2-ethenediyl.[11] To get a more quantitative assessment on the E (trans) and Z (cis) content in selected polymers (A, E-1, and E-2), ^{1}H NMR was employed. Parts a and b of Figure 2 show ^{1}H NMR spectra of A and E-1, respectively, and are consistent with the overall repeat units for the polymers. The spectra also show that both polymers contain appreciable (Z)-1,2-ethenediyl. The Z/E ratio for polymer A is 0.29 versus 0.81 for E-1 (Figure 2c,d). In the case of E-1, a solvent study was conducted to see if the preferred E isomer could be increased, but no appreciable effect was found (see Table II). The relatively low isolated yields of polymer prepared in ethanol and low η_{inh} explain the high E isomer content—the more soluble Z isomer would be left in solution. This result is consistent with results found in the synthesis of stilbene in EtOH using the Wittig reaction where the E/Z ratio was found to be 55:45.[12] Here, the E isomer was isolated from ethanol by precipitation into aqueous HBr, leaving the soluble Z isomer to be isolated by extraction with ether followed by distillation.

The ^{1}H NMR spectrum of polymer E-2, a copolymer of E-1 and its parent, is less informative with respect to E/Z ratio due to insufficient resolution in the 1,2-ethenediyl range (Figure 3). However, it is clear from the NMR spectrum that the copolymer contains a large amount of the Z isomer.

Fluorescence and Structure. All of the polyhydrocarbons prepared in this work exhibit a high degree of fluorescence and are brilliantly colored (chartreuse in the case of polymer A; orange for B and D; and yellow for C, E-1, and E-2). The fluorescence exhibited by these polymers is in line with observations by other workers who studied the effect of degree of polymerization for poly(1,4-phenylene-1,2-ethenediyl) on fluorescence.[8] Polymer A with three 1,4-phenylene units in resonance with two 1,2-ethenediyl units fluorescences at 515 nm (when excited at 467 nm from a xenon lamp), somewhat higher wavelength than for an oligomer with DP of 2 which has the same number of 1,4-phenylene and 1,2-ethenediyl units. The latter exhibited maxima at 444, 474, and 500 nm versus 449 and 581 nm for the highest molecular weight

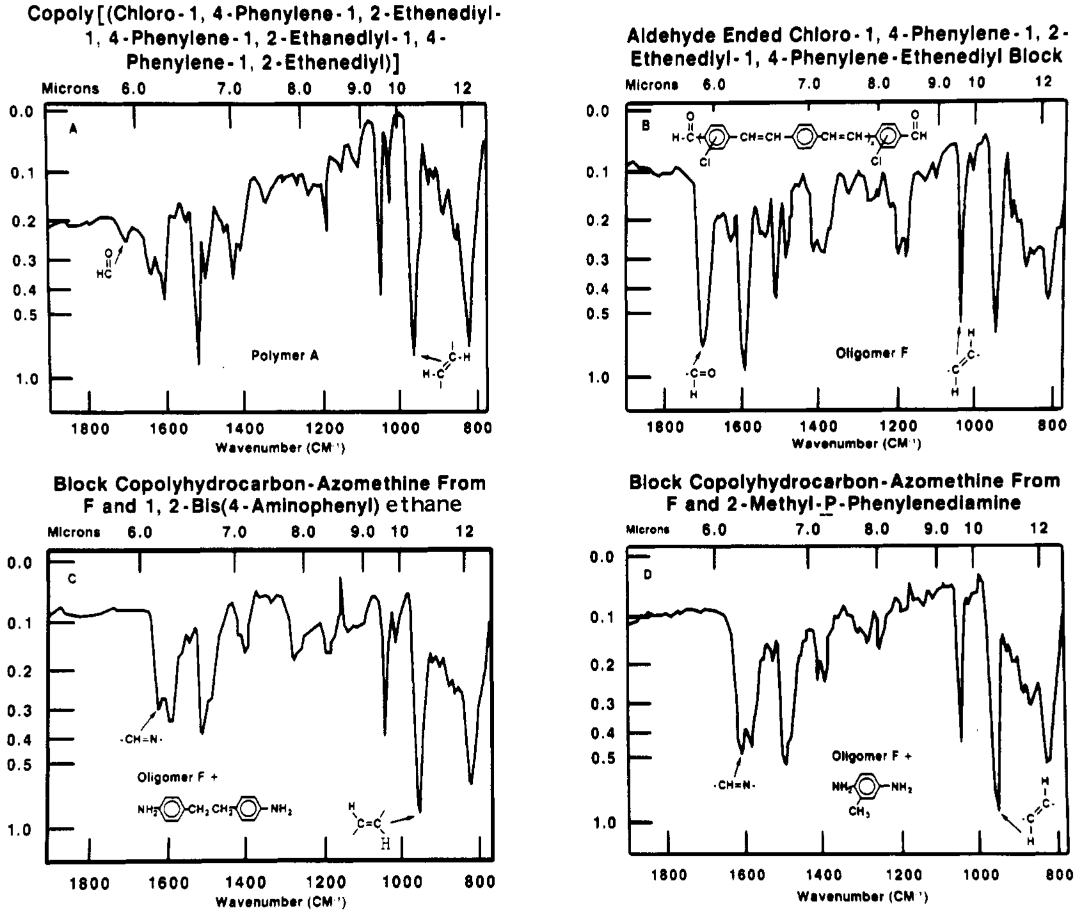


Figure 1. Infrared spectra of polymer A, oligomer F, polymer F, and polymer F-2.

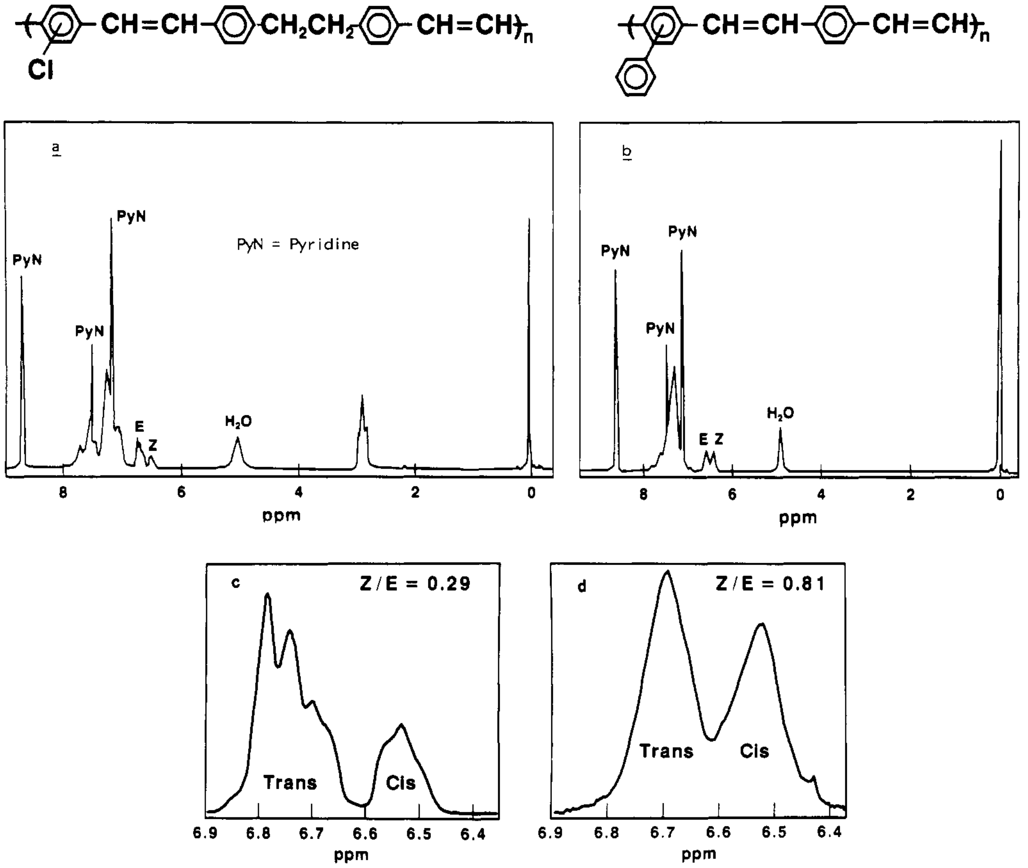


Figure 2. (a, b) ^{1}H NMR spectra of polymers A and E-1 in pyridine-d_5 versus TMS at 0 ppm. (c, d) ^{1}H NMR spectra of *cis*- and *trans*-1,2-ethenediyl of polymers A and E-1 in pyridine-d_5 versus TMS at 0 ppm.

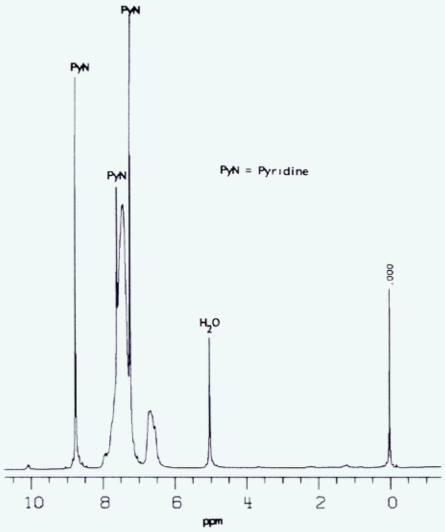


Figure 3. ^{1}H NMR spectra of polymer E-2 in pyridine-d_5 versus TMS at 0 ppm.

polymer. Fluorescence spectra of E-1 and E-2 were not taken but these materials would be expected to fluoresce in the same range as poly(1,4-phenylene-1,2-ethenediyl).

Thermal Properties. The thermal properties of the polymers were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in nitrogen and polymer melt temperature (PMT) and results are tabulated in Table I. With the exception of polymer C which exhibits a T_m strong endotherm at 195 °C which is consistent with the PMT on a hot bar at 200 °C, the DSC's of the other polymers give very little information with respect to polymer T_g's and T_m's. The virtual absence of T_m's in DSC thermograms may be rationalized by the presence of both *Z* and *E* 1,2-ethenediyl units in the polymer chains which result in low crystalline order and therefore low heats of fusion. Polymers B, D, and E-1 exhibited strong exotherms at 319, 330, and 330 °C, respectively, and most probably correspond to a crystallization. (The polymers do not have long-term melt stabilities but solidify after standing for awhile.)

In general, the polymers exhibit high TGA decomposition temperatures. Surprisingly, introduction of the 1,2-ethanediyl unit does not seem to adversely affect the thermal stability (compare polymer A with B–E-1). The very good thermal behavior of polymer A is in contrast to the poor results for poly(*p*-xylylene) (from pyrolysis of *p*-xylene) which exhibits major TGA decomposition at only 323 °C in nitrogen and retains only 16% of its initial weight when recovered at 522 °C.[13] Poly(*p*-xylylene) when heated above decomposition volatilizes to monomer while polymer A no doubt decomposes to less volatile fragments giving much higher weight retention. It is also worthwhile to note that the polymers, with the exception of D, have thermal stabilities equal to or greater than those reported previously for poly(1,4-phenylene-1,2-ethenediyl) prepared via the Wittig reaction.[2] This may be explained by the overall higher molecular weights of polymers in the current work.

Characterization of Melts. The above polyhydrocarbons were characterized by making visual observations using a polarizing microscope while heating the polymers on a hot stage and by measuring light transmission through cross optical polarizers while heating at a programmed rate. The latter technique has been previously described and is termed the thermal optical test (TOT).[6] With the exception of polymer E-1, the polymers exhibit melt anisotropy. Figures 4 and 5 show polarized light micrographs of polymer A and D melts, respectively. The texture for A is the usual one for a nematic thermotropic melt whereas that for D appears to be atypical. No definite explanation can be given for the unusual texture of D at this time, but it may be related to the presence of the large 9,10-anthracenediyl moiety in the copolymer which results in formation of a second phase, especially if the polymer contains blocks.

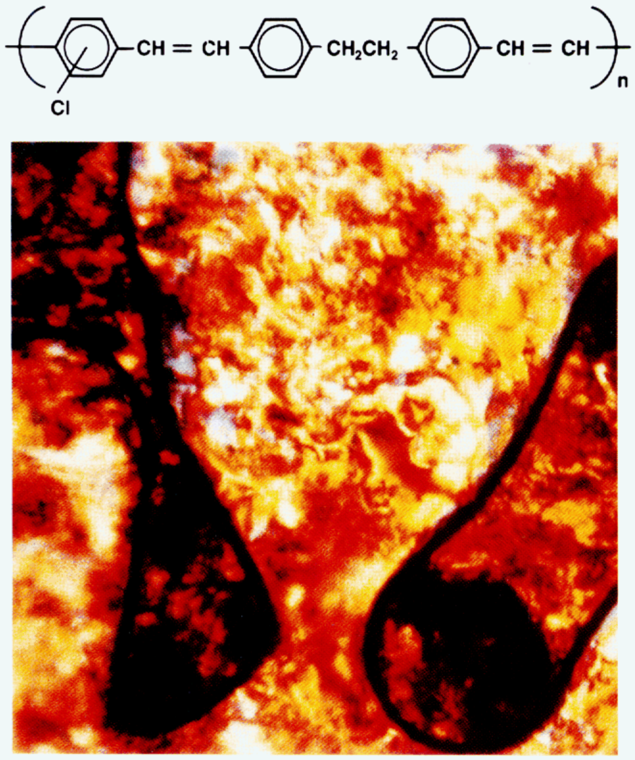


Figure 4. Polarized light micrograph of polymer A [η_{inh} 0.35 (*p*-chlorophenol/*p*-dichlorobenzene 70/30 v/v)] at 270 °C.

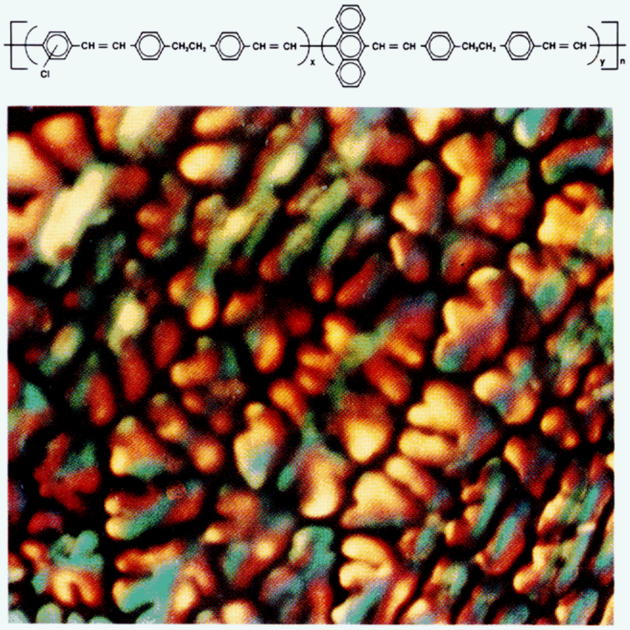
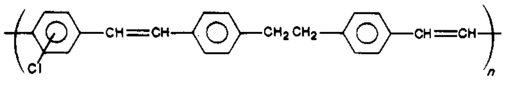
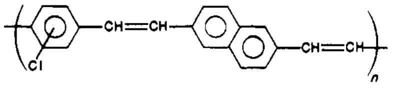
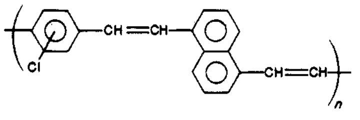
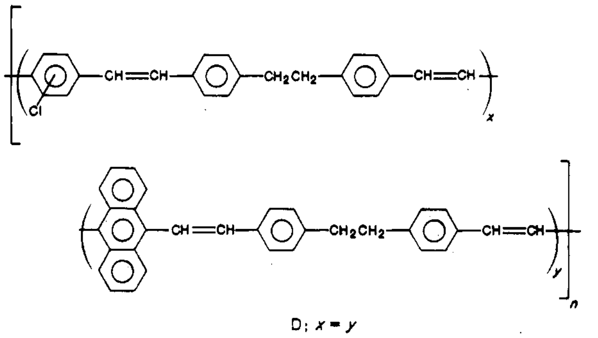
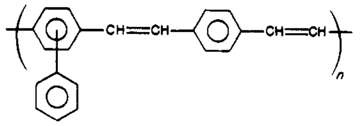
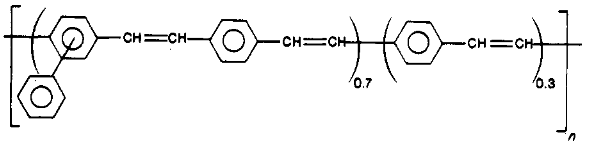
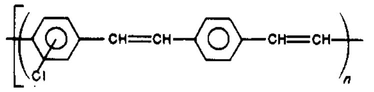
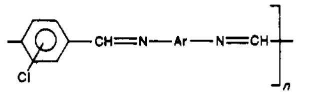
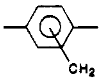
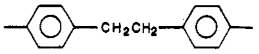


Figure 5. Polarized light micrograph of polymer D [η_{inh} 0.35 (*p*-chlorophenol/*p*-dichlorobenzene 70/30 v/v)] at 270 °C.

Figure 6a shows the TOT curve for polymer A. In a typical TOT, there is very little light transmission below the flow temperature of the polymer. However, since the polymer disk used in the test was pressed at 192 °C, some strain birefringence was introduced and the solid exhibited

Table I
Thermal Properties of Polyhydrocarbons and Block Poly(hydrocarbon-azomethines)

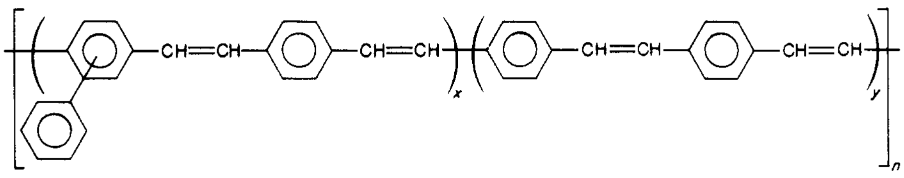
polymer	η_{inh}, dL/g	PMT, °C	melt structure	DSC[c] endo	DSC[c] exo	TGA[c] dec, °C	TGA[c] % wt ret (700 °C)
 A	0.35[a]	230	anisotropic			487	66
 B	0.23[a]	270	anisotropic	160 (w)	319 (s)	492	80
 C	0.24[a]	200	anisotropic	195 (s)		450	72
 D; $x = y$	0.35[a] (135 °C)	300	anisotropic	250 (w)	330 (s)	450	50
 E-1	0.93[b]	207	shear anisotropic		330 (s)	490 500	60 42 (air)
 E-2	0.93 (pt. sol)[b]	220	anisotropic				
	insol[d]	300	anisotropic		325 (s) 500 (vs)	470	72 60 (510 °C)
 F-1; Ar =  F-2; Ar = 	insol[d]	280	anisotropic	276 (s)	476 (s)	460	72 90 (510 °C)

[a] 0.50 g/dL in p-chlorophenol/p-dichlorobenzene (70/30 v/v). [b] 0.063 g/dL in o-dichlorobenzene/1,2,4-trichlorobenzene (50/50 v/v). [c] 20 °C/min in nitrogen. [d] Concentrated H_2SO_4.

appreciable light transmission below its melting point due to the partially crystalline nature of the solid. On heating, the birefringence of the solid decreases due to loss of crystallinity. However, on melting the molecules were able to align themselves to form a liquid crystalline phase and birefringence returned and persisted to above 360 °C with no sign of an isotropic clearing point. In contrast to the behavior of this sample of polymer A, lower molecular weight (η_{inh} equal to or less than 0.14) samples exhibited isotropic clearing points at less than 360 °C. The apparent lower degree of liquid crystalline order for the lower molecular weight polymers manifests itself in poorly ordered fibers (see the following discussion).

Melt Anisotropy and Structure. As mentioned above, all of the polyhydrocarbons listed in Table I, with the exception of E-1, exhibit melt anisotropy. For the purpose of this discussion, the key points to be made about this new class of material can be made by focusing attention on polymers A, E-1, and E-2. First, polymer A exhibits optical anisotropy in spite of a fairly high (Z)-1,2-ethenediyl content: Z/E = 0.29. In this polymer, the presence of a crankshaftlike 1,2-ethanediyl connecting link

Table II
Polymerization Solvent Effect on Yield and Properties of



x	y	polymerztn solvent (v/v)	yield	η_{inh} [1,2,4-TrClPh/o-DClPh (50/50 v/v)] polym concn, g/dL 0.125	0.063	0.031	PMT, °C	Z/E[a]	melt structure
1	0	1,2,4-TrClPh/EtOH (53/47)	80		0.47	0.63	215	0.81	shear anisotropic
1	0	(52/48)	108[b]	0.62	0.95	0.95	207		shear anisotropic
1	0	(26/74)			0.63	1.86	202	0.91	shear anisotropic
1	0	EtOH/NMP (74/26)	96		1.08	1.86	202	0.94	shear anisotropic
1	0	(47/53)	72		0.47	0.63	202	0.93	shear anisotropic
1	0	EtOH	52		0.16	0.32	171	0.04	shear anisotropic
0.7	0.3	1,2,4-TrClPh/EtOH (52/48)	82		0.95 (pt sol)		220		anisotropic + isotropic regions[c]

[a] ^{1}H NMR in pyridine-d_5. [b] >100% yield probably due to presence of solvent. [c] Melt contained infusible particulates.

Table III
Melt Spinning of Polyhydrocarbons and Copoly(hydrocarbon–azomethines)

polymer	η_{inh}	PMT	molding temp for spinning cylinder, °C	spinneret hole size $D \times L$, μm	spinneret temp, °C	extrusn pressure, MPa	windup speed, m/min	tensile properties[a] T, g/denier	E, %	M_i, g/denier	den	OA 2θ
A	0.14	140	140	178 × 356	146	22	238	0.5	3.0	28	7	trace
	0.20		140	178 × 356	172	4.5–6.9	48	1.0	3.4	32	16	trace
	pt sol	150	160	178 × 890	202	2.6–2.9	16	0.9	4.0	56	42	42
	0.30	180	290	230 × 760	305	0.69	411	1.4	2.7	120	13	31
	0.3	180	290	230 × 760	305	0.69	456	1.4	1.1	170	11	<31
	0.33		240	230 × 890	300–312	5.5–6.9	<1	1.3	1.7	127	84	
	0.35	230	230	230 × 890	310–370	5.5–14	free fall	1.6	1.7	113	284	28
D	0.35	300	260	230 × 770	305–320	>5.5	<10		brittle			~60
E-1	0.93	207	190	230 × 690	230	5.5	102		brittle			none
F-2	insol	250	245	230 × 890	295	0.69	320	0.7	0.5	131	22	

[a] To convert to dN/tex = decinewtons/tex (tex = wt in grams per 10 000 meters of fiber), multiply by 0.883.

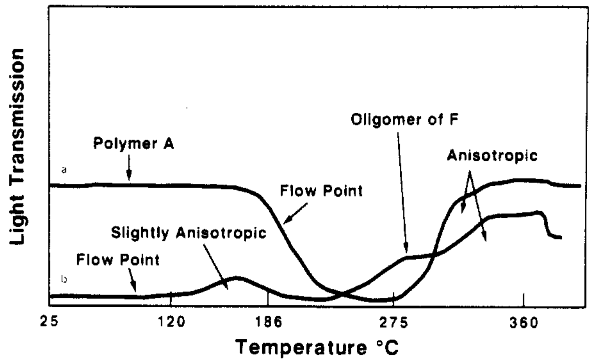
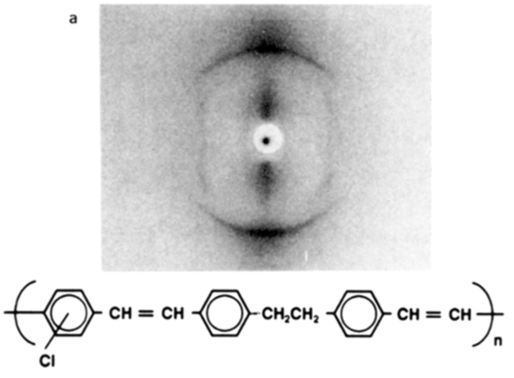


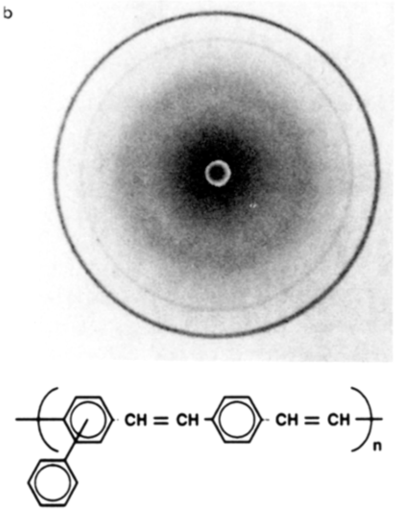
Figure 6. Thermal optical test on polymer A and the aldehyde-ended oligomer of polymer F. Particles of polymer A and oligomer F were pressed at 192 and 135 °C. Heating rate was 48.6 °C/min.

probably helps to damp out chain perturbations from linearity due to (Z)-1,2-ethenediyl links. (The crankshaftlike 1,2-ethanediyl linkage is responsible for the dramatic configurational difference between the α and β forms of poly(p-xylylene); the α form's benzene rings lie parallel but stepwise, whereas the β form's benzene rings lie both parallel and coplanar.[14]) On the other hand, polymer E-1 has an even higher Z isomer content (Z/E = 0.81–0.94) and does not contain connecting linkages which damp out the effects of the Z units. Furthermore, E-1 contains the large lateral side group, phenyl, which is another disturbing influence to melt anisotropy. The effect of the latter can be reduced by the copolymerization with a substituent-free comonomer as in E-2, which does indeed result in melt anisotropy. Unfortunately, the polymerization procedure employed, due to unequal reactivity of monomers, apparently introduces too many high melting blocks of the unsubstituted repeat units in the polymer which form infusible particulates that persist in the melt to >400 °C. To increase the degree of anisotropy for this type of polymer without particulate formation, it would probably be more desirable to keep to a minimum the substituent-free repeat unit and use a modification of the synthesis which might give more E isomer such as that reported recently with phosphorus ylides based on the dibenzophosphole ring system.[15] Iodine catalyzed Z to E would be an alternative if a suitable medium could be identified for the transformation either on polymer or a fabricated form of it.

Preparation of Fibers of Polyhydrocarbons and Their Properties. Fibers have been demonstrated from all of the polyhydrocarbons listed in Table I. However, only A, D, and E-1 were continuously melt extruded. Fibers from B, C, and E-2 were prepared by pulling from the polymer melts on a hot bar and were all brittle and virtually unoriented by X-ray diffraction. For B and C, the poor quality fibers were probably due to low molecular weight and for E-2 the presence of particulates in the melt. Of the systems which were melt extruded, substantial effort was put into spinning A and E-1. Conditions for spinning A are shown in Table III. Again, at the lowest molecular weights, fibers obtained were virtually unoriented because they were spun from melts with low degrees of anisotropy and fast relaxation times. (This means



Anisotropic



Shear anisotropic

Figure 7. WAXS pattern of free fall (no spin stretch) filament from polymer A versus polymer E-1 wound up at 109 m/min.

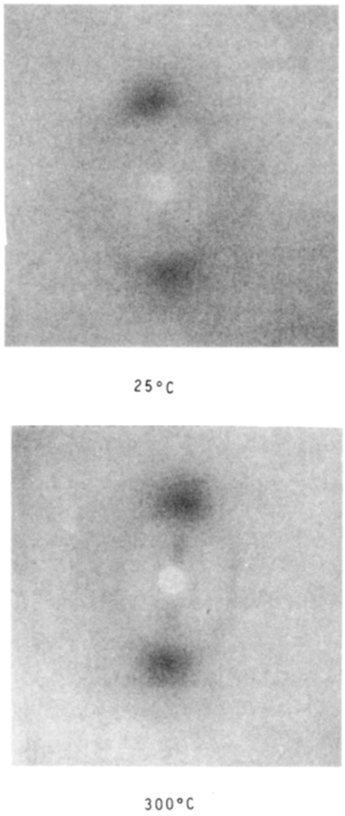


Figure 8. WAXS pattern of as-spun fibers of polymer A at 25 °C and after heating to 300 °C in an X-ray diffraction chamber.

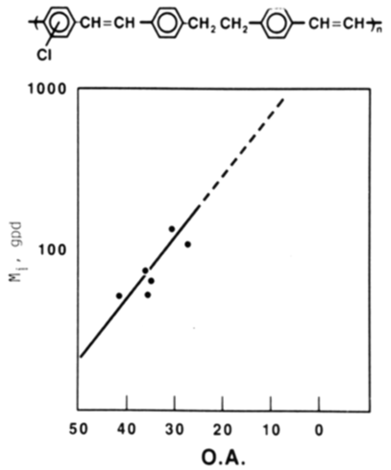
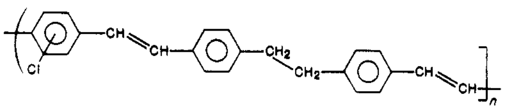
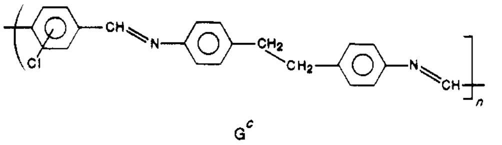
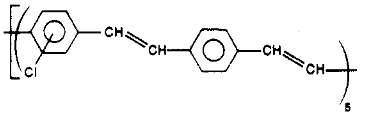
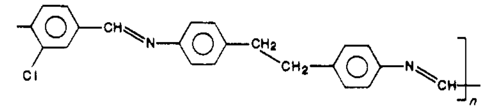


Figure 9. Initial modulus versus X-ray OA for polymer A.

that the orientation achieved in the melt is lost quickly.) On the other hand, higher molecular weight anisotropic melts gave fibers with significant orientation along the fiber axis as measured by X-ray diffraction (see Figure 7a) even when no spin stretch was applied to the extrudate. The latter behavior is characteristic of liquid crystalline melts with long relaxation times. [It is worth noting that orientation is maintained at 300 °C, which is greater than the PMT (see Figure 8).] Unfortunately, the extrudates from the higher molecular weight samples could not be attenuated very well (compare the sample with η_{inh} 0.14 with that of η_{inh} 0.35), which prevents the achievement of very high levels of molecular orientation for development of high mechanical properties, especially initial modulus. Figure 9 shows a plot of initial modulus versus orientation and illustrates the latter point: the curve extrapolates to much higher modulus as chain orientation improves along the fiber axis. This projection gains support when one considers that polymer A is the hydrocarbon analogue of a polyazomethine already (see polymer G, Table IV) demonstrated to give high modulus fibers[9] and that the hydrocarbon in an all *E* configuration would be expected to be at least as rectilinear as or perhaps more rectilinear than a trans azomethine. For the hydrocarbon there is appreciably less twisting of the benzylidine rings out of the C—C=C—C plane (X-ray evidence shows 3.4° and 6.8° for the two centrosymmetric centers in (*E*)-stilbene[16]) than for the aromatic rings in an azomethine.[17] For benzylidineaniline in the solid-state, X-ray evidence shows that the aniline ring is twisted out of the C—N=C—C plane by 55° and the benzylidine ring is twisted in the opposite direction by 10°. Nevertheless, the angles in the azomethine unit have been determined to deviate from parallel extension by only 2.8°.[17] What this all adds up to is that there is probably little difference in the two classes of polymers with respect to chain extension but the hydrocarbon chains may pack together better because there is less twisting of the aromatic rings. Strength development is also a function of molecular orientation but is highly dependent on molecular weight. The end groups in these polymers prepared via the Wittig reaction do not appear to undergo solid-state coupling for increasing molecular weights, therefore their strengths do not increase upon heat treatment unlike a number of other classes of thermotropic melt polymers.[6] On the other hand, aldehyde ended oligomers can be chain extended with diamines to give pseudo-polyhydrocarbons which develop good strength

Table IV
Fibers of Polymer A versus Its Poly(azomethine) Analogue and Block Copolymer from 1,2-Bis(4-aminophenyl)ethane Coupled Aldehyde-Ended (Chloro-1,4-phenylene)-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl Oligomer

polymer	η_{inh}	PMT, °C	tenacity, g/denier	elongation, %	init modulus, g/denier	X-ray OA 2θ
 A	0.35[a]	230	AS, 1.6 HT, little change[b]	1.5	133	28
 G[c]	0.40[d]	260	AS, 3.6 HT,[e] 21	1.3 4.3	400 447	25 9
	insol[d]	250	AS, 0.7	0.5	131	
			HT,[f] 3.6	1.8	201	
	insol[d]	280	HT,[g] 9–13	1.7–1.9	565–710	15
 F-2						

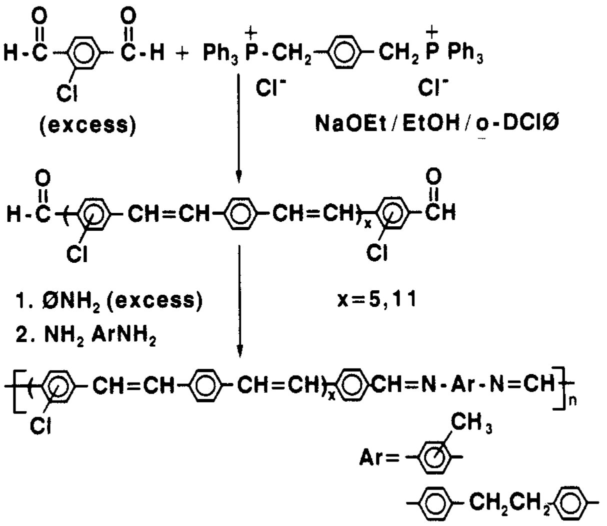
[a] Concentration, 0.5 g/dL *p*-chlorophenol/*p*-dichlorobenzene (70/30 v/v) at 30 °C. [b] Heat treatment at ≥180 °C. [c] Data from: Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729. [d] Concentration, 0.5 g/dL concentrated H_2SO_4. [e] Heated 2 h, 150 °C; 2 h, 260 °C. [f] Heat treatment was 0.5 h, 200 °C; 0.5 h, 240 °C; 1.6 h, 280 °C. [g] Heat treatment was 1 h, 220 °C; 1.5 h, 275 °C.

upon heat treatment [see discussion below on block copoly(hydrocarbon–azomethines)].

In contrast to polymer A, polymer E-1, which exhibits only shear anisotropy (anisotropy imparted via a shear force) with fast relaxation times, gave unoriented (see X-ray diffraction pattern in Figure 7b) relatively brittle fibers even when well attenuated during spinning (Table III). The high level of disorder imparted to the system by the high *Z*/*E* ratio simply overwhelms local order within the polymer melt which gives rise to shear anisotropy and which apparently is not sustained during spinning. In case of polymer D which exhibits melt anisotropy, the melt could not be easily attenuated during spinning (Table III) and gave poorly oriented brittle fibers versus polymer A.

Preparation and Characterization of Block Copoly(hydrocarbon–azomethines). The copoly(hydrocarbon–azomethines) were prepared in three stages as shown in Scheme II. The aldehyde ended hydrocarbon block was prepared via the Wittig reaction as described above but using an excess of the dialdehyde. The oligomer was isolated and its aldehyde end groups determined via oximation (see Experimental Section) in hexamethylphosphoramide (*carcinogen*, take appropriate safety precautions). The polymers described in this paper were prepared from oligomers with degrees of polymerization of 5 and 11. The assumption made in calculating the degree of polymerization is that the bis(triphenylphosphorous) based end group concentration is small versus the aldehyde concentration. In the case of oligomer with DP of 11, the phosphorus content was only 23 equiv/g versus 673 equiv of aldehyde/g. The infrared spectra of the oligomers showed the expected aldehyde absorption at 1695 cm^{-1} (see Figure 1b for oligomer with a DP of 5). The oligomers were fusible materials with a PMT on hot bar of 140 °C for a DP of 5 and 160 °C for a DP of 11. They also exhibit thermotropic behavior when observed with a polarizing microscope and passed the thermal optical test (TOT).[6] Figure 6 shows the TOT curve for the oligomer with a DP of 5.

Scheme II
Prepartion of Block Copoly(hydrocarbon–azomethines)



The next step in the scheme for preparation of the copoly(hydrocarbon–azomethines) was conversion of aldehyde ends to azomethines by treatment with aniline. This was done to moderate the rate of final coupling of the oligomers with diamines so that the molecular weight of the resulting polymers would remain low enough to maintain fusibility and therefore processibility. The technique of moderating the rate of polymerization via use of dianils in place of dialdehydes was described previously for preparation of high molecular weight azomethine via melt polymerizations.[9] Without isolation, the anil ended oligomers were treated with either 1,2-bis(4-aminophenyl)ethane or 2-methyl-1,4-phenylenediamine to form high molecular weight polymers. The infrared spectra of poly(hydrocarbon–azomethines) prepared from hydrocarbon oligomer with a DP of 5 and these diamines are shown in parts C and D of Figure 1, respectively, where

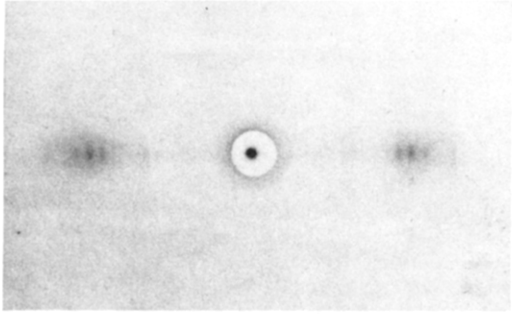


Figure 10. WAXS pattern of heat-treated fibers of polymer F-2.

the azomethine absorption is at 1618 cm^{-1}. Note the complete absence of aldehyde absorption at 1695 cm^{-1}.

A number of solvents including sulfuric acid were tried for η_{inh} measurements but none dissolved the polymers. The polymers were fusible but their melting points increase on heating due to postpolymerization to the point where they became infusible. This behavior is similar to that recently described for aromatic poly(azomethine) and aromatic poly(azomethine) polymers containing flexible units.[9,18]

Optical Melt Anisotropy. The copoly(hydrocarbon–azomethines) shown in Table I exhibit melt anisotropy as would be expected from the melt anisotropic nature of the hydrocarbon oligomers from which they were prepared. These polymers can be viewed as pseudo-polyhydrocarbons since they contain only a small number of azomethine connecting linkages in chain which are similar to the 1,2-ethenediyl links. This allows one to judge the potential of the polyhydrocarbon systems for forming materials with high mechanical properties if they could be formed in and/or postpolymerized to high molecular weight.

Preparation of Fibers of Block Copoly(hydrocarbon–azomethines). Because of the rapid postpolymerization of anisotropic melts of copoly(hydrocarbon–azomethines) to infusible solids, fabrication was generally carried out from small pools formed from melting the polymers on a gradient temperature bar. Fibers several inches long were spun by withdrawing forcep tips from the melt in a steady but rapid motion as previously for aromatic polyazomethines.[9] Fibers could be withdrawn from the melt pools just above the melting point for F-1 and F-2 shown in Table I, but these gave relatively poor properties versus those withdrawn at higher temperatures, e.g., 390 °C for both F-1 and F-2. The exception to this method of fabrication was an extrusion of a fairly low melting sample of polymer F-2 (Table IV). After spinning, the fibers were then heat treated as described previously for aromatic polyazomethines[9] in order to increase molecular weight and crystalline order for improved properties. For polymer F-2, properties for as-spun and heat-treated (conditions for heat treatment shown in footnotes of table) fibers are shown in Table IV. For fibers prepared by extrusion, properties increased upon heat treatment but only to moderate levels. In contrast, properties of heat-treated fibers obtained from the melt pool are quite high. Although the strength is lower than for aromatic polyazomethines reported on previously (e.g., see entry G in Table IV), the modulus is quite high and compares favorably with polymer G and a number of other aromatic polyazomethines[9] and also with aromatic polyazomethines containing short flexible connecting linkages.[18] The high initial modulus for fibers of F-1 and F-2 (Table IV) are in accord with their very good orientation (see Figure 10 for X-ray orientation of heat-treated F-2). The diamine effect on properties does not appear to be all that significant based on the work done to date. Polymers F-1 and F-2 give properties in the same general range. This is to be expected since the crankshaftlike 1,2-ethanediyl link in F-2 would be expected to conform to the major component of the polymer, i.e., the hydrocarbon block, about as well as an azomethine or a 1,2-ethenediyl link.

Summary and Conclusions

Thermotropic melt forming main-chain polyhydrocarbons have been prepared for the first time. The key to the preparation of this new class of thermotropic polymers was the preparation of relatively high molecular weight polymers, via the Wittig reaction, containing appropriately arranged arylene (1,4-phenylene, 2,5- and 2,6-naphthalene, or 9,10-anthracene), 1,2-ethenediyl and -ethanediyl subunits in the polymer backbone, and asymmetric substitution (chloro and phenyl) of 1,4-phenylene. The latter resulted in reduction of the polymer melt temperature to below decomposition. Melt anisotropy was enhanced by the presence of *trans*-1,2-ethenediyl versus *cis*-1,2-ethenediyl subunits in the polymer chains. The large lateral group, phenyl, inhibits melt anisotropy versus the smaller chloro substituent. This is especially true for the polymers examined which contain a large number *cis*-1,2-ethenediyl units in their backbone. The thermotropic melts, given sufficient molecular weights, form oriented fibers which do not improve in their strength when heat treated due to lack of reactive end groups for solid-state reaction. On the other hand, the initial modulus was a function of polymer orientation and extrapolated to very high values at high degrees of orientation.

The high mechanical property potential of the above hydrocarbons was demonstrated by using a procedure where aldehyde ended hydrocarbon blocks were coupled with diamines to give thermotropic block copoly(hydrocarbon–azomethines). These pseudo-polyhydrocarbons (a few of the CH=N units replace CH=CH) can be melt spun into fibers which can be postpolymerized in the solid state by heat treatment to give high tenacity and high modulus fibers.

Experimental Section

Intermediates. Terephthalaldehyde. Terephthalaldehyde was purchased from Aldrich Chemical Co. and purified by sublimation at reduced pressure. The melting point was 115 °C, and the purity by vapor pressure chromatography (VPC) was 99.4–99.6%.

2-Chloroterephthalaldehyde. 2-Chloroterephthalaldehyde was prepared from 2-chloro-*p*-xylene as described by Naylor[19] for dihalogeno-substituted terephthalaldehyde. The intermediate chloroterephthalaldehyde tetraacetate, recrystallized from methanol, melted at 105–108 °C. The acetate was hydrolyzed with sulfuric acid in aqueous ethanol. The aldehyde was recrystallized from *n*-hexane and melted at 79–80.5 °C.

2-Methyl-1,4-phenylenediamine. The diamine was purchased in an impure form as the dihydrochloride or the sulfate. The free diamine is exceptionally air and light sensitive.

The diamine was obtained as the free base by treating the salt with aqueous concentrated ammonium hydroxide, separating the diamine as an oil, distilling the oil from granular zinc (5–10 mol %) through an efficient column, and collecting the water-white diamine in 50-mL flasks for storage in a drybox in low light. The flasks were opened and used only in the nitrogen-filled drybox. The pure diamine has a melting point of 64 °C and a boiling point of 274 °C (760 Torr).

4,4′-Diaminodiphenylethane. The diamine was purchased from Eastman Chemical Co. and sublimed at 140 °C and 0.25 Torr prior to use: mp 138–140 °C.

4,4′-Bis[(triphenylphosphonio)methyl]bibenzyl Dibromide. This material was prepared via a sequence of reducing 4,4′-dicarbomethoxybibenzyl with $LiAlH_4$ in THF and converting the diol to 4,4′-bis(bromomethyl)bibenzyl [mp 114–119 °C, NMR

CD_3COCD_3 singlets at d 2.90 (4 bibenzyl H) and 4.58 (4 dibromomethyl H)] in $CHCl_3$ followed by treating the dibromide as follows with triphenylphosphine to give the bisphosphonium salt: 27.2 g (0.074 mol) of 4,4′-bis(bromomethyl)bibenzyl in 230 mL of DMF was treated with 42.9 g (0.16 mol) triphenylphosphine at reflux overnight. The solid which precipitated during this time was collected by suction filtration and washed several times with DMF and then with ether. The phosphonium salt was dried in a 100 °C vacuum oven. Yield, 60 g (91%); mp >400 °C; IR max 1430 cm^{-1} (C—P=). The material was used without further purification.

4,4′-Bis[(tributylphosphonio)methyl]bibenzyl Dibromide. The bisphosphonium salt was prepared from 4,4′-bis(bromomethyl)bibenzyl and tributylphosphene in an analogous way to the above reaction. The melting point range was broad: 66–74 °C.

***p*-Xylylenebis(triphenylphosphonium bromide).** Aldrich Chemical Co.: mp >300 °C.

***p*-Xylylenebis(tributylphosphonium chloride).** Prepared from *p*-xylylene dichloride and tributylphosphine in *N*,*N*′-dimethylformamide mp 276-279 °C.

1,5-Bis[(triphenylphosphonio)methyl]naphthalene dibromide was prepared according to a procedure described in the ref 20.

2,6-Bis[(triphenylphosphonio)methyl]naphthalene dibromide was prepared via a procedure analogous to that for the 1,5-isomer above.

Preparation of Polymers. Low Molecular Weight Polymer A. To a 1-L 3-necked round-bottom flask equipped with a mechanical stirrer, drying tube, N_2 line, and dropping funnel were added 450 mL of *o*-dichlorobenzene (dried over molecular sieves), 100 mL of absolute ethanol, 5.62 g (33.3 mmol) of 2-chloroterephthalaldehyde, and 29.74 g (33.3 mmol) of 4,4′-bis[(triphenylphosphonio)methyl]bibenzylidene dibromide. To the heterogeneous mixture stirring at room temperature was added dropwise over a 3-h period a solution of 3.77 g (69.8 mmol) of NaOMe in 250 mL of absolute ethanol. The reaction mixture was stirred overnight at room temperature during which time the polymer coagulated into a gum. After a total reaction time of 22 h the somewhat translucent yellow solution phase was decanted and discarded. About 500 mL of ethanol was added to the gummy residue. Addition of the ethanol caused the polymer to harden. The ethanol extract was decanted and discarded. The polymer was stirred with ~300 mL of EtOH and filtered by suction over a sintered glass Buchner funnel. The filter cake was washed with ethanol in the funnel and was ground with a pestle. The polymer was washed four times in a beaker with 50% hot aqueous ethanol and then with hot ethanol. The filter cake was dried in a 100 °C vacuum oven. Yield, 5.6 g (54%) canary yellow polymer; η_{inh} 0.14 (benzyl benzoate); percent phosphorus 0.19%. The spectrum exhibits strong absorption at 960 cm^{-1} (CH out-of-plane (*E*)-1,2-ethenediyl) and weak absorption at 1686 cm^{-1} (unreacted aldehyde). The ^1H NMR spectrum (Figure 2a,b) determined in $CDCl_3$ is consistent with assigned structure.

High Molecular Weight Polymer A. To a solution of 3.36 g (20 mmol) of 2-chloroterephthalaldehyde and 15.46 g (20 mmol) 4,4′-bis(tributylphosphoniomethyl)bibenzylidene dibromide in 300 mL of *o*-dichlorobenzene and 30 mL of absolute ethanol was added a solution of 2.26 g (41.8 mmol) of sodium methoxide in 100 mL of ethanol from a dropping funnel over a 2-min period. During addition of the methoxide solution the polymer began to precipitate. The reaction was stirred for 2.5 days. Polymers was worked up in similar fashion to that described above. Yield, 5.5 g (81% theory); η_{inh} 0.35 (*p*-dichlorobenzene/*p*-chlorophenol 30/70 v/v) at 135 °C. The infrared spectrum exhibited less absorption due to unreacted aldehyde than above polymer from the bis(triphenylphosphonium) salt.

Poly(1,4-phenylene-1,2-ethenediyl-1,4-phenylene-1,2-ethanediyl-1,4-phenylene-1,2-ethenediyl). To a 500-mL 3-necked round-bottom flask with a condenser, drying tube, mechanical stirrer, and nitrogen line were added 300 mL of *o*-dichlorobenzene, 30 mL of absolute ethanol, 15.46 g (0.02 mol) of 4,4′-bis[(tri-*n*-butylphosphonio)methyl]dibenzylidene dibromide, and 2.68 g (0.02 mol) of terephthalaldehyde. To the slurry was added over a 1-min period 2.26 g (0.042 mol) of sodium methoxide in 100 mL of absolute ethanol. The polymer began to precipitate immediately and the yellow slurry was stirred for 68 h at 55 °C and then cooled to room temperature. Ethanol (200 mL) was added and the reaction mixture was filtered by suction over a sintered glass Buchner funnel. The polymer was washed thrice in a beaker with hot ethanol/water (50/50) followed by hot ethanol. The polymer was dried in a 100 °C vacuum oven. Yield, 4.7 g (76%); polymer melt temperature (PMT) >400 °C on a hot bar.

Polymer B. To a slurry of 8.38 g (10 mmol) of 2,6-bis[(triphenylphosphonio)methyl]naphthalene dibromide and 1.68 g (10 mmol) of 2-chloroterephthalaldehyde in 150 mL of *o*-dichlorobenzene and 15 mL of absolute ethanol at 55 °C was added from a dropping funnel over a 1-min period a solution of 1.13 g (20.9 mmol) of sodium methoxide in 50 mL of ethanol. The yellowish orange polymer began to precipitate during the next hour from the initially translucent opaque reaction mixture. The reaction was stirred overnight at ~55 °C after which 200 mL of ethanol was added. The reaction mixture was allowed to cool to room temperature. The polymer was collected by suction filtration over a sintered Buchner funnel. The polymer was washed twice in a beaker on hot plate containing 50% aqueous ethanol and then with ethanol. The polymer was dried in a 100 °C vacuum oven. Yield, 0.3 g (10%). The low isolated yield was probably due to polymer solubility in workup media. η_{inh} 0.23 (*p*-dichlorobenzene/*p*-chlorophenol 30/70 v/v at 150 °C).

Polymer C. To a slurry of 8.38 g (10 mmol) of 1,5-bis[(triphenylphosphonio)methyl]naphthalene dibromide and 1.68 g (10 mmol) of 2-chloroterephthalaldehyde in 150 mL of *o*-dichlorobenzene and 15 mL of ethanol at 55 °C was added over a 1-min period a solution of 1.13 g (20.9 mmol) of sodium methoxide. The reaction became a translucent solution during the next minute and gave a precipitate during the next hour. The reaction was stirred overnight, and then 200 mL of ethanol was added. The reaction mixture was allowed to cool to room temperature and then filtered by suction. The gummy product was triturated with ethanol by means of a mortar and pestle. The resulting granular polymer was washed successively thrice with hot 50% aqueous ethanol and once with ethanol. The polymer was dried in a 100 °C vacuum oven. Yield, 1.2 g (42%); η_{inh} 0.24 (*p*-dichlorobenzene/*p*-chlorophenol 30/70, v/v at 150 °C); PMT 200 °C.

Polymer D. To a solution of 2.34 g (10 mmol) of 9,10-anthracenedicarboxaldehyde, 1.68 g (10 mmol) of 2-chloroterephthalaldehyde, and 15.45 g (20 mmol) of 4,4′-bis[(tributylphosphonio)methyl]bibenzylidene dibromide in 300 mL of *o*-dichlorobenzene and 30 mL of ethanol at 55 °C was added a solution of 2.26 g (41.8 mmol) of sodium methoxide in 100 mL of ethanol. The polymer began to precipitate during addition of the NaOMe. The reaction was stirred over the weekend and worked up by adding 200 mL of ethanol followed by filtration. The polymer was washed by stirring magnetically in 60 mL of boiling 50% aqueous ethanol. This was repeated four times after which the polymer was washed with hot ethanol. The polymer was dried in a vacuum oven. Yield, 6.5 g (87%); η_{inh} 0.35 (*p*-dichlorobenzene/*p*-chlorobenzene 30/70 v/v at 135 °C).

Polymer E-1. To a dry 500-mL 3-necked round-bottom flask were added 7.76 g (0.01 mol) of (2-phenyl-*p*-xylylene)bis(triphenylphosphonium chloride), 1.34 g (0.01 mol) of terephthaldehyde, 75 mL of 1,2,4-trichlorobenzene, and 7.5 mL absolute ethanol. A glass stirrer with a Teflon blade was inserted and a condenser with a drying tube was attached and the assembly transferred to a hood and connected to a nitrogen line and "Motomatic" stirrer. The mixture was warmed to 50 °C whereupon a solution was obtained. After the solution cooled to room temperature, a solution of 1.2 g (0.022 mol) of NaOMe in 62 mL of absolute ethanol was added from a dropping funnel over ~70 s. A deep reddish brown color developed where the two solutions came into contact. After a few minutes the cloudy orange mixture turned yellow and became more fluorescent and after a total of 10 min a gummy product began forming. The mixture was stirred overnight (~17 h) and then allowed to stand for about 1 h. At this point 100 mL of the translucent upper liquid layer was removed by pipeting. Ethanol (100 mL) was added to the residual material and the mixture was stirred and cooled in "dry ice". The mixture was filtered by suction and the filter cake washed thrice by stirring at room temperature in 200-mL aliquots of ethanol. After the mixture was dried overnight in a 100 °C vacuum (~380 mm) oven, 3.0 g (108%) of a bright yellow fluorescent solid was obtained. The >100% yield is probably due to retained solvent (based on TGA in N_2). The η_{inh} (dL/g)/concentration (g/dL) data in 1,2,4-trichlorobenzene/*p*-chlorophenol (50/50, v/v) were as follows: 0.62/0.125; 0.93/0.063; 0.95/0.031. PMT 207 °C.

Polymer E-2. To a dry 500-mL round-bottom flask were added 5.43 g (0.007 mol) of (2-phenyl-*p*-xylylene)bis(triphenylphosphonium chloride), 2.34 g (0.003 mol) of *p*-xylylenebis(triphenylphosphonium bromide), and 1.34 g (0.01 mol) of terephthaldehyde, all in 75 mL of 1,2,4-trichlorobenzene and 75 mL of ethanol. To this slurry was added a solution of 1.2 g (0.022 mol) of sodium methoxide in 62 mL of ethanol. The slurry dissolved upon addition of the ethanol and the solution remained clear for ~3 min then became progressively cloudier. The mixture was stirred overnight and allowed to stand over the weekend. The upper portion of liquid was decanted and the solid filtered by suction and washed 3× with 100-mL aliquots of ethanol. After drying at 90 °C in a vacuum oven, the yield of polymer was 2.1 g (82%). Polymer stick temperature (PST) ~211 °C; PMT 220 °C.

Preparation of Copoly(hydrocarbon-azomethines). Aldehyde-Ended Oligomer F. To 30 mL of absolute EtOH and 300 mL of *o*-dichlorobenzene at room temperature in a three-necked 1-L round-bottom flask with mechanical stirrer, N_2 bleed, drying tube, and dropping funnel were added 26.07 (0.045 mol) of 1,4-bis[(triphenylphosphonio)methyl]benzene dichloride and 10.11 g (0.060 mol) of 2-chloroterephthalaldehyde. To the resulting solution 5.1 g (0.094 mol) of NaOMe in 250 mL of absolute ethanol was added over a 50-s period during which time the reaction became cloudy. The mixture was stirred for 2 h; then to the precipitate which formed, 500 mL of absolute EtOH was added. The product was filtered by suction and the filter cake was collected and transferred to a beaker and stirred magnetically under N_2 near the boil in 50 mL of each EtOH and water. The product was filtered by suction. The agglomerated filter cake was ground in EtOH in a mortar with a pestle and refiltered. The filter cake was washed thrice more with EtOH/water as above and then twice with hot EtOH. The product was dried overnight in a 65 °C vacuum oven. Yield, 6.7 g (51%). The material had an η_{inh} of 0.08 (0.5 wt % in 1,2,4-trichlorobenzene/*o*-dichlorobenzene 50/50 v/v. PMT ~140 °C. Brittle fibers were pulled from hot bar at 170 °C. The melt exhibits some degree of anisotropy (see TOT test, Figure 6b). Aldehyde end groups (see Figure 1B for infrared spectrum) were determined by oximation[21] in hexamethylphosphoramide with 2-chloroterephthalaldehyde as a standard. The oximation procedure applied was a modification of that used in ref 21 in that it was necessary to use hexamethylphosphoramide to dissolve the oligomers. Aldehyde ends, 1494 μequiv/g; calculated molecular weight, 1340 equiv per 5 repeat units. An oligomer with 673 μequiv/g (molecular weight 2870, 11 repeat units) was prepared by a similar procedure starting with 0.0203 mol of bis(phosphonium salt and 0.0225 mol of dialdehyde. This sample also showed the presence of 23 μequiv/g of phosphorus. PMT 160 °C; η_{inh} 0.10.

Preparation of Copoly(hydrocarbon-azomethine) F-2. To a polymerization tube equipped with a side-arm takeoff were added, in order, 2.2 g (1.6 mmol) of aldehyde ended oligomer F, 2.2 g (2.3 mmol) of aniline, and 5 mL of *o*-dichlorobenzene. This was followed by 1,2-bis(4-aminophenyl)ethane (0.56 g, 2.6 mmol) and 2 mL of *o*-dichlorobenzene. A capillary was inserted into the reaction mixture and the system purged with nitrogen. The mixture was heated in an *o*-dichlorobenzene vapor bath (179 °C) for 45 min during which time it began to form an orange precipitate. The mixture was then transferred to a 222 °C vapor bath (methyl salicylate) where bumping occurred and aniline solid collected in the receiver flask. The collected material was transferred back to the polymerization tube. Another attempt gave similar results. The total time at 222 °C was 90 min. Again the material which came over was transferred back to the polymerization tube and distillation was carried out instead by using a 179 °C vapor bath over 0.5 h. The tube was again heated in 222 °C vapor bath for 40 min and finally in a 259 °C vapor bath (diphenyl ether) under 380 mmHg vacuum. The polymerization tube was allowed to cool to room temperature and 2.5 g of polymer collected. Figure 1C shows the IR spectrum of the product and indicates complete reaction of aldehyde. PMT was 280 °C. The sample contained some volatile material, likely *o*-dichlorobenzene, and was not completely homogenous in the melt. Fibers could be pulled from the hot bar at 320 °C but these were brittle compared to those pulled at a higher temperature (390 °C). By using a similar procedure but with an oligomer having a DP of 11, versus 5 above, and 0.20 g (0.94 mmol) of the diamine, 2 g of polymer was isolated which left a trail on hot bar at 370 °C but did not give a true melt even at 400 °C. This polymer when analyzed by TGA in nitrogen retained 80% of its weight at 700 °C.

Preparation of Copoly(hydrocarbon-azomethine) F-1. This polymer was prepared by a procedure similar to that for F-2 except for using 2-methyl-1,4-phenylenediamine. See Figure 1D for infrared spectrum. PMT 300 °C.

Characterization of Polymers. NMR Spectra. ^{1}H NMR spectra were recorded on a Nicolet NT-300 spectrophotometer.

Dilute Solution Properties. Inherent viscosity, $\eta_{inh} = \ln(\eta_{rel})/c$, values were determined in several solvents as given in I, II, and IV. It should be noted that in all cases, the solutions were found not stable and gave precipitates of the polymers upon standing.

Polymer Melt Temperature (PMT). Polymer melting was determined on a dry polymer on a chrome-plated gradient temperature bar[22] and is noted as the temperature at which the polymer under moderate sliding pressure leaves a molten trail.

Thermal Analysis. DSC and TGA measurements were made by using Du Pont 900 series instruments. Samples were run at heating rates of 20 °C/min in flowing nitrogen.

Thermal Optical Test. See ref 9 for a detailed description of the test procedure.

Fiber Spinning. Cylinders of polymers molded at temperatures generally below their PMT (see Table III) were spun according to procedure described in ref 9. In those cases where fibers were obtained from a melt pool, the procedure is also described in ref 9.

Fiber Tensile Properties. See ref 9 for procedure.

X-ray Orientation Angle. Wide-angle X-ray diffraction patterns were obtained with a Warhus pinhole camera and Phillips generating unit Model 12045 having a copper fine-focus diffraction tube and nickel β filter. The distance from the film was 50 mm. The arc length in degrees between the half-maximum intensity points of the principal equatorial diffraction spot is reported as the orientation angle of the sample. For measurements made at elevated temperature, the sample holder was surrounded by a heating element.

Acknowledgment. X-ray diffraction patterns were prepared and interpreted by H. Thielke. NMR measurements were made by J. E. Anderson and R. Narvaez.

Registry No. A (copolymer), 118018-57-8; A (SRU), 118101-97-6; B (copolymer), 118018-60-3; B (SRU), 118101-95-4; C (copolymer), 118018-61-4; C (SRU), 118101-94-3; D (copolymer), 118041-61-5; E-1 (copolymer), 118018-63-6; E-1 (SRU), 118101-96-5; E-2 (copolymer), 118018-64-7; F-1 (copolymer), 118018-65-8; F-2 (copolymer), 118018-66-9; (4,4′-bis(tributylphosphoniomethyl)bibenzylidene dibromide)(2-chloroterephthalaldehyde) (copolymer), 118041-60-4; (4,4′-bis(tributylphosphoniomethyl)bibenzylidene dibromide)(terephthalaldehyde) (copolymer), 118018-59-0; (4,4′-bis(tributylphosphoniomethyl)bibenzylidene dibromide)(terephthalaldehyde) (SRU), 118018-67-0.

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Liquid Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 7. Molecular Weight and Composition Effects on the Phase Transitions of Poly(methylsiloxane)s and Poly(methylsiloxane-*co*-dimethylsiloxane)s Containing 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane Side Groups[†]

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ABSTRACT: The synthesis of poly(methylsiloxane)s with different molecular weights and of poly(methylsiloxane-*co*-dimethylsiloxane)s with different molecular weights and compositions, both containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecan-1-yl)-1,2,3-dioxaborinane as side groups, is described. Copolymers containing around 50/50 weight ratios between the polymer backbone and the polymer side chains exhibit two changes in their heat capacity. Sequence distribution considerations, dynamic mechanical thermal analysis measurements, and influence of both molecular weight and copolymer composition on the width of isotropization and transitions are all suggesting that these changes in the heat capacity are most probably associated with two glass transition temperatures. One glass transition temperature was assigned to the independent motion of the polymer backbone and the other to the cooperative (but independent from the polymer backbone) motion of the side groups. Therefore, these copolymers should exhibit an intramolecular microphase-separated morphology. Extrapolation of these two glass transition temperatures suggests that the poly(methylsiloxane) containing mesogenic side groups may also exhibit two glass transition temperatures.

Introduction

Recently we critically reviewed the molecular engineering of thermotropic side-chain liquid crystalline polymers and outlined some of the major problems of synthetic interest which require additional research.[1]

One of the principal problems which deserves additional research is the spacer concept introduced by Ringsdorf et al.[2,3]

This simple and invaluable structural concept led to the development of the entire field of side chain liquid crystalline polymers. However, the spacer concept provides only a partial decoupling of the motions of the side groups from that of the backbone in the liquid crystalline phase.[4-6] Below the glass transition temperature, the motion of the side groups is frozen. This is a very important result based on which many applications of side-chain liquid crystalline polymers are presently considered.

Recently, by analogy with the behavior of block and graft copolymers, we have proposed that highly or even completely decoupled side-chain liquid crystalline polymers would be realized for systems in which the side groups and the polymer backbone are highly immiscible.[7-12] In such systems, for a proper weight ratio between the polymer backbone and its side groups, an intramolecular microphase separation of the side groups from the polymer backbone is realizable and has been observed both by our group[7-12] and by Ringsdorf's group.[13,14] It is expected that for a suitable ratio between the domain sizes of the polymer backbone and the side groups, almost independent motion of the two sybsystems would be achievable. We have observed for a series of systems two changes in heat capacity on the DSC curves and suggested that they are due to the independent motion of the polymer backbone and the cooperative (but independent from the polymer backbone) motion of the side groups. Without any additional support, we have assigned these two changes in the heat capacity to the glass transition temperatures

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[†] Part 6 in this series: ref 64.

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