Although we do not expect true rodlike characteristics at short length scales, we do expect that properties which are sensitive to distances larger than b will be adequately represented by this model.

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(21) If the distance between interchain contact points is ξ and the number of monomers between contact points is g, they are related by the two relations

$$g = \rho\xi^3$$

$$\xi = g^{1/2}(ab)^{1/2}$$

The first of these relations expresses the fact that each monomer has to be between two contact points; the second says that between two contact points we have an ideal single-chain behavior. Solving these equations yields $\xi = (\rho ab)^{-1} = \xi_\rho^{\Theta}$
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Thermal Oligomerization of Bis[4-(3-ethynylphenoxy)phenyl] Sulfone and 4-(3-Ethynylphenoxy)phenyl Phenyl Sulfone

J. M. Pickard* and S. C. Chattoraj

Research Applications Division, Systems Research Laboratories, Inc., Dayton, Ohio 45440

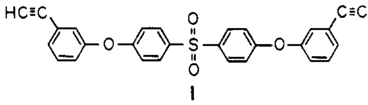
G. A. Loughran and M. T. Ryan

Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433. *Received March 4, 1980*

ABSTRACT: Infrared, ^{1}H NMR, and ^{13}C NMR characterization data are presented for oligomers isolated from the thermal reaction of bis[4-(3-ethynylphenoxy)phenyl] sulfone (**1**) in the initial stages of reaction and 4-(3-ethynylphenoxy)phenyl phenyl sulfone (**2**) up to 90% conversion. Thermal reaction of each monomer at 434 K yields conjugated oligomers having molecular weights of about 2800 as well as lower molecular weight species presumed to consist of dimer and trimer. The IR spectrum of oligomer **1** and its deuterated analogue exhibit bands at 3290 and 2550 cm^{-1}, respectively, which indicates that pendant ethynyl moieties exist in the oligomer. The presence of unsaturation in both oligomers is indicated by the ^{1}H and ^{13}C NMR spectra. Assignments for the aromatic carbons in the ^{13}C NMR spectra for the oligomers are derived from group additivity and are confirmed for oligomer **2** by changes in the ^{13}C NMR spectrum which are induced by the addition of a shift reagent, Eu(fod)$_3$. Tentative assignments are proposed for the α and β carbons of the polyene chains. It is suggested that both oligomers possess a trans-cisoidal conformation.

Introduction

Thermal polymerization of aromatic and heteroaromatic acetylene-terminated monomers yields condensed resins which possess unique thermooxidative and mechanical properties.[1-3] While the mechanism of the reaction is poorly understood, studies based upon observations involving model compounds and selected monomers have suggested that the principal reaction involves dimerization,[4,5] chain extension,[5] and cyclotrimerization.[5,6] Recently, the complexity of the cure reaction has also been eloquently revealed by Schaefer and co-workers,[7] who demonstrated by magic-angle ^{13}C NMR studies that only about 30% of the ethynyl moieties react by cyclotrimerization. Analogies based upon the reactivity of simpler arylacetylenes[8-11] suggest that the primary reaction in the initial curing stage might be one involving the formation of low-molecular-weight polyenes. In order to



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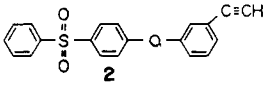

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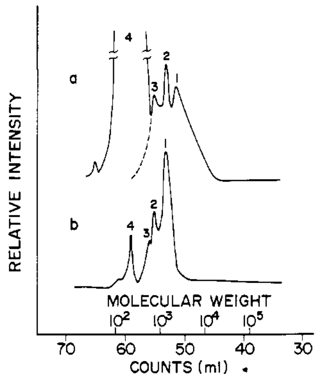


Figure 1. Gel permeation chromatograms at 243 nm for thermal reaction products of acetylene-terminated monomers: (a) monomer 1; (b) monomer 2. Fractions 1–4 refer to oligomer, trimer, dimer, and monomer, respectively. Molecular weights are relative to polystyrene.

examine this possibility, it is of interest to characterize the polymer formed in the pregel stage of thermal reaction of monomer 1, bis[4-(3-ethynylphenoxy)phenyl] sulfone, and that of a suitable model compound, 4-(3-ethynylphenoxy)phenyl phenyl sulfone (2).[12]

The model compound exemplified by monomer 2 would be expected to possess a reactivity comparable to that of monomer 1 as well as those observed for the simpler arylacetylenes. In the present paper, IR, ^1H NMR, and ^{13}C NMR data are presented which support the formation of low-molecular-weight polyenes in the thermal reaction of monomers 1 and 2.

Experimental Section

Monomer Synthesis. Samples of bis[4-(3-ethynylphenoxy)phenyl] sulfone (1) and 4-(3-ethynylphenoxy)phenyl phenyl sulfone (2) were provided by the Polymer Branch of the Air Force Materials Laboratory. The methods of monomer synthesis, which were based upon nucleophilic displacement of halogen from suitable derivatives of diphenyl sulfone, have been described in detail elsewhere.[13]

Briefly, for monomer 1, this involved heating 57.4 g (0.2 mol) of 4,4′-dichlorodiphenyl sulfone with 93.7 g (0.6 mol) of potassium 3-ethynylphenoxide in dry Me_2SO at 100 °C for 144 h. The reaction mixture was extracted with methylene chloride, and the product was subsequently isolated by column chromatography. Final purification was achieved by freeze-drying from benzene, which resulted in 45.0 g (50%) of crystalline monomer 1: mp 14 °C; IR (KBr) 3300 (ethynyl H), 2110 (triple bond) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.9 (m, 2, aromatic H), 7.3 (m, 6, aromatic H), 3.1 (s, 1, ethynyl H); CI mass spectrum, m/z 451 (M + 1); vapor phase osmometry (VPO in CH_2Cl_2), calcd $M_r = 450$, found 434. Anal. Calcd for $C_{28}H_{14}O_4S$: C, 74.64; H, 4.02. Found: C, 74.32; H, 4.00.

Deuteration of 4.0 g (0.0088 mol) of monomer 1 was performed by exchange with excess n-butyllithium and hydrolysis of the resultant lithium salt with excess D_2O. The product was recrystallized three times from a 90:10 (v/v) mixture of hexane and THF to yield 2.0 g (50%) of the deuterated monomer. Subsequent analysis by ^1H NMR indicated that the isotopic composition exceeded 98.2 mol % D.

Monomer 2 was synthesized by heating 5.90 g (0.025 mol) of 4-fluorophenyl phenyl sulfone in dry DMAC with 3.92 g (0.025 mol) of potassium 3-ethynylphenoxide at 80 °C for 1 h. The reaction mixture was quenched with water and the product was extracted with chloroform. After concentration of the chloroform extract, recrystallization from hexane resulted in 6.26 g (75%) of monomer 2: mp 112–113 °C; IR (KBr) 3265 (ethynyl H), 2100 (triple bond) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9 (m, 4, aromatic H), 7.0–7.5 (m, 9, aromatic H), 3.1 (s, 1, ethynyl H). Analysis of monomer 2 by gel permeation chromatography (GPC) revealed that the purity exceeded 99%.

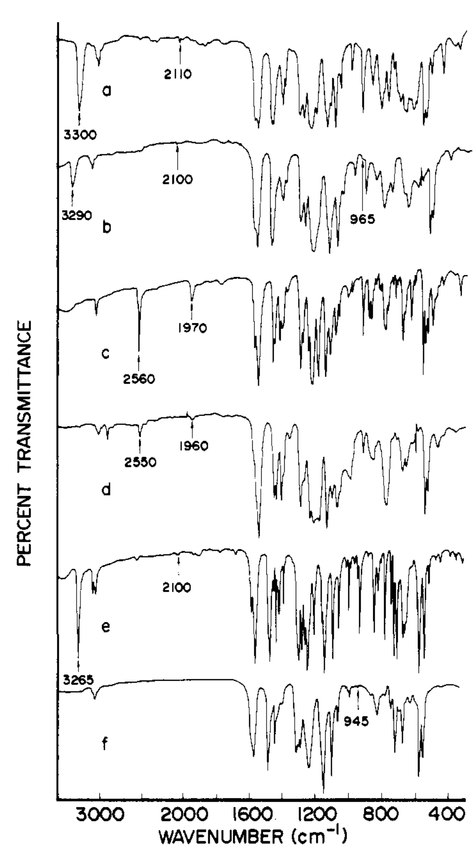


Figure 2. IR spectra of acetylene-terminated monomers and oligomers (KBr matrix): (a) monomer 1; (b) oligomer 1; (c) deuterated monomer 1; (d) oligomer obtained from c; (e) monomer 2; (f) oligomer 2.

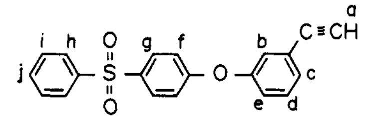
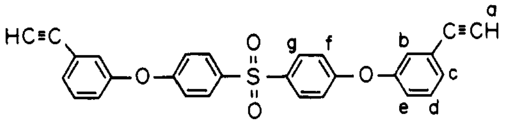
Oligomer Synthesis. Thermal oligomerization of each monomer was conducted in a sealed tube at 434 K under a nitrogen atmosphere. The reaction time for monomer 1 and its deuterated analogue was limited to 0.75 h (~25% conversion) in order to minimize the formation of insoluble cross-linked polymers. Monomer 2 was reacted for 3 h in order to obtain a conversion approaching 90%.

The reaction products for each monomer were dissolved in methylene chloride, and product distributions were determined by GPC analysis at 243 nm in THF with 10^4-, 10^3-, 2 (5×10^2), and 10^2-Å μ-Styragel columns. The reaction products were subsequently isolated from methylene chloride by precipitation with methanol; this precipitation process was repeated three times in order to obtain methanol-insoluble fractions having narrow-molecular-weight distributions. The purified fractions were dried under vacuum at 25 °C for 24 h. Number-average molecular weights for the oligomers were determined with a Mechrolab vapor phase osmometer calibrated against polystyrene standards which, in turn, were standardized against benzil.

Oligomer Characterization. Infrared spectra of the monomers and oligomers were recorded with a Perkin-Elmer 521 infrared spectrophotometer in KBr matrices. Nuclear magnetic resonance spectra were recorded with a Varian XL 100/15 NMR spectrometer interfaced with a Varian VFT-100 computer and gyrocode decoupler. Proton spectra of the monomers (0.2 M in $CDCl_3$) and polymers (0.05 g/mL in $CDCl_3$) as well as those obtained after addition of 0.01–0.07 M tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium, $Eu(fod)_3$, were recorded in the CW mode at 100.1 MHz.

Pulsed FT ^{13}C NMR spectra at 25.2 MHz for monomer and oligomer 1 were recorded in 1.7-mm tubes, while the spectra for monomer and oligomer 2 were recorded in 12-mm tubes. Proton-noise-decoupled spectra of the monomers were obtained with a 65° pulse and a repetition time of 4.8 s, while those of the oligomers and the undecoupled spectra of the monomers were obtained with a 25° pulse and a repetition time of 0.8 s. Noise-off-resonance-decoupled (NORD)[14,15] spectra of the oligomers were recorded in 12-mm tubes. Chemical shifts were measured relative to internal Me_4Si.

Table I
Summary of ^1H NMR Chemical Shifts for Bis[4-(3-ethynylphenoxy)phenyl] Sulfone and 4-(3-Ethynylphenoxy)phenyl Phenyl Sulfone

Structure	Monomer		Oligomer	
	Obs. δ, ppm	Assign.[a]	Obs. δ, ppm	Assign.[a]
	7.9, 8.0	g,h	7.8	g,h
			7.5	i,c,e
	7.5	i,e	6.0 - 7.2	b,d,f, =CH
	7.3	b,e		
	7.2	d		
	7.0	f,j		
	3.1	a		
	7.9	g	7.9	g
	7.3	b,e	7.4	b,e
	7.1	d	6.0 - 7.1	e,d,f,=CH
	7.0	f,c	3.1	a
	3.1	a		

[a] Based on first-order analysis of multiplets.

Results

Oligomer Properties. Figure 1 illustrates the cumulative differential molecular weight distribution obtained by GPC analysis at 243 nm for the thermal reaction products of each monomer. The indicated molecular weights refer to polystyrene. Examination of Figure 1 reveals that oligomerization of each monomer is accompanied by the formation of two lower molecular weight species, which, in view of their relative intensities and elution volumes, may consist of dimer and trimer. A VPO analysis of the methanol-insoluble components (fractions 1 in Figure 1) indicated number-average molecular weights of 2785 and 2620 for oligomers **1** and **2**, respectively. The observed product distributions of each monomer and the molecular weights of the oligomeric fractions closely resemble those obtained from simpler arylacetylene monomers, which are known to form conjugated polymers by thermal polymerization.[8-11]

In order to obtain a qualitative indication of oligomer reactivity, oligomer **2** was subjected to low-pressure reduction over a Pd/charcoal catalyst. This resulted in an absorption of 0.6 mol of H_2/mol of monomer, based upon the number-average degree of polymerization, $DP_n \sim 8$, as determined by VPO analysis. The observed reactivity is similar to those previously reported for thermal polymers derived from simpler monomers,[11] namely, phenylacetylene ($DP_n \sim 20$, 0.2 mol of H_2/mol of monomer) and (3-phenoxyphenyl)acetylene ($DP_n \sim 12$, 0.4 mol of H_2/mol of monomer). Without additional characterization of the reduced oligomers, it is inappropriate to draw definitive conclusions from these data; however, it is of interest to briefly mention two possible explanations for the observed reactivities. First, the mean molecular weight of the three polymers corresponds to 2400; therefore, if the same reaction mechanism were operative, then these data could reflect the presence of a common precursor or end group in each polymer.[8] Secondly, one should recognize that these data also suggest a reactivity which is inversely proportional to the degree of polymerization. This effect might then arise from greater delocalization of π electrons along the polymer backbone, thereby resulting in a more stable polymer. Such a view is consistent with reported kinetics[10] as well as molecular orbital calculations on the polymerization of acetylenic monomers[16,17] which suggest a reduced reactivity with increasing molecular chain length.

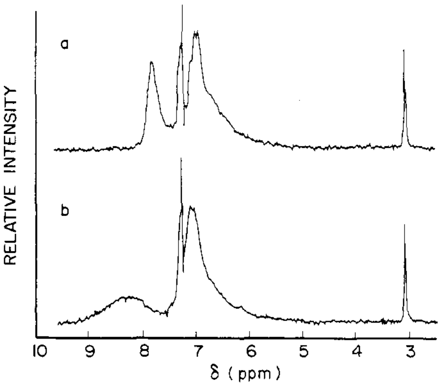


Figure 3. ^1H NMR spectra of oligomer **1**: (a) 0.05 g/mL oligomer in $CDCl_3$ vs. Me_4Si; (b) 0.05 g/mL oligomer with 0.07 M $Eu(fod)_3$ in $CDCl_3$ vs. Me_4Si.

IR Spectra. Infrared spectra of the monomers and the oligomers, corresponding to fraction 1 of the product distributions, are given in Figure 2. The spectra of the normal monomers, Figure 2a,e, exhibit intense bands in the region of 3300 cm^{-1} and weak bands at 2100 cm^{-1} that are characteristic of the carbon-hydrogen and triple-bond stretching motions of the ethynyl groups.[18] In the deuterated monomer, Figure 2c, these vibrations occur at 2560 and 1970 cm^{-1}. In the spectrum of oligomer **2**, shown in Figure 2f, the carbon-hydrogen stretch of the ethynyl moiety is absent. This contrasts sharply with spectra 2b and 2d, which reveals that pendant ethynyl groups, having about half the intensity observed in the initial monomers, are present in oligomer **1**.

Structural and symmetry considerations suggest that all

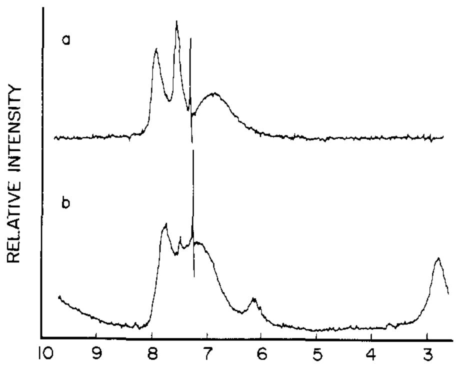


Figure 4. ^1H NMR spectra of oligomer 2: (a) 0.05 g/mL oligomer in $CDCl_3$ vs. Me_4Si; (b) 0.05 g/mL oligomer with 0.05 M $Eu(fod)_3$ in $CDCl_3$ vs. Me_4Si.

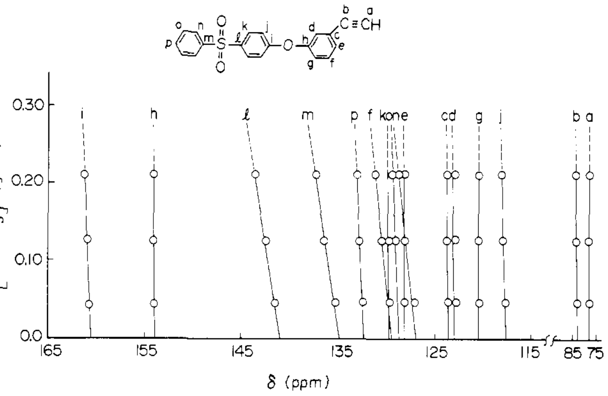
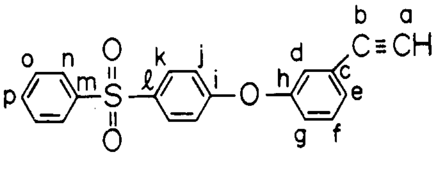


Figure 5. Variation of ^{13}C NMR chemical shifts of 4-(3-ethynylphenoxy)phenyl phenyl sulfone with concentration of $Eu(fod)_3$: 0.2 M monomer in $CDCl_3$ vs. Me_4Si.

normal modes of vibration of both monomers are infrared active and nondegenerate.[19] This inference makes quantitative comparison of the monomer and oligomer spectra in the region below 1600 cm^{-1} difficult; however, certain qualitative comparisons can be made. The possibility that the recurring unit of oligomer 1 is a symmetrical cyclic trimer is unlikely, since none of the oligomer spectra appear to contain a strong band at 1480 cm^{-1}, characteristic of 1,3,5-triarylbenzene moieties.[20] Comparison of the strong bands characteristic of symmetric and antisymmetric stretching of the aryl ether and sulfone moieties[21] in the 1350–1200- and 1150–1060-cm^{-1} regions in the spectra of the monomers and oligomers indicates that these motions are not appreciably perturbed by polymerization. On the other hand, oligomer 1 exhibits a shoulder at 965 cm^{-1}, and oligomer 2 exhibits a weak, but rather distinct, band at 945 cm^{-1}. In the deuterated oligomer, Figure 2d, the expected band or shoulder at 965 cm^{-1} has either shifted due to isotopic substitution or it is obscured by small perturbations associated with adjacent bands. Olefinic carbon–hydrogen deformations of poly(phenylacetylenes)[8,9] are known to occur in this region; although not confirmed from the spectra given in Figure 2, the weak bands observed at 965 and 945 cm^{-1} in the polymers may be associated with unsaturation along the oligomer backbone.

^{1}H NMR Spectra. Proton spectra in the region 3–10 ppm for the oligomers and changes induced by addition of the shift reagent $Eu(fod)_3$ are given in Figures 3 and 4. The spectra of both oligomers exhibit characteristic broad absorption in the region 6–8 ppm which is analogous to that observed in the spectra of poly(phenylacetylenes).[9]

Table II
Summary of ^{13}C NMR Chemical Shifts
for 4-(3-Ethynylphenoxy)phenyl Phenyl Sulfone



Monomer			Oligomer		
δ, ppm			δ, ppm		
Obs.	Calc.	Assign.	Obs.	Calc.	Assign.
78.3		a	128.3		a
82.2		b	153.9		b
117.5		j	117.4		j
120.4	119.3	g	120.0	119.0	g
123.1	123.3	d	118.0	117.5	d
123.6	124.4	c	141.1	140.0	c
126.9		n	126.9		n
128.1	127.3	e	119.0	121.5	e
128.7		o	128.7		o
129.4		k	129.4		k
129.6	130.9	f	129.4	130.7	f
132.4		p	132.5		p
134.9		m	134.7		m
141.2		ℓ	141.1		ℓ
154.0	157.9	h	154.4	157.7	h
160.6		i	160.9		i

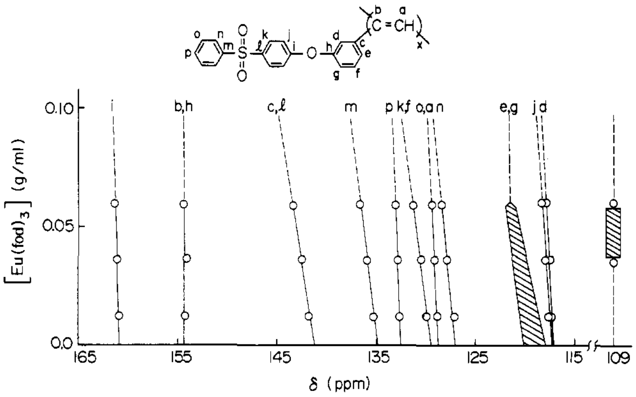
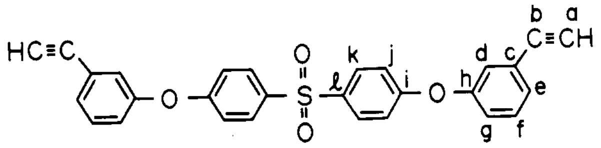


Figure 6. Variation of ^{13}C NMR chemical shifts of oligomer 2 with concentration of $Eu(fod)_3$: 0.05 g/mL oligomer in $CDCl_3$ vs. Me_4Si. Hatched areas represent broad resonance.

Oligomer 1 in Figure 3a shows broad absorption at 7.9, 7.4, and 7.0 ppm with half-band widths, i.e., $\Delta\nu_{1/2}$, of 35, 10, and 35 Hz, respectively, as well as a sharp resonance at 7.2 ppm due to a $CHCl_3$ impurity in the solvent. The absorption at 7.0 ppm is asymmetric and decreases toward the base line at 6.0 ppm. There is also a resonance centered at 3.1 ppm, indicative of pendant ethynyl moieties. The ratio of intensity of the total aromatic and vinyl protons to that of the ethynyl protons (~17:1) in the ol-

Table III
Summary of ^{13}C NMR Chemical Shifts for Bis[4-(3-ethynylphenoxy)phenyl] Sulfone



Monomer			Oligomer		
Obs. δ, ppm	Calc. δ, ppm	Assign.	Obs. δ, ppm	Calc. δ, ppm	Assign.[a]
			123.6		a'
79.7		a	79.8		a
			155.3		b'
82.4		b	82.4		b
					j'
117.9		j	117.9		j
			120.7	119.0	g'
120.7	119.3	g	120.7	119.3	g
			118.0	117.5	d'
123.4	123.3	d	123.4	123.3	d
			141.3	140.0	c'
123.9	124.4	c	123.9	124.4	c
			119.0	121.5	e'
128.5	127.3	e	128.5	127.3	e
					k'
129.6		k	129.6		k
			130.0	130.7	f'
130.0	130.9	f	130.0	130.9	f
					ℓ'
135.7		ℓ	135.6		ℓ
			154.6	157.7	h'
154.6	157.9	h	154.6	157.9	h
					i'
161.1		i	161.1		i

[a] Prime denotes equivalent carbons of the (3-phenoxyphenyl)acetylene moieties altered by polymerization.

igomer is consistent with that expected for a conjugated polyene. It should be noted that the indication of a polyene structure is qualitatively consistent with the approximate 50% reduction of the intensity of the ethynyl band in the IR spectrum of monomer 1 that occurs upon reaction. The spectrum of oligomer 2 in Figure 4a exhibits absorption from 6 to 7.2 ppm with $\Delta\nu_{1/2} \sim 80$ Hz, a sharp $CHCl_3$ impurity at 7.2 ppm, and broad absorptions with $\Delta\nu_{1/2} \sim 20$ Hz at 7.5 and 7.8 ppm. Assignments for the proton spectra, based upon a first-order analysis of multiplets, are summarized in Table I.

Coordination of the shift reagent with the oligomers would be expected to occur at the sulfone moiety, and this is supported experimentally by the spectral changes shown in Figures 3b and 4b. Figure 4b for oligomer 2 shows that the aromatic protons shift downfield, revealing a broad resonance at 6.2 ppm. Similar behavior, but less intense due to more extensive line broadening, is observed in the spectrum of oligomer 1, given in Figure 3b. The resonance observed at 6.2 ppm for each oligomer is in the region reported for the olefinic protons of *trans*-poly(arylacetylenes),[9,22] and this offers strong support for polyene structures with similar conformations. The possibility of a cis conformation can be ruled out since the resonance

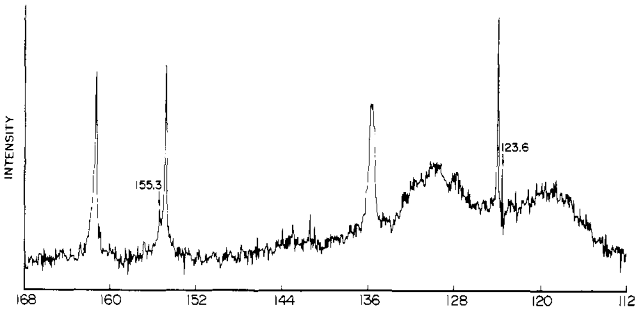


Figure 7. NORD spectrum of oligomer 1: 0.05 g/mL oligomer in $CDCl_3$ vs. Me_4Si.

of the olefinic protons would be expected to occur at a higher field.[9]

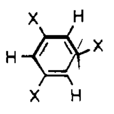
^{13}C NMR Spectra. Assignments for aromatic carbons are based upon intensity considerations and additivity rules for substituted benzenes. Calculated chemical shifts were derived from substituent constants for a *m*-ethynylphenoxy group.[21] The proposed assignments for the monomers and oligomers are summarized in Tables II and III. These assignments are supported by the shifts induced by additions of $Eu(fod)_3$ to solutions of monomer and oligomer 2, as shown in Figures 5 and 6. The largest downfield shifts occur for the carbon atoms near the sulfonyl group.

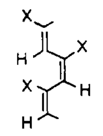
The calculated chemical shifts for the aromatic carbons in the oligomers are based upon values expected if the ethynyl group is converted to a vinyl group by polymerization. In Tables II and III, it should be noted that C_c, C_d, and C_e are calculated to occur at 140.0, 117.5, and 121.5 ppm, respectively, in the polymer. The shifts observed in monomer 2 for these carbons occur at 123.6, 123.1, and 128.1 ppm, as can be seen in Figure 5. After reaction, as indicated in Figure 6, absorption from 123 to 124 ppm is no longer evident. The chemical shifts observed for these carbons in the oligomer occur at 141.1, 118.0, and 119.0 ppm and are in good agreement with the calculated values.

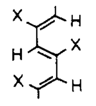
The resonances expected for the vinyl carbons in the oligomers are obscured by overlapping absorption of the aromatic carbons. Therefore, NORD spectra were obtained in order to determine whether absorption of the vinyl carbons could be observed. The NORD spectrum of oligomer 1, shown in Figure 7, exhibits resonances at 155.3 and 123.6 ppm. In the NORD spectrum of oligomer 2, an absorption at 128.3 ppm and a splitting of the resonance at 154.4 ppm were observed. Also in oligomer 2, a broad absorption (as indicated by the hatched area in Figure 6) was observed at 109.0 ppm. After several days, the oligomer solutions showed evidence of gel formation; thus, the possibility that some of these absorptions peaks arise from cross-linked polymer cannot be excluded.[24] On the other hand, the chemical shifts for α and β carbons of styrenes[25] are reported to occur in the 135–160- and 108–120-ppm regions, respectively. Therefore, the resonances observed at 155.3 and 123.6 ppm in oligomer 1 and 153.9 and 128.3 ppm in oligomer 2 are tentatively assigned to the α and β carbons of the polyene chains.

Summary and Conclusion

Conjugated polyenes may be conveniently classified according to the stereochemistry of the carbon–carbon double bonds within the polymer chain.[8,9] Three possible isomers, arising from rotation about the σ bonds of the polymer chain, consist of (a) cis-cisoidal, (b) cis-transoidal, and (c) trans-cisoidal conformations


a


b


c

where X represents the pendant aromatic moieties attached to the polymer chains.

Poly(phenylacetylenes) with a and b conformations may be synthesized with coordination catalysts,[8,9,26–30] while isomer c is obtained by cationic[31,32] and free-radical[8,33,34] initiation.

In the present work, product distributions for monomers 1 and 2 are remarkably similar to those obtained from thermal polymerization of simple arylacetylenes, since these monomers yield oligomers of comparable reactivity and molecular weight. In addition, thermal reaction of each of the monomers is accompanied by the formation of two lower molecular weight species which may consist of dimer and trimer. The ^1H NMR spectra obtained for the oligomers after addition of the shift reagent $Eu(fod)_3$ exhibit a resonance at 6.2 ppm which is characteristic of the olefinic protons of *trans*-poly(arylacetylenes).[9,22] The possibility of a cis conformation can be excluded since the olefinic protons would exhibit resonance at higher fields.[9] In oligomer 1 the ratio of the total aromatic to ethynyl protons is consistent with a polyene structure, and this, in turn, provides a qualitative explanation for the approximate 50% reduction of the intensity of the ethynyl band in monomer 1 that occurs upon reaction. Assignments for the aromatic carbons in the ^{13}C NMR spectra were derived from group additivity, and these were confirmed for oligomer 2 by changes in the chemical shifts induced by the addition of $Eu(fod)_3$. Tentative assignments for the vinyl carbons of the polyene chains were also proposed for each oligomer. The IR, ^1H NMR, and ^{13}C NMR characterization data for both oligomers are in accord with a polyene structure, as opposed to that expected for a oligomer in which the recurring unit is formed by cyclotrimerization. From the characterization data, the thermal origin of each oligomer,[8,9,11] and the steric constraints imposed upon the oligomer chains, it is suggested that both oligomers possess trans-cisoidal conformations.

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Vibrational Analysis of *trans*-1,4-Polypentadiene. 1. Single-Chain Model

N. Neto*

Centro di Studio Sulla Chimica e Struttura dei Composti Eterociclici, CNR, 50121 Firenze, Italy

M. Muniz-Miranda

Istituto di Chimica Fisica, Università di Firenze, 50121 Firenze, Italy

E. Benedetti, F. Garruto, and M. Aglietto

Centro di Studio per le Macromolecole Stereordinate ed Otticamente Attive, CNR, 56100 Pisa, Italy.

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ABSTRACT: The vibrational spectrum of crystalline isotactic *trans*-1,4-poly(1,3-pentadiene) is compared with results of a normal-mode calculation of the isolated chain, using a set of force constants transferred from *trans*-1,4-polybutadiene. The dynamical equation of a vibrating chain is presented in terms of linear coordinates, and it can be easily extended to include interactions among different chains. Normal coordinates are obtained in terms of internal, translational, and rotational displacements for each repeat unit, and vibrational frequencies, computed for a wave vector **k** = 0, are compared with observed data. Calculations are carried out for two possible conformations of the polymer chain and show a better agreement for a conformation characterized by side methyl groups in a skew arrangement with respect to the neighboring double bonds.

The infrared spectrum of isotactic *trans*-1,4-poly(1,3-pentadiene), hereafter referred to as ITPP, was first studied by Natta and co-workers,[1] who showed that the absorption pattern in the region 650–5000 cm^{-1} is little influenced by interactions between polymer chains in the crystal. The crystal structure was later determined by Bassi et al.,[2] who proposed a chain conformation in the crystalline state characterized by side methyl groups in a cis arrangement with respect to the neighboring double bonds. This conformation, hereafter referred to as the cis form, is schematically shown in Figure 1a while in Figure 1b a possible alternative form is given in which the side methyl groups are in a skew arrangement relative to the double bonds. It was suggested[3] that the energy difference between these two different conformations is small, and a skew form was in fact found for similar compounds (see discussion given in ref 2).

In the present paper we report the results of a vibrational analysis of a single polymer chain of ITPP, assuming, as stated in ref 1, that interchain interactions are relatively unimportant for this polymer. This assumption is supported by the observation that very few factor group splittings occur in the infrared spectrum, despite the presence of four monomers per unit cell, each belonging to a different chain. Besides, the spectrum of the crystal is very similar to that of the paracrystalline modification, obtained from the crystalline sample by melting and fast cooling, in which three-dimensional order does not exist. It must be pointed out, however, that the assumption of a crystal made up of noninteracting chains is an approx-

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