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Optically Active Polymers of 1-Alkynes

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ABSTRACT: The already-known polymers of (*S*)-3-methylpentyne (I) and (*S*)-4-methyl-1-hexyne (II) as well as the new ones from (*S*)-5-methyl-1-heptyne (III), (*S*)-6-methyl-1-octyne (IV), and (*S*)-3,4-dimethylpentyne (V) have been prepared by iron tris(acetylacetonate)–aluminum triisobutyl catalyst. The primary structure with alternate double bonds along the main chain has been confirmed for all above polymers. Spectroscopic data (ir, nmr, and uv) show that conjugation is only partial according to a nonplanar conformation of the chains due to mutual steric repulsion of side chains in "1,3" relative positions. The CD spectra from 400 down to 200 nm show, according to absorption spectra, a system of optically active bands attributed to the presence of an inherently chiral polyene chromophore in the macromolecules main chains.

The polymerization of 1-alkynes gives, in the presence of the catalytic system obtained by reacting iron(III) chelates with aluminum trialkyls or dialkyl hydrides, head-to-tail linear macromolecules with alternate double bonds along the main chain.[2-6]

The first optically active 1-alkyne, (*S*)-4-methyl-1-hexyne, was polymerized in 1967 and it was demonstrated that no racemization occurs during the polymerization.[3] Analogous polymers of (*S*)-3-methylpentyne (I) and (*S*)-4-methyl-1-hexyne (II) were more recently investigated.[7,8]

In the present paper the synthesis of polymers of additional optically active 1-alkynes, such as (*S*)-5-methyl-1-heptyne (III), (*S*)-6-methyl-1-octyne (IV), and (*S*)-3,4-dimethylpentyne (V), is described. The chiroptical properties down to 200 nm of these last polymers as well as those of the polymers from I and II are investigated and related to the conformational equilibrium in solution.

Experimental Section

Materials. The solvents used were purified according to standard procedures; they were deoxygenated by distillation under nitrogen and by bubbling dry nitrogen through them.

$Al(i\text{-}C_4H_9)_3$ was obtained by distillation from a 25% commercial solution in *n*-heptane.

Iron tris(acetylacetonate) was prepared as reported in the literature[9] and purified by two crystallizations from methanol-water mixture.

The monomers I–IV and 3,3-dimethylbutyne (VI) were prepared by adding bromine to the corresponding olefins and causing the obtained dibromides to react with $NaNH_2$ in mineral oil at 160°.[10] Their purity was checked by gas chromatography. A sample of V was kindly supplied by Dr. A. M. Caporusso.

Polymerization Experiments. All experiments were carried out under nitrogen atmosphere in a two-necked 100-ml flask fitted with magnetic stirrer. Catalyst was prepared by introducing in the flask $Fe(AcAc)_3$; this last was dried under vacuum (0.5 mm) at 60–65° for several hours. A few milliliters of *n*-heptane were then introduced and $Al(i\text{-}C_4H_9)_3$ was added under stirring. The flask was heated for 15 min at 60° and the monomer was successively added at room temperature. The polymerization was interrupted by dissolving the polymer in diethyl ether and by decomposing the catalyst with deoxygenated HCl (1:1). The organic layer was then washed with deoxygenated water, treated with saturated $NaHCO_3$ solution, and finally washed with water.

Polymer was precipitated by methanol from the ethereal solution, isolated by filtration, and dried under vacuum. Details concerning each polymerization run are reported in Table I.

Measurements. Fractionation of the polymers and viscosity measurements were carried out as previously reported.[3]

Nuclear magnetic resonance spectra were obtained with a Jeol JNM-100 spectrometer on polymer solution in CCl_4; all chemical shifts are reported in δ (ppm) with Me_4Si as internal standard.

Infrared spectra were obtained with a Perkin-Elmer double-beam spectrophotometer Model 225. The spectra were recorded at 25° on polymer films, prepared by evaporation of the solvent from solution of the polymer in CS_2, placed on NaCl plates.

Ultraviolet spectra were recorded at room temperature by a Cary 14 spectrophotometer. Polymers solutions in Spectrograde *n*-heptane with concentrations between 0.3 and 0.5 g per l. were used.

Optical rotatory power at 589 nm was measured with a Schmidt–Haensch polarimeter. Polymer solutions in Spectrograde *n*-heptane with concentrations between 3 and 5 g per l. were used.

Circular dichroism spectra were carried out on a Roussel Jouan Model II dichrograph. The solutions were the same used for uv spectra. For the low-temperature spectra, ellipticities were calculated assuming as density of the solution the density of the solvent at each temperature. No correction has been made for refractive index of the solvent.

Results and Discussion

Polymerization. No detailed kinetic studies have been performed, but the collected data (Table I) already show that the polymerization rate is strongly affected by monomer structure and particularly by the steric obstruction of the alkyl group bound to the triple bond. In fact the homologous series from I to IV, where the methyl branching goes from the α position in I to the δ position in IV, the polymerization rate seems to increase in the order, even if high conversion can be reached for all monomers I–IV in a few hours. A remarkable decrease in polymerization rate is observed going from I to V and even more to VI. This decrease of capability to polymerize must be attributed to steric reasons. In fact V in addition to the methyl in the α position, as in I, has a second methyl group in the β position. In VI the carbon atom bound to the triple bond is fully substituted and in each monomer conformation the approach of the catalyst to the unsaturation is strongly hindered. Accordingly the corresponding α-olefin, *tert*-butylethylene[11] does not polymerize at all.

The marked steric effect resembles that observed[12] in the α-olefins polymerization by Ziegler–Natta catalysts. This supports the formation of main chain double bonds having a predominantly "cis" or "trans" configuration as observed in the polymerization of nonchiral 1-alkynes.[4,13]

Polymer Structure. The polymerization of terminal acetylenes[3-6] and of acetylene[14] by ferric acetylacetonate or dimethylglyoximate and organoaluminum leads to linear

Table I
Polymerization of 1-Alkynes in the Presence of Iron Tris(acetylacetonate)–Aluminum Triisobutyl Catalyst[a]

Monomer	mmol	Polymerization Conditions: Duration (hr)	Polymerization Conditions: Temp (°C)	Conversion[b] (%)	Wt % of Polymer Extracted with[c]: n-C_5H_{12}	Wt % of Polymer Extracted with[c]: CH_2Cl_2	Wt % of Polymer Extracted with[c]: $CHCl_3$
I	12.20	17	20–35	92.4	44.0[d]	14.3	40.4
II	10.40	25	20–25	79.7	87.9[e]		8.9
III	9.09	20	20–25	75.4	95.7[f]		2.7
IV	8.06	20	20–25	76.3	97.8		0.2
V	3.70	50	20–35	7.6	0	35.5	64.5
VI	12.20	23	20–35	5.3	0	0	89.5

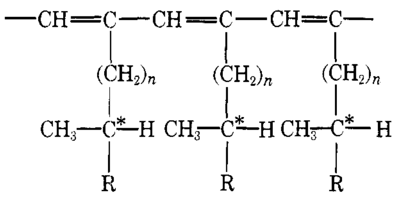
[a] Molar ratios: AlR_3–Fe(AcAc)$_3$ = 3; monomer–Fe(AcAc)$_3$ = 20; solvent: n-heptane. [b] To polymeric products insol in methanol. [c] 2–3% of the polymer was previously extracted with boiling acetone. [d] $[\eta]$ = 1.03 dl/g in chloroform at 30°; $[\eta]$ = 0.2 dl/g in tetralin at 120° after hydrogenation: $\bar{M}_n$ = 10,000–30,000 [P. L. Luisi and F. Pezzana, *Eur. Polym. J.*, **6**, 259 (1970)]. [e] $[\eta]$ = 1.40 dl/g in chloroform at 30°; $[\eta]$ = 0.3 dl/g in tetralin at 120° after hydrogenation: $\bar{M}_n$ = 10,000–30,000 (see note *d*). [f] $[\eta]$ = 1.22 dl/g in chloroform at 30°.

Table II
Nmr, Ir, and Uv Absorption Data for Polymers of 1-Alkynes

Polymer from	Nmr Olefinic Proton δ (ppm)	Ir: Out-of-Plane C—H Bending (cm^{-1})	Ir: C=C Stretching (cm^{-1})	Uv[a] Longest Wavelength Absorption Band: λ_{max} (nm)	Uv[a] Longest Wavelength Absorption Band: ϵ_{max}[b]
I	5.7	900	1610	294	2400
II	5.9	880, 905	1618	323	2500
III	5.8	880–910	1626	290	1950
IV	5.8	875	1622	322	2250
V	n.d.	900	1607	~315[c]	~2200[c]
VI	n.d.	875	1602	262[c]	700[c]

[a] In n-heptane if not otherwise indicated. [b] Per monomer unit. [c] In chloroform.

polymers having alternate mainly "cis" double bonds along the main chain.



poly(I), R = C_2H_5; n = 0
poly(II), R = C_2H_5; n = 1
poly(III), R = C_2H_5; n = 2
poly(IV), R = C_2H_5; n = 3
poly(V), R = i-C_3H_7; n = 0

The polymers of I–V are very sensitive to oxygen, light, and heat and must be stored in refrigerator under nitrogen and in the dark. Therefore spectroscopic measurements have been performed on freshly prepared polymers. Extraction with boiling solvents was carried out under nitrogen and with solvents having boiling points lower than 56° (acetone). Above this temperature strong variations of polymer properties occurred promptly.

In general the characterization was carried out on the fraction extracted with n-pentane or dichloromethane from the purified polymer previously extracted with acetone. The above fraction was in general a large part of the polymer obtained from I to IV; however in the case of I about 40% of the polymer was extractable with boiling chloroform but the data obtained on this fraction were not reliable (Table I). In the case of the polymers from V and VI because of very low conversion and small amount of soluble polymer available, the data reported here have to be considered as preliminary.

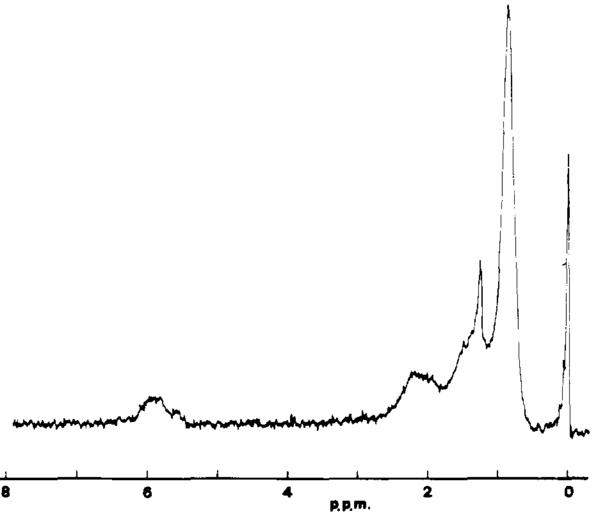


Figure 1. Nuclear magnetic resonance spectrum (100 MHz) of poly[(*S*)-4-methyl-1-hexyne] in CCl_4.

Nmr spectra are rather complex because of the presence of a large number of protons only slightly magnetically nonequivalent. Figure 1 reports the spectrum of poly(II) in CCl_4 at 100 MHz. The spectra of polymers of I–IV are similar and show a band at 2.0 ppm associated with the methynic proton of the *sec*-butyl group, and at about 1.2 and 0.7 ppm the bands of methylenic and methyl hydrogens, respectively, in a variable relative ratio according to the different structure. The most interesting result is the presence, between 5.7 and 5.9 ppm, of the band related to the olefinic proton (Table II). The position of this band is intermediate between that of conjugated open-chain polyenes[15,16] and that of internal monoolefins.[17] No nmr investigation was carried out for polymers of V and VI.

The ir spectra (Figure 2) are in agreement with the pro-

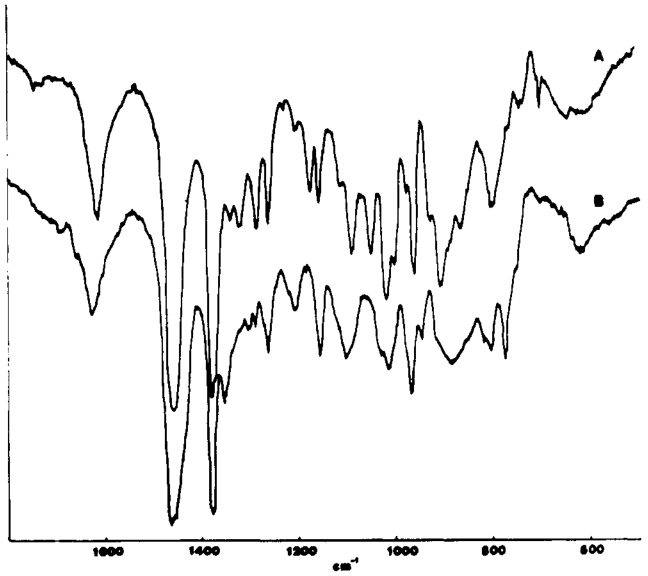


Figure 2. Infrared spectra of poly[(*S*)-3-methylpentyne] (curve A) and poly[(*S*)-5-methyl-1-heptyne] (curve B); films from solutions in carbon disulfide.

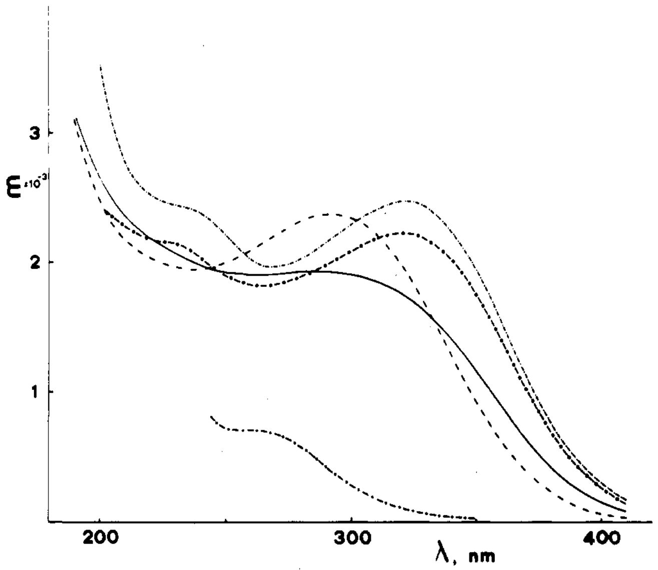


Figure 3. Uv absorption spectra of poly[(*S*)-methylpentyne] (- - - -), poly[(*S*)-4-methyl-1-hexyne] (–·–·–), poly[(*S*)-5-methyl-1-heptyne] (——), and poly[(*S*)-6-methyl-1-octyne] (- O - O -), in *n*-heptane, and of poly(3,3-dimethylbutyne) (- + - + -) in chloroform. ε is based on one monomer unit.

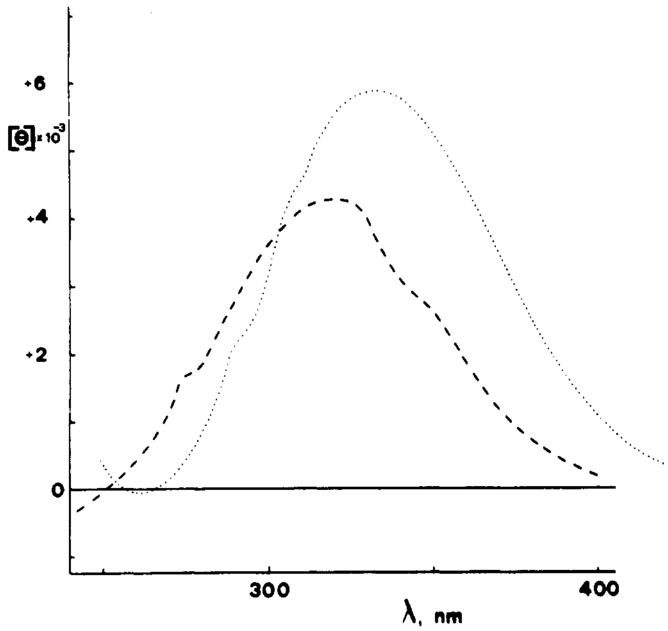


Figure 4. CD spectra between 400 and 250 nm of poly[(*S*)-3-methylpentyne] (----), monomer optical purity 43.7%, in *n*-heptane and of poly[(*S*)-3,4-dimethylpentyne] (····), monomer optical purity 44.4%, in chloroform. The molar ellipticity [*θ*] is based on one monomer unit.

posed structure and after hydrogenation they are very similar to those of the polymers from the corresponding α-olefins.[3] The bands in the 1626–1602- and 910–875-cm^{-1} spectral region disappear with hydrogenation and can be related to the stretching vibrations of the C=C double bonds and to the out-of-plane C—H bending vibrations in $-(CH{=}CR)_x-$, respectively. The former band moves toward smaller wave numbers (Table II) going from poly(IV) to poly(I) and from this last to poly(V) and -(VI). As $\nu_{C=C}$ is about 1600 cm^{-1} in fully conjugated dienes[18] and increases to about 1670 cm^{-1} in internal isolated double bonds,[18] conjugation seems to increase with increasing the bulkiness of the side chains. A likely explanation is that $\nu_{C=C}$ is very sensitive to deformation of double bond in plane[19] as shown by the wave number of the corresponding band in strained cyclic monolefins.[19,20] As previously reported[3,13] the presence of a single band in the carbon—carbon double-bond stretching vibration region and its shape substantiate that the double bonds have for the main part the same configuration. The latter band at 910–875 cm^{-1} (Table II) is analogous to that of poly(phenylacetylene) prepared by the same catalyst. This band has been assigned[4] to the out-of-plane C—H deformation in cis $-(CH{=}CR)_x-$. Poly(phenylacetylene) having trans configuration shows bands around 980–960 cm^{-1}; the absorption observed in the same region by the polymers from I to IV cannot be associated with the massive presence of "trans" double bonds as it is not appreciably affected by hydrogenation. Rather than to main-chain unsaturation, this band is to be assigned to CH_3 rocking vibrations in the side chains.

A strong broad absorption band with the maximum at about 295–315 nm and ϵ_{max} (for monomeric residue) of about 2000–2500 is present in the uv spectra of polymers from I to IV (Figure 3). Poly(VI) shows a much smaller absorption (ϵ_{max} ~700) at 262 nm (Figure 3 and Table II). These spectra are not appreciably affected by solvent ($CHCl_3$ and *n*-heptane) and temperature (20–60°) changes. The main peculiarities are the much lower value of ϵ_{max} per double bond with respect to planar fully conjugated polyenes[21] and the relatively short wavelength of this maximum. In fact these polymers contain (see viscosity data in Table I) a few hundred double bonds per macromolecule and if fully conjugated they should absorb in the visible spectral region like polyacetylene[22] and planar polyenes.[21,23,24]

The uv absorption spectra can be interpreted by considering that a loss of conjugation occurs as the macromolecules have a nonplanar conformation due to the mutual steric repulsions of the side chains on alternate carbon atoms. The skew angle between two adjacent double bonds should have a constant value as the steric interactions are the same for each couple of monomeric units. The macromolecules assume a coiled conformation if both clockwise and counterclockwise skew angles are present. Helical conformations are expected if the double bonds have the same configuration and are skewed predominantly in a single sense. In the actual case this will be true for relatively short-chain sections. In fact folding points can exist in the

Table III
Chiroptical Properties of Polymers of 1-Alkynes and of Some Low Molecular Weight Structural Analogs, All Having (*S*) Absolute Configuration

Polymer from	Monomer Optical Purity (%)	$[\Phi]^{25}\text{D}$[a]	Longest Wavelength CD Band at 27° $\lambda_{\max}$ (nm)	 $[\theta]_{\max}$[a]	Low Mol Wt Structural Analogs	$[\Phi]^{25}\text{D}$[b,c]	$\lambda_{\max}^{\text{CD}}$ (nm)[d]
I	43.7	+268	319	+4300	VIII (n = 0; R = C_2H_5)	+32.1	<210
	87.3	+498	317	+8200	IX (n = 0; R = C_2H_5)	+39.4	~230
II	83.5	−10.6	392	+290	VIII (n = 1; R = C_2H_5)	−3.0	<210
					IX (n = 1; R = C_2H_5)	−10.8[e]	nd
III	89.3	−146	335	−2350	VIII (n = 2; R = C_2H_5)	+12.2	<210
IV	89.7	−3.4	356	−260	VIII (n = 3; R = C_2H_5)	+13.7	<210
V	44.4	+470[f]	331[f]	+5900[f]	VIII (n = 0; R = i-C_3H_7)	+42.2	<210

[a] Based on monomer unit; in *n*-heptane if not otherwise stated. [b] Neat; maximum value. [c] Values taken from ref 15 and 29–34. [d] From ref 15 and 35. [e] In benzene, ref 34. [f] In chloroform.

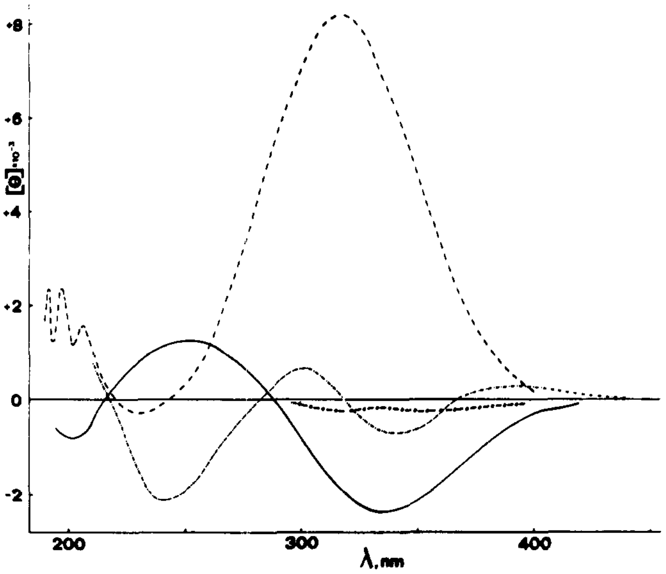
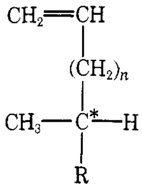


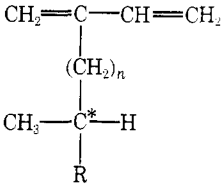
Figure 5. CD spectra at 27° in *n*-heptane of polymers from (*S*)-3-methylpentyne (- - - -), (*S*)-4-methyl-1-hexyne (-·-·-), (*S*)-5-methyl-1-heptyne (——), and (*S*)-6-methyl-1-octyne (- O - O -), all having high optical purity. The molar ellipticity [*θ*] is based on one monomer unit.

main chain due to the occasional irreversible shift of the double bond in the side chain[13] or to the presence of saturated units[25] which interrupt the sequence of alternate double bonds and then the even partial conjugation. On the other hand, the possibility of nonenergetic "bond reversal" has been foreseen even theoretically.[26] Other factors[19] can affect the uv spectrum, such as distortion in the plane of the angle C—C=C or distortion out of the plane of the double bond caused by the bulky substituents about the double bond. The existence of these effects is shown by the ir data discussed above. However both the short wavelength of absorption maxima and the low values of $\epsilon_{\max}$ per double bond with respect to expectation should be mainly caused by deviation from planarity of the system of alternating double bonds.[21,27] This does not allow to relate the $\epsilon_{\max}$ to the number of double bonds, and then of monomeric units, included in a partially conjugated chain section. In fact as the skew angle becomes larger, the transitions have a tendency to shift to higher energies; for instance $\lambda_{\max}$ goes from 220 in 2,3-dimethyl-1,3-butadiene to 185 nm in 2,3-di-*tert*-butyl-1,3-butadiene.[28] In any case, the number of units interacting in a conjugative way in the polymers investigated is probably markedly larger than that expected on the basis of absorption maxima position. The similar shape of the uv spectra (Figure 3) of the polymers of I-IV and also of V should indicate that the above number as well as the value of the skew angle are probably not very different in the series.

Optical Activity. According to uv spectra the examined polymers show optically active bands in their CD spectra between 400 and 200 nm (Figures 4 and 5). Taking into account the large number of optically active bands in the near-uv region and their high rotational strength and opposite sign, the optical rotation values at 589 nm are practically of no use and the comparison with low molecular weight structural models VII[29-33] and VIII[15,34] is of little significance. Similarities observed are in fact most probably fortuitous (Table III). As expected from absorption data the chromophoric system responsible of the optical activity in the models VII and VIII is completely different from that of the poly(1-alkynes). In fact compounds VII do not show dichroic bands at wavelengths larger than 210 nm[35] and VIII at wavelengths larger than 230-240 nm.[15]



VII



VIII

The ellipticity of the longest wavelength CD band of the poly(1-alkynes) (Figures 4 and 5, and Table III) is strongly affected by the distance between asymmetric carbon atom and main chain. Poly(IV) for instance, where the asymmetric carbon atom is in *δ* position, show a broad negative band with very low ellipticity. On the contrary poly(I) and poly(V), where the asymmetric carbon is in *α*, show a strong positive band the ellipticity of which resembles in order of magnitude that of inherently chiral cyclic rigidly fixed dienes.[36,37] In the case of poly(II) the longest wavelength CD band is still positive but its ellipticity is much lower and it is shifted to the red, while in poly(III) it becomes negative and shifted again toward uv, even if the presence of an inflexion point at about 400-410 nm could indicate the presence of a weak positive CD band.

At least as far as the longest wavelength band is concerned no strong solvent effect seems to exist: the small differences between the maxima of poly(I) in *n*-heptane and chloroform can be associated to the different refractive indexes of the solvents.

In the case of the polymers from I, II, and III the CD spectrum has been also investigated down to 200 nm thanks to their solubility in saturated hydrocarbons. The system of bands at shorter wavelength is rather complex

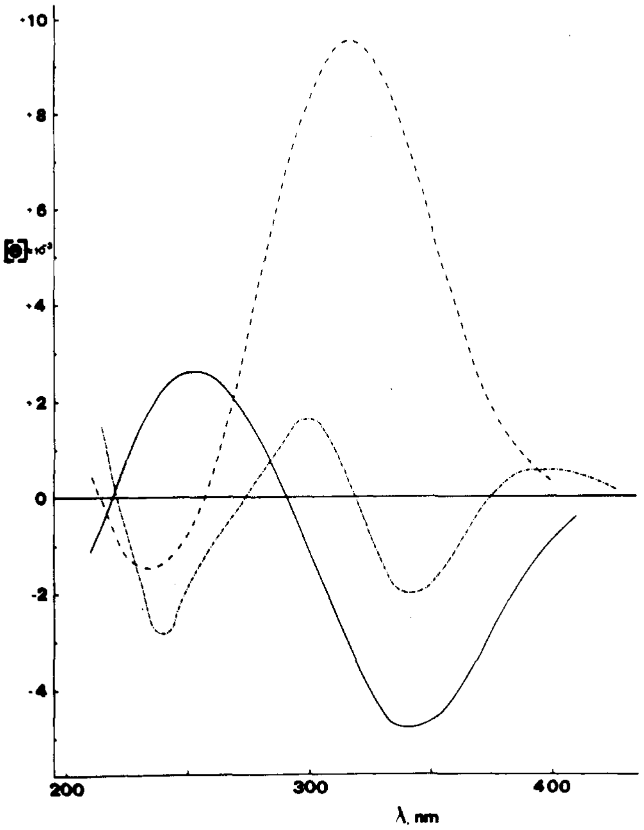


Figure 6. CD spectra at −60° in *n*-heptane of poly[(*S*)-3-methylpentyne] (----), poly[(*S*)-4-methyl-1-hexyne] (-·-·-), and poly[(*S*)-5-methyl-1-heptyne] (——). The molar ellipticity [*θ*] is based on one monomer unit.

and no simple dependence of ellipticity on structure seems to exist. A similar system of optically active bands has been observed in carotenoids[38,39] and in polyisocyanates[40] where the possibility of conjugation between several double bonds exists.

The absence of a definite relationship between structure and CD features is not surprising as the same occurs in the case of cyclic dienes which are structurally simpler.[41] In fact both the chirality "diene rule"[42] and the correlation by Burgstahler and Barkhurst[43] must be accommodated to fit with experimental data now available.

A lowering of the temperature down to −60° produces in all polymer examined (from poly(I) to poly(III)) an increase of the ellipticity, in absolute value, of all CD bands without appreciable changes of the maxima position. The slight red shift of the longest wavelength band negative maximum of poly(III) seems to be mainly due to structural features of this band (Figure 6). The maximum ellipticity for all bands varies linearly with temperature and the percent variation is different from polymer to polymer; in fact poly(I) spectrum varies only slightly while poly(II) and poly(III) show a strong variation of their spectra, the ellipticity values at −60° being more than two times those at room temperature. It is of interest to remark that at −60° also these two polymers show values of the order of magnitude of inherently chiral dienes.[37] These results are consistent with the fact that the optically active bands system observed between 400 and 200 nm for the poly(1-alkynes) is connected to the presence of an inherently chiral polyene chromophore. A conformational analysis based on molecular models indicates that when, as in our case, the side-chain asymmetric carbon atom has (*S*) absolute configuration the macromolecules assume preferentially a left-handed helical conformation if all double bonds are either cis or trans. The effect of monomer structure and of temperature on CD curves can be interpreted by assuming the existence of a dynamic equilibrium between the two opposite screw senses.

Conclusions

The results presented in the previous sections can be summarized as follows. (1) Polymers of 1-alkynes having a branched side chain assume in solution a nonplanar conformation because of steric repulsions of the side chains with a consequent loss of conjugation. (2) The presence of chiral side chains having the same absolute configuration leads to skew angles having predominantly a single sign. Main-chain sections consisting of double bonds with the same configuration assume a helical conformation with a predominant screw sense. Construction of molecular models shows that when the side chain asymmetric carbon atom has (*S*) absolute configuration the preferred screw sense is the left-handed, or counterclockwise, one. (3) The absolute value of the skew angle does not seem to change markedly with temperature; in fact uv spectra do not change and CD variations can be better explained with a variation of the position of the equilibrium between helical sections with opposite screw sense.

Even if the conclusions which can be drawn at the present are not definitive, the above points suffice to give a tentative picture of the conformational situations of optically active polyenes in solution.

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Photopolymerization Studies. III. Thermal Sensitization and Desensitization Effects[1]

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ABSTRACT: Heating and pH effects on the dark storage are studied for photopolymerizable solutions of barium acrylate in water. Methylene Blue and sodium *p*-toluene- or benzenesulfinate are used as photopolymerization-initiating agents. When solutions of pH 6 are heated, the photosensitivity initially increases and then gradually decreases until desensitization is complete. The sensitization process is partly due to a decrease in sulfinate quenching of the excited dye, but a decrease of oxygen inhibition due to its reaction with monomer appears to be the major factor. The desensitization is due to the ionic dark addition of the elements of *p*-toluenesulfinic acid to monomer double bond, forming a sulfone which is unreactive with the excited state of the dye. Photopolymerization rates measured as a function of prior heating are used to make a kinetic analysis of the dark reactions. Desensitization occurs faster at lower pH because the ionic addition is much faster with acrylic acid than with the acrylate ion. Desensitization is slower at higher pH due to absence of acrylic acid, and due to an equilibrium of sulfinate ion and sulfone at high hydroxide ion concentrations. Long storage times are possible at high pH; however, the photopolymerization efficiency is also decreased in the high pH range.

We have already described[2,3] a direct imaging system based on photopolymerization of acrylic monomer solutions containing a phenothiazine dye and a salt of an arylsulfinic acid. Polymerization is initiated by transient free radicals resulting from the redox reaction between the dye-triplet state and the sulfinate ion.[4] The photopolymer image is due either to the light-scattering properties of polymer or to refractive index differences within the partially polymerized film. Applications for rapid-access, large-screen display devices[5] and holographic recording have been demonstrated.[5-8]

This paper describes the sensitizing and desensitizing effects obtained by heating photopolymerizable aqueous compositions of barium acrylate, Methylene Blue, and sodium *p*-toluene- or benzenesulfinate. A kinetic analysis is made on the thermal dark desensitization reaction. Comparisons are made with other studies[9] in which the rate constants (*k* in eq 1) for the ionic addition of sulfinate ions to acrylic monomers were measured by techniques not involving polymerization.

$$\mathrm{RSO_2^-} + \mathrm{CH_2{=}CHY} + \mathrm{H_2O} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{RSO_2CH_2CH_2Y} + \mathrm{OH^-} \quad (1)$$

The effects of low pH and high pH on the room-temperature stability and photosensitivity of these photopolymerizable solutions are also described. The reverse reaction of eq 1 (k' direction) is followed at high pH by analysis of the benzenesulfinate ions produced from the reaction of hydroxide ions with 3-(benzenesulfonyl)propionate ions.

Experimental Section

Materials. Barium acrylate solutions were prepared by neutralizing aqueous solutions of acrylic acid with an equivalent amount of barium hydroxide. The pH was adjusted with excess acrylic acid, and the solutions were treated with activated carbon and filtered. The concentrations were determined by atomic absorption spectroscopy or by heating measured volumes of solution to dryness; the results of the two methods agreed within 2%. Concentrations of sulfinate solutions were determined by a potentiometric titration with standard sodium nitrite solution,[10] which indicated that the commercial sodium *p*-toluenesulfinate and sodium benzenesulfinate were better than 97% pure. Photosensitive solutions were prepared by mixing aqueous solutions of barium acrylate, Methylene Blue, and the sodium salt of either *p*-toluenesulfinic or benzenesulfinic acid. The compositions of these solutions are summarized in Table I.

When basic barium acrylate solutions were prepared, we noted that often they spontaneously consumed hydroxide ion and gradually became less basic. This is attributable to the presence of β-acryloyloxypropionic acid as an impurity in the glacial acrylic acid.[11] This ester "dimer" undergoes hydrolysis in base, consuming $\mathrm{OH^-}$. We found that after barium acrylate solutions were allowed to stand for about 1 week with an excess of base they would remain nearly constant at a given pH in the 9-12 range.

3-(Benzenesulfonyl)propionic acid was synthesized by the reaction of sodium benzenesulfinate with methyl acrylate in aqueous methanol and hydrolysis of the resulting methyl 3-(benzenesulfonyl)propionate in 6 *N* hydrochloric acid. The melting point was 124° (lit. mp 125-126°,[12] 125.5-127°[13]).

Photopolymerization Rate Measurements. Photopolymerization was followed optically, since the polymer that is formed scatters light. It has been shown[2] that, at least in the region of low monomer conversion, the apparent optical density of a light-scattering photopolymer film is proportional to the amount of polymer formed. The sample of photosensitive composition was held between two glass slides separated by a peripheral plastic shim 0.15 mm thick. For expt 1 and 2 unfiltered light from a 500-W tungsten filament projection lamp was used to induce polymerization, and the light transmitted by the sample was attenuated with neutral density filters and detected with an RCA 931A phototube. For the remaining experiments the polymerization was followed by passing through the polymerizing spot an analyzing light beam having a low intensity and a wavelength that was in-