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Effects of Elongation on the Photochemistry of Poly[ethylene-*co*-(carbon monoxide)]

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ABSTRACT: Films of poly[ethylene-*co*-(carbon monoxide)], P(E/CO), were cold drawn to various extensions. IR dichroism measurements showed that the molecular chains in the amorphous region were oriented along the direction of drawing. After UV irradiation ($\lambda < 290$ nm, 300 °C, nitrogen atmosphere), the percent crystallinity and average crystallite size, as determined by X-ray diffractometry, increased for both undrawn and drawn samples. Also, the orthorhombic form in drawn samples increased at the expense of the monoclinic form during UV exposure. The formation of vinyl end groups increased with exposure and with extent of elongation as determined by IR spectroscopy, while the formation of acetyl end groups was strongly suppressed by orientation as determined by NMR spectroscopy. Molecular chain tension increased the overall scission rate slightly and shifted the reaction mechanism from mostly Norrish type II scission in unoriented P(E/CO) to predominantly Norrish type I scission in oriented samples.

Introduction

Most reactions in semicrystalline polymers are confined to amorphous regions above the glass temperature.[1,2] Little is known about how constraints, imposed on the intercrystalline tie chains in these regions, may affect the rates and mechanisms of reactions. We have now found that the photolysis rate and mechanisms of films of poly[ethylene-*co*-(carbon monoxide)], P(E/CO), are affected by elongation.

P(E/CO) is an appropriate model for this study, since its carbonyl groups are located primarily in the backbone chain, rather than in branches, and the groups are distributed randomly throughout the solid polymer.[3] The photolysis of P(E/CO) consists of two well-defined competing processes (Scheme I), which are free of diffusion-related complications.

It seemed likely that the Norrish type II reaction, the predominant process at room temperature in an unelongated polymer, would be inhibited by constraints on molecular motion since it requires a cyclic intermediate. The slower Norrish type I reaction might be less affected, since it is not as dependent on chain conformation. The photolysis reactions described in this report are consistent with these postulates.

Experimental Section

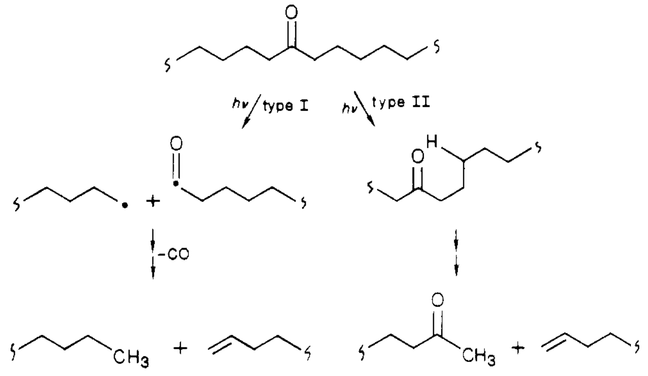
Compression-molded films of a noncommercial P(E/CO) obtained from E. I. DuPont de Nemours and Co. and of a low-density polyethylene (Union Carbide Co. DYNK) were prepared as described previously.[3] Dumbbell-shaped specimens were drawn on an Instron tensile test instrument at room temperature and a draw rate of 25 mm/min. The drawn samples were then inspected visually for defects prior to use.

Irradiation Procedure. Films were mounted on aluminum-backed holders and placed in a sealed cell equipped with $^1/_8$-in. Pyrex windows. The cells were filled with nitrogen and exposed to a 400-W medium pressure mercury lamp, while the temperature at the surface of samples was maintained at 32 ± 1 °C with a circulating water bath. The filters permitted only light of wavelength $\lambda > 290$ nm to illuminate samples.

IR Spectroscopy. Transmission infrared spectra were obtained by using either a Perkin-Elmer Model 330 IR spectrophotometer or a Pye Unicam Model 3-300 IR spectrophotometer and a Model 3-080 data acquisition system.

Dichroic spectra were recorded by using a Molectron Model 16P225 KRS-5 polarizer (70% $T_{\max}$, 93% minimum polarization). Samples and polarizer were mounted at an angle of 45° to the instrument axis to minimize instrumental polarization effects.

Scheme I



The determinations of methyl end groups were made by using an IR difference method.[4] Spectra were obtained by digital averaging of 10 runs and using a 16-point curve smoothing procedure.

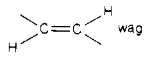
UV Spectroscopy. The extent of light scattering of samples was measured by using a Perkin-Elmer 320 UV–vis double-beam spectrophotometer. Absorbance spectra of P(E/CO) samples were measured with a low-density polyethylene in the reference beam to compensate for light scattering.

NMR Spectroscopy. Carbon-13 NMR spectra were obtained at 110 °C with a JEOL FX90Z spectrometer operating at 22.53 MHz. Proton decoupling was used while accumulating 12 000–22 000 scans with a pulse angle of 90° and a pulse delay of 4 s. Polymer samples (~13 wt %) were dissolved in a 4:1 v/v solution of 1,2,4-trichlorobenzene and *p*-dioxane-d_8. Hexamethyldisiloxane (HMDS) was used as an internal chemical shift reference (2.00 ppm versus Me_4Si), and dioxane-d_8 provided the internal deuterium lock.

X-ray Diffraction. X-ray diffractometry was performed on specimens in the reflection geometry by using Ni-filtered Cu Kα radiation at a scanning rate of 0.50° 2θ/min. While single films were used for the unoriented samples, their elongated counterparts were carefully cut into small pieces and placed on the X-ray holder in randomized fashion in order to remove the effects of preferred orientation on the reflection intensities. For crystallite-size estimates, removal of instrumental broadening was made by using large single crystals of mica. For crystallinity determinations, the amorphous profile was obtained by a diffractometer scan above the melting temperature.

Gel Permeation Chromatography. Weighed samples of films were dissolved at 135 °C in 1,2,4-trichlorobenzene containing 3,5-di-*tert*-butylcatechol as an antioxidant. Chromatograms were recorded by using a Waters 150C ALC/GPC with a Shadex column set and a refractive index detector. Average molecular weights were computed from elution curves compared to those

Table I
Selected IR Bands, Assignments, and Dichroic Ratios of Unelongated and Elongated P(E/CO)

		dichroic ratio, $R(1/R)^a$	
band, cm^{-1}	assignment	elong 450%	no elong
1895	CH_2 rock, crystalline	0.23 (4.35)	1.10
1720	C=O stretch	0.33 (3.00)	1.07
1410	C=O bend	0.14 (7.25)	1.13
1370	CH_2 wag, crystalline	2.51	0.99 (1.01)
1305	CH_2 twist, amorphous	1.15	0.96 (1.04)
1260		0.37 (2.69)	1.08
1080	C–C skeletal stretch, amorphous	2.90	1.24
965		9.10	1.19
732	CH_2 rock, crystalline		0.98 (1.02)
722	CH_2 rock, crystalline + amorphous		1.20
~720	multiple including monoclinic	0.35 (2.90)	

[a] $R = A_{\parallel}/A_{\perp}$ relative to the direction of elongation, $1/R$ shown for relative comparison of magnitudes.

of the NBS 1476 standard linear polyethylene fraction.

Results

Many of the stress-related changes that are observed in IR spectra of polyethylene are observed for P(E/CO). The intensities of various bands change with the extent of stress. For example, the 1720-cm^{-1} carbonyl stretch band broadens with increasing elongation of the copolymer. The 720–730-cm^{-1} doublet broadens and appears to merge. This is due in part to the crystalline change from an orthorhombic phase to a monoclinic phase, which has an overlapping band at about 717 cm^{-1}.[5] Other evidence for the orthorhombic to monoclinic phase change was found by using X-ray diffraction and will be discussed later.

Polarized IR spectra, parallel and perpendicular to the orientation direction of a sample of P(E/CO) stretched 450%, showing several bands with significant polarization. An unelongated sample showed little or no polarization for most bands. Some selected bands, their assignments, and dichroic ratios are summarized in Table I. The 1305-cm^{-1} band assigned to amorphous CH_2 twist showed the least amount of polarization. This band will be used as a reference in comparing the observations of samples with varying degrees of elongation. The vinylene (trans-olefinic) band at 965 cm^{-1} showed polarization parallel to the direction of elongation. Since the dipole moment for this vibration is parallel to the chain axis, parallel polarization indicates that as expected the chains are oriented along the stretch direction. The 1720- and 1410-cm^{-1} bands assigned to the carbonyl group show polarization perpendicular to the stretch direction. A model of an extended chain containing a C=O group would have the C=O group oriented perpendicular to the chain axis. The polarization observed for both C=O and vinylene bands confirms that the orientation of the molecular chains is along the stretch direction. The magnitudes of the dichroic ratios shown here are in agreement with those reported by Read and Stein[6] and Glenz and Peterlin[7] except for the peak at 1080 cm^{-1}. This peak is considerably broader in the spectrum of P(E/CO) than in the corresponding one for polyethylene. It may be due to an unknown vibration overlapping that of the 1080-cm^{-1} C–C skeletal stretch and having a different polarization.

X-ray diffractograms of unoriented P(E/CO) before and after 24-h photodegradation are shown in Figure 1. The patterns are very similar to those obtained by Alfonso et al.[8] for copolymers containing higher amounts of ketonic groups (9–37%). The diffractograms could be resolved into contributions from the crystalline orthorhombic phase and from the amorphous phase, after determination of the profile of the latter at temperatures above the melting point. Each of the crystallographic peaks was modeled by different linear combinations of Lorentzian and Gaussian line shapes until the best overall match with the experi-

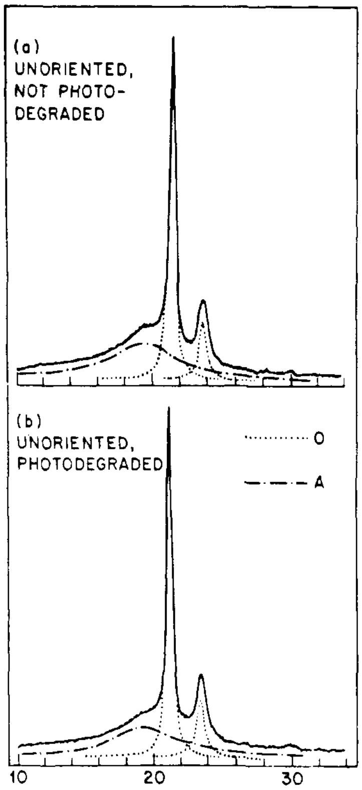


Figure 1. X-ray diffractograms of unoriented P(E/CO) before (a) and after (b) 24-h UV exposure. The resolved components of orthorhombic (···) and amorphous (–·–) domains are shown.

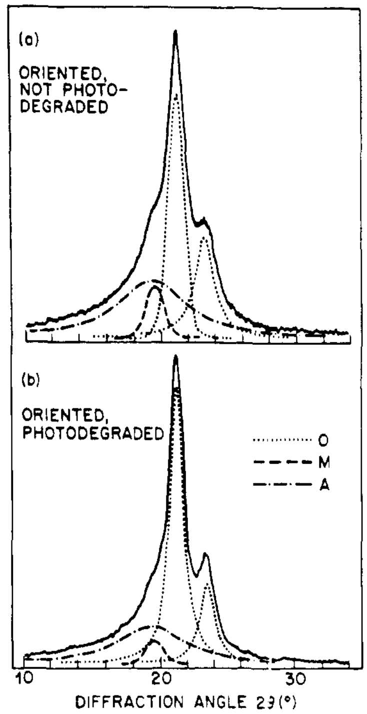


Figure 2. X-ray diffractograms of 390% elongated P(E/CO) before (a) and after (b) 22-h UV exposure. The resolved components of orthorhombic (···), monoclinic (- - -), and amorphous (–·–) domains are shown.

Table II
P(E/CO) Crystalline Structure from X-ray Diffractometry

		crystallinity, %			crystallite
elong, %	photodegr, h	total	orthorh	monocl	size, nm
0	0	37	37		22.9
0	24	42	42		22.9
0	575	48	48		27.0
390	0	47	41	6	6.1
390	22	55	52	3	7.8

mental diffractogram was attained.

The same procedure was used to resolve the diffractometric traces from P(E/CO) oriented by 390% elongation before and after photodegradation (Figure 2). However, in this case, no combination of the experimentally determined amorphous background and of the orthorhombic peaks (within the entire Lorentzian–Gaussian range) could reproduce the observed diffractograms; presence of an additional peak at 19.5° 2θ was required, as seen in Figure 2, parts a and b. This peak is attributed to the monoclinic phase, which is indeed known to be generated in polyethylene as a result of mechanical deformation.[9,10] The two additional, weaker reflections of monoclinic polyethylene in this 2θ range could not be observed.

Comparison of the major features of Figures 1 and 2 shows the following: (a) in both oriented and unoriented samples, photodegradation causes a reduction in the amorphous contribution; (b) in elongated samples, crystalline line widths are broader—and therefore crystallite sizes are smaller—than in their unoriented counterparts, both before and after photodegradation; (c) in oriented specimens, photodegradation causes a reduction in crystalline line widths, as well as in both monoclinic and amorphous content.

These features are summarized quantitatively in Table II. Here, estimates of crystallinity are given by using the Hermans–Weidinger method,[11] which is in good agreement with the more elaborate method of Ruland.[12] Crystallite-size estimates are given for the (110) planes by using the Scherrer equation, with the caveat that lattice-distortion effects could not be subtracted,[13] since multiple orders of the reflections were not available. However, for the low-order (110) peak chosen, the overall broadening is known to arise predominantly from crystallite-size effects.[14]

From Table II photodegradation of the unoriented sample for 24 h causes an increase in crystallinity of about 14% (37–42%) with no apparent change in crystallite size. Prolonged irradiation (575 h) increases the crystallinity by 30% (37–48%), and an 18% increase in crystallite size is observed. The changes caused by photodegradation for 22 h (equivalent absorbed dose for the 24-h exposure of the unoriented sample) of the oriented sample were greater. The total crystallinity increased by 17% (47–55%), the orthorhombic crystallinity increased by 27% (41–52%), and the monoclinic form decreased by half (6–3%). The average size of crystallites increased by 28% due to UV irradiation.

The molecular weight distribution of these samples before and after UV irradiation is summarized in Table III. The apparent difference in M_n for the elongated and unelongated samples is probably due to experimental error rather than to some process leading to an increase in molecular weight caused by stretching the polymer. Elongation would be expected to lead to a net decrease in molecular weight due to mechanical scission of chains.[15,16] As expected, irradiation caused a similar decrease in average molecular weight to nearly equal values for both samples and led to a narrower molecular weight distribution, P. Therefore, the average number of scissions is similar for the two samples and presumably identical if both are assumed to have the same starting molecular weights.

Table III
Summary of Gel Permeation Chromatographic Determinations

sample	$10^{-4}M_n$	$10^{-5}M_w$	P^a (M_w/M_n)	scission molecule
no elong	2.2	1.4	6.4	
elong 390%	2.7	1.2	4.4	
no elong 24-h UV	0.78	0.24	3.1	1.8
elong 390%, 22-h UV	0.77	0.27	3.5	2.5

^{a} Polydispersity.

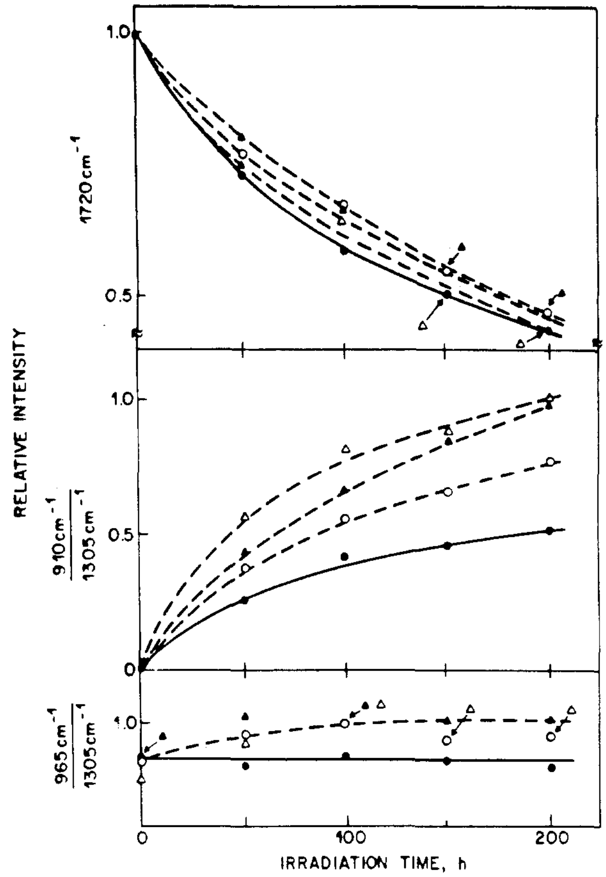


Figure 3. Time dependence of changes in IR intensity of carbonyl (1720 cm^{-1}), vinyl (910 cm^{-1}), and vinylene (965 cm^{-1}) bands for P(E/CO) samples elongated 0 (●), 222 (○), 420 (▲), and 520% (△).

The concentration of carbonyl and vinyl groups can be monitored over time by tracking the intensities of the 1720- and 910-cm^{-1} IR bands, respectively. Intensities of these bands are normalized relative to that of the 1305-cm^{-1} band. The variances in CO, vinyl, and vinylene (965 cm^{-1}) with irradiation time and of samples elongated 0, 222, 420, and 523% are shown in Figure 3.

The CO band was found to decrease rapidly at the onset of degradation. A slower rate at longer exposure times is due to the depletion of CO groups in the amorphous region, which react faster than those in the crystalline region.[3] However, the loss of CO does not appear to be affected by elongation in a regular fashion. Within a spread of about 10%, the extent of CO loss is the same for all samples regardless of extent of elongation. Vinyl groups increased with irradiation time and with extent of elongation. At the earlier exposure times (<50 h), the 523% elongated sample showed a rate of vinyl formation over twice as fast

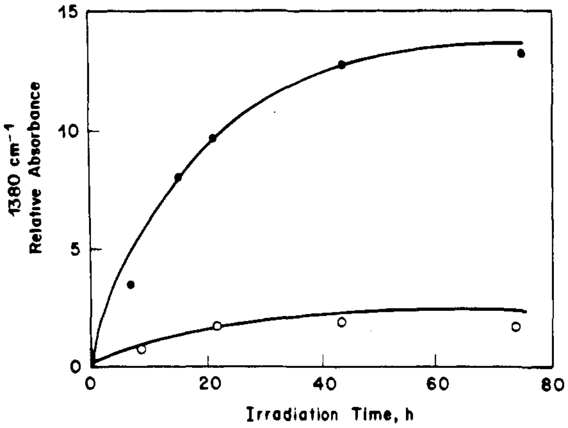


Figure 4. Time dependence of formation of methyl end band at 1380 cm^{-1} for 400% elongated (●) and unelongated (○) samples. Values are taken from difference IR spectra of samples exposed to UV irradiation at various times minus unexposed samples. The values are an average of 10 scans, which were digitally smoothed.

as that of the 0% elongated sample. At prolonged times, the rates of all samples leveled off due to the depletion of vinyl-forming groups. The relative differences in the intensities of the vinyl band samples of different elongation should directly correspond to relative differences in concentration of vinyl groups. Vinyl groups are located at the ends of molecular chains and should show little if any effect of stress. The vinylene groups occur to an extent of less than 10% of the vinyl groups at 200 h and show little change due to irradiation.

The formation of methyl end groups can be determined by monitoring an IR band at 1378 cm^{-1}, assigned to the symmetric bend for a methyl group.[4,17] This band can be resolved by appropriate spectral subtraction techniques. The time dependence of change in the band at 1380 cm^{-1} due to UV exposure for 400% elongated samples and unelongated samples is shown in Figure 4. The elongated samples show a faster increase in methyl end formation and reach a value at about 7 times greater than that for unelongated samples. As in the case of vinyl groups, this band should be relatively insensitive to stress, since it represents a functional group at the end of a molecular chain.

Selected regions of the ^{13}C NMR spectrum of a 390% elongated sample after 22-h UV exposure are compared with those of an unelongated sample with 24-h UV exposure in Figure 5. These regions show peaks assigned to acetyl C_α at 43.8 ppm and acetyl C_β at 22.1 ppm. The peak at 43.8 ppm is clearly due to acetyl and not aldehyde as determined from the spectra of model mixtures. After UV exposure, the unelongated sample shows both vinyl and acetyl groups. The 390% elongated sample shows solely vinyl groups of a comparable amount to that of the unelongated sample but none of the peaks associated with acetyl groups. Although the spectra were not run under conditions for quantitative analysis, the relative concentrations can be estimated within 20%. It is concluded that under the conditions of this experiment comparable amounts of vinyl groups have been formed in both samples, and the extent of formation of acetyl groups for the 390% elongated sample was only one third or less than that in the unelongated sample.

Undrawn P(E/CO), photolyzed in nitrogen at 30 °C, degraded by a two-step process as shown in Figure 6. Cumulative loss of CO after 575-h UV exposure was about 90%. Since CO content varies inversely with gas evolution, the reaction rate for gas evolution leveled off at a point that corresponds to a CO loss of about 55%. This value is roughly equal to the amorphous fraction determined by X-ray diffraction (Table II). The rapid initial rate of gas evolution is consistent with fragmentation reactions in amorphous regions, while the slower subsequent step evidently involves loss of CO from crystalline regions.

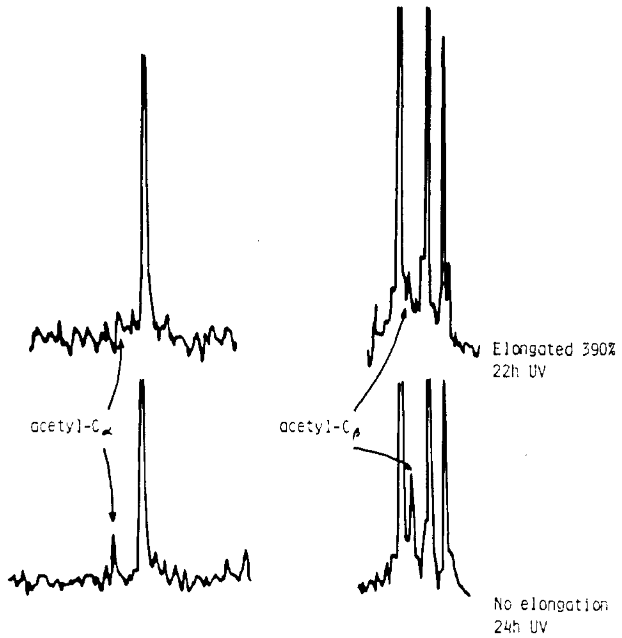


Figure 5. ^{13}C NMR spectral regions showing acetyl C_α and C_β peaks for 390% elongated P(E/CO) after 22-h UV exposure and unelongated P(E/CO) after 24-h UV exposure.

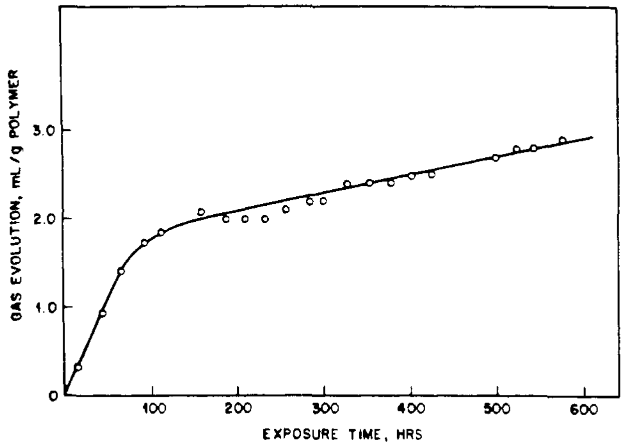


Figure 6. Time dependence of gas evolution of unelongated P(E/CO) due to UV exposure at 30 °C, under nitrogen atmosphere.

Discussion

Mechanical stress causes changes in the physical properties and chemical reactivity of polymers.[18] For semicrystalline polymers, the physical effects of uniaxial elongation include changes in the crystalline content, the nature of crystalline and amorphous regions, and the volume and dimensions of voids.[5,19] These morphological changes dramatically influence physical properties such as the diffusion and solubility of smaller molecules in the polymer. Macroscopic extension of a polymer film causes anisotropic orientation and extension of polymer chains. Stress can cause chain breaks and introduce radicals, which can initiate degradative processes such as oxidation or microcracking.

Ketonic carbonyl groups in the backbone of a polyethylene chain are also probes for studying the effects of molecular orientation on the photochemistry of the polymer. Ketonic groups undergo photochemical scission by two primary pathways, the type I radical process and the type II nonradical process. Type II scission is strongly conformationally dependent and should be sensitive to restrictions on motion of the polymer chain.[20] Analysis of the end groups formed by scission reactions should indicate the effect of molecular chain tension on the relative importance of type I and type II processes. Before the chemistry is discussed, the morphology and structure of P(E/CO) and changes due to orientation should be discussed.

The IR dichroism of peaks associated with carbonyl and vinyl groups showed that elongation caused the molecular chains to be oriented in the direction of stretch. The dichroic ratios of other measured peaks were in agreement with those for polyethylene reported by Read and Stein[6] and Glenz and Peterlin,[7] with the exception of the peak at 1080 cm^{-1}. This peak may be due to some unknown vibration rather than the assigned C–C skeletal stretch.

Several morphological changes due to elongation were observed in X-ray diffraction patterns of oriented samples before UV irradiation. During 390% elongation, the average crystallite size decreased by 75%, and the percent crystallinity increased by 25%. Stress-induced deformation leads to breakup of crystallites and to extension and alignment of chain segments in the amorphous region into new crystallites. This process is analogous to strain-induced crystallization of rubbers.[21] Another effect of mechanical stress is the generation of the monoclinic phase, whose relative amount (based on the total crystallinity) was 6%, in excellent agreement with the value determined by Siesler for 400% elongated polyethylene using an IR spectral difference method.[5]

The most significant changes in morphology due to chain scission caused by UV irradiation can be summarized as follows: (1) an increase in crystallinity due to alignment of broken chains in both unelongated and elongated samples; (2) an increase in crystallite size (28%) for the elongated sample, while the larger crystallites of the unelongated sample remain essentially unchanged (on prolonged irradiation, the crystallite size does increase about 10%); (3) an increase in the orthorhombic form at the expense of the monoclinic form in elongated samples. The relief of stress by scission of tie chains accounts for the decrease in monoclinic content, while the accompanying increase in chain mobility leads to increases in overall crystallinity and crystallite sizes.

Changes in chemical functional groups caused by mechanical degradation or elongation of polymers have been studied by IR spectroscopy.[22,23] Complementary studies of the reactivities and ESR spectra of polymer radicals generated by mechanical degradation have been reviewed by Sohma and Sakaguchi.[24] Our present study uses IR and ^{13}C NMR spectroscopy to observe changes in chemical functional groups formed by UV irradiation of elongated P(E/CO) copolymer.

The type and extent of chain scission in P(E/CO) were determined by monitoring the newly formed end-group functionalities. With ^{13}C NMR, it is possible to unambiguously detect acetyl end groups, which arise solely from type II scission. Methyl end groups, formed primarily from type I scission, were analyzed by IR and ^{13}C NMR spectroscopy. Vinyl end groups, formed by both types of scission, were monitored by IR and NMR spectroscopy.

As discussed earlier, the initial formation of vinyl end groups showed a direct dependence on extent of orientation, with the rate of formation increasing with elongation. If vinyl groups were formed primarily by type II scission in oriented samples, as is the case in unelongated P(E/CO), then the decrease in concentration of carbonyl groups should show a similar dependence. In the case of unelongated P(E/CO), 80% of chain scission occurs at the onset by a type II scission mechanism.[6] There was apparently no direct correlation between the initial rate of CO loss and the extent of elongation of samples. From difference IR, the number of new methyl end groups was about 7 times larger for an oriented sample than for an unelongated one. The NMR peaks for acetyl groups were present at a signal-to-noise ratio of >3 for the oriented sample exposed to the same light dose. This evidence indicates that the predominant photochemical scission mechanism in oriented P(E/CO) is type I and differs from the predominant type II scission in unelongated P(E/CO). The initial rate of vinyl group formation increased over 2 times in going from unelongated to oriented samples. Therefore, the rate of type I scission was increased by over an order of magnitude, after 390% elongation.

Orientation has a dual effect on photochemical reactivity of P(E/CO). Orientation retards the ability of polymer chains to twist into the conformation necessary for type II scission. Additionally, tension on tie chains enhances type I scission by reducing cage recombination by the radical pairs. This study provides a clear demonstration of the effect of molecular chain orientation on both the rate and mechanism of photoreactions.

These scission processes should respond in a way similar to those caused by other forms of stress on molecular chains. In accordance with the kinetic theory of rubber elasticity, thermal stress on chain segments in amorphous P(E/CO) should also accelerate type I scissions. Such an effect has indeed been noted by Hartley and Guillet,[25] who reported that the quantum yield of type I scission was nearly the same as that for type II scission at 120 °C in P(E/CO), but at room temperature the quantum yield for type I scission was only one-fifth that of type II scission. Other studies have probed effects of elongation on the photooxidation of polyethylene,[18] on the orientation of molecules in polyethylene,[26] and on the photochemistry of a conformationally labile molecular dopant in polyethylene.[27]

Conclusions

Tension on molecular chains may either inhibit or promote reaction rates. For example, P(E/CO) photolyzes by competing Norrish type I and type II processes. The type II reaction rate is about 8 times faster in undrawn film, but the type I rate is at least 3 times faster in film cold drawn 400%. Evidently, constraints on intercrystalline tie chains suppress formation of the cyclic intermediate in the nonradical type II process and reduce the probability of cage recombination of radical chain ends formed in the type I reaction. Similar effects may be caused by thermal stress. Photolysis in nitrogen at wavelengths above 290 nm causes both loss of CO by chain scission in crystalline regions and extensive chemicrystallization in amorphous regions at 30 °C, about 70 °C below the softening temperature of the polymer.

Registry No. (E)(CO) (copolymer), 25052-62-4.

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Synthesis of a Chemically Ordered Liquid Crystal Polymer

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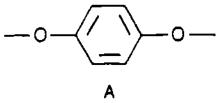
ABSTRACT: Links between chemical sequence structure in self-ordering polymers and their physics are still to be established. In order to address this problem we have proceeded to synthesize a sequentially ordered and regioregular terpolymer which exhibits liquid crystallinity. Neglecting end groups, this polymer is a constitutional isomer of a chemically random liquid crystal polymer reported previously. The synthesis of ordered–disordered chemical analogues has been difficult in the past either because of the absence of liquid crystallinity in highly regular chains or because of difficulties in developing regioregular polyesters. The mesogenic chain synthesized here contained dioxyphenyl (A), oxybenzoate (B), and pimeloate (C) structural units and was built from the condendation reaction between the symmetric monomer ABCBA and pimeloyl chloride. The structure of the regular polymer was verified by ^{13}C NMR analysis of tetrachloroethane solutions and additional characterization was carried out through DSC and dilute solution viscometry.

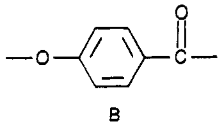
Introduction

Links between molecular structure and the physics of liquid crystal polymers are still to be established. An intriguing question is how chemical disorder along the backbone affects phase structure in the fluid state. It is also puzzling how chemically random mesomorphic chains order to form partly crystalline solids. These questions are important since many liquid crystal polymers are synthesized by transesterification reactions that lead to chemically disordered backbones. For example, Blackwell and co-workers have shown through calculated X-ray diffraction patterns that some aromatic liquid crystal polyesters can be described as chemically random.[1] Recent work from our laboratory also describes an aromatic–aliphatic polyester as random at the diad level by ^{13}C NMR analysis.[2] One possible consequence of chemical disorder is the description of the system as chain segments or chains with a flexibility distribution rather than a single persistence length. This nonuniform rigidity and chemical disorder could affect chain dynamics by controlling the density of interchain associations and entanglements. Molecular organization and phase behavior of the fluid and solid states should also be affected by chemical disorder and nonuniform rigidity.

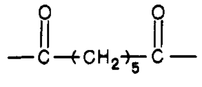
It is in this context that we have proceeded to synthesize a chemically regular analogue to the liquid crystal polymer containing the following three structural units:



A



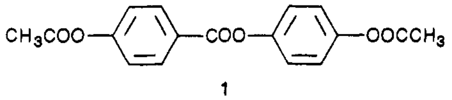
B



$$-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-$$

C

We reported earlier[2] on the synthesis of the random chain from the following two monomers:

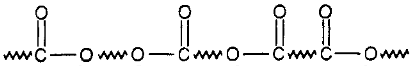


1

$HOOC{-}(CH_2)_5{-}COOH$

2

A random chain grows during this polymerization reaction for two reasons. One is that the central ester bond in 1 participates in transesterification reactions and the second is the non-symmetric nature of monomer 1 leading to an aregic chain.



We describe herein the synthesis and chemical characterization of the regular mesogen. In two following papers