

Synthesis and Photodegradation Behavior of Polyethylene Containing Side-Chain Keto Ether Groups

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Synopsis

The synthesis and photochemical behavior of the polymers obtained by grafting diazoacetophenones and *p*-substituted diazoacetophenones onto an ethylene-vinyl alcohol copolymer were studied. Photodegradation proceeds through a primary process with generation of acetophenone (or the *p*-substituted acetophenone) and "in chain" keto groups. A secondary photochemical process sensitized by these two units leads to oxidative photodegradation. The degradation leads to lowering of the molecular weight in prevalence to crosslinking. The effect of the *p*-substitution on the acetophenone with electron-withdrawing substituent has little effect on the degradation rate.

INTRODUCTION

The photochemical behavior in solution of a series of α -keto ethers has been reported by Turro and Lewis¹; the results were interpreted in terms of the type II photoelimination and cyclization reaction.

The variations in quantum yields and rate constants for product formation as compared with intramolecular photoelimination and cyclization in alkyl aryl ketones are interpreted in terms of a lowering of bond dissociation energy for the γ -hydrogen due to the ether oxygen or more probably of a lowering of the entropy requirements for the formation of the six-membered transition state due to the presence of the oxygen atom.

We report here the preparation and characterization of polymeric α -keto ethers through the grafting of diazo derivatives of acetophenones and *p*-substituted acetophenones on an ethylene-vinyl alcohol copolymer in order to study the photochemical behavior of the grafted polymers in view of obtaining photodegradable polymers.

EXPERIMENTAL

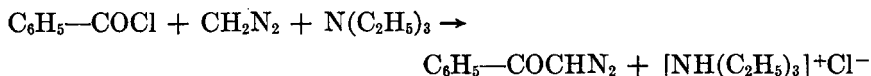
Ethylene-Vinyl Acetate Copolymer. The polymer used in the experiment was a commercial sample of a modified polyethylene supplied by ANIC.

In Table I, molecular weights and vinyl acetate contents of a fractioned copolymer are reported.²

TABLE I
Characterization of Ethylene-Vinyl Acetate Copolymer

Fraction no.	Weight of fraction, %	Vinyl acetate content, % w/w	M_n
1	14.6	4.2	12,100
2	50.6	5	29,000
3	7.1	4.5	29,800
4	5	4.6	37,200
5	7	4.5	56,200
6	9	4.6	87,000
7	6.7	5	119,000

Diazoacetophenone. The product was synthesized by the reaction of the corresponding acylchloride with diazomethane in the presence of triethylamine according to the scheme



To a solution of 11.76 g (0.28 mol) diazomethane in ether was added 40.2 cc (0.28 mole) triethylamine. To the solution cooled to 0°C and under stirring was added dropwise 40 g (0.28 mole) of the corresponding acyl chloride in 90 cc dry ether. The solution was kept at 0°C overnight under stirring. At the end of the reaction, the solution was concentrated under vacuum and the residue dissolved in a 10:1 ether-alcohol mixture. Crystallization from this solution gave 28 g (77% yield) of diazoacetophenone (mp 47°C). The product was characterized by IR and NMR spectra.

p-Nitro- and *p*-chlorodiazoacetophenone were prepared according to the same procedure. Yields were in the same range as for diazoacetophenone.

Ethylene-Vinyl Alcohol Copolymer. To a 1% solution of an ethylene-vinyl acetate (5% in vinyl acetate) copolymer in toluene at 85°C, a 1% solution of NaOH in isopropanol (3 mmoles NaOH/g polymer) was added dropwise under stirring. The reaction was maintained for 4 hr.

At completion of the reaction, the solution was added under stirring to two volumes of methanol. The polymer which precipitated was collected on a filter, washed with methanol, and dried at 50°C under vacuum. IR spectra of a thin film of the polymer show a broad band around 3300 cm⁻¹ for the formation of the alcoholic OH, while the 1745 cm⁻¹ band due to the acetate group has almost completely disappeared, indicating almost quantitative hydrolysis. A weak $\nu_{\text{C=O}}$ band is also observed at 1710 cm⁻¹ as evidence of partial oxidation of the polymer.

Grafting. To a 0.7% solution of the ethylene-vinyl alcohol copolymer (120 g) in toluene (17 liters) at 65°C, 5 ml of BF₃·OEt₂ was added dropwise and, in succession, a toluene solution of the diazo ketone to be grafted (mole diazo/mole —OH = 1.3). The reaction was carried out under nitrogen and in absence of light. At completion of the reaction, the solution was added under stirring to two volumes of methanol. The polymer precipi-

tated was collected on a filter washed with methanol and dried at 50°C under vacuum (115 g).

Photodegradation. Transparent films of the grafted polymer obtained by hot press (0.15 mm thick) were irradiated with a 6000-W xenon arc fitted with a water-cooling Pyrex glass jacket (effective wavelength above 290 m μ) at a distance of 47 cm. In order to keep the temperature of the sample at 30° \pm 2°C, the film was sprinkled with water spray.

The films were exposed in a stepwise fashion, and changes in IR spectra, carbonyl and vinyl absorbances, per cent elongation, and intrinsic viscosities were measured at each interval.

Per cent elongation was measured on microtensile specimens according to ASTM D-1708. Carbonyl absorbances referred to the thickness of the specimen were measured at 1715 cm⁻¹ on a P.E. Model 325. Vinyl double-bond concentration was measured as absorbance of the 908 cm⁻¹ band referred to the thickness of the specimen on the same IR spectrometer. Data on carbonyl and vinyl formation under irradiation were referred to a low-density polyethylene as standard.

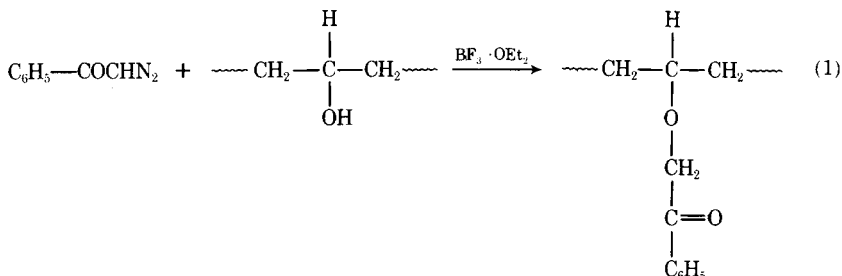
Viscosities were measured in decalin (concn. 0.1% g/cc) at 135°C on a Schott Viscotimer. Intrinsic viscosities were calculated according to

$$[\eta] = \frac{1}{C} (2 (\eta_{spec} - \ln \eta/\eta_0))^{1/2}$$

Molecular weights M_n and M_w were obtained by elaboration of elution volumes distribution of the sample injected in a Waters 200 GPC according to the Drott and Mendelson⁷ method for branched polyethylene. Measurements were carried out in 1,2,4-trichlorobenzene at 130°C.

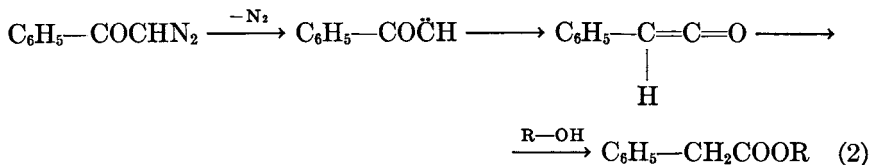
RESULTS AND DISCUSSION

Grafting on the resulting ethylene-vinyl alcohol copolymer was carried out through the diazo derivate⁸ of the aryl alkyl ketone, according to eq. (1):



For the reaction with *p*-chloro- and *p*-nitrodiazocetophenone, the extent of grafting was evaluated by the mean of the analytical determination of the chlorine and nitrogen content, respectively. The yields, slightly higher for the *p*-chloro derivate, were in both cases around 60%. Under the experimental conditions, a certain amount of the corresponding phenylacetic ester is formed owing to phenyl group migration to form a ketene which adds to

the hydroxyl groups in the polymeric backbone according to a Wolff rearrangement of diazoketones⁴:



In order to minimize this rearrangement, the grafting was carried out also with *p*-nitro- and *p*-chlorodiazooacetophenone, that is, with *p*-substituted aromatic groups being less prone to migrate than the unsubstituted phenyl group.

It should be pointed out that the presence of electron-withdrawing substituents in the para position, besides decreasing the possibility of a Wolff rearrangement, should also have an effect on the photochemical behavior of the alkyl aryl ketones insofar as it increases the n, π^* character of the triplet state of the excited ketone group, thereby increasing the efficiency of hydrogen abstraction. The IR spectra of the polymer grafted with diazoacetophenone show two distinct carbonyl absorptions of medium intensity at 1682 cm^{-1} and 1715 cm^{-1} and a weak third band at 1725 cm^{-1} . The 1682 cm^{-1} band, stronger than the other two, is in agreement with the formation of the α -keto ether group while the 1725 cm^{-1} band is evidence of a partial Wolff rearrangement with formation of the phenylacetic ester.

The band at 1715 cm^{-1} that preexists in the ethylene-vinyl alcohol copolymer can be related to the presence of keto groups due to partial oxidation of the vinyl acetate copolymer or to a partial oxidation of the ethylene-vinyl alcohol copolymer during the hydrolytic reaction or the subsequent treatment.

Mass-gas chromatography of the products of pyrolysis of the polymer previously subjected to repeated extractions in boiling hexane, besides the multiplicity of hydrocarbon products from the pyrolysis of the polyethylene units, shows evidence of acetophenone and benzaldehyde from the thermal

degradation of the ether bond and formation of $\phi\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}\dot{\text{C}}\text{H}_2$ and $\phi\text{—}\dot{\text{C}}=\text{O}$ radicals that can extract hydrogen from the polymer.

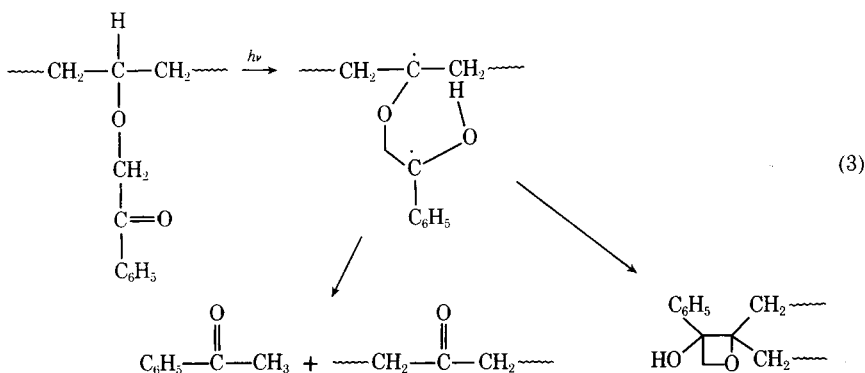
When the grafting is carried out with the *p*-chloro- and *p*-nitrodiazooacetophenone, the carbonyl stretching bands for the α -keto ether group fall at 1685 cm^{-1} for the *p*-chloro derivative and at 1692 cm^{-1} for the *p*-nitro derivative.

Upon irradiation, the carbonyl band of the grafted α -keto ether group disappears, whereas the 1715 cm^{-1} band increases in intensity according to the progress of the degradation process. At the same time absorption bands appear at 908 cm^{-1} , 1010 cm^{-1} and 1635 cm^{-1} according to the formation of vinyl groups following the Norrish type I and II reactions⁵ of keto groups in a polymeric matrix.

In the case of the polymer grafted with *p*-nitrodiazoacetophenone, besides the reported evolution of the carbonyl absorptions and vinyl formation, in the IR spectra a decrease of the absorption bands at 1528 cm⁻¹ and 850 cm⁻¹ due to the stretching and deformation modes of vibrations of the NO₂ group is observed. This is probably due to a photochemical reaction of the nitro group that, in the presence of abstractable hydrogens, can undergo a photoreduction process.

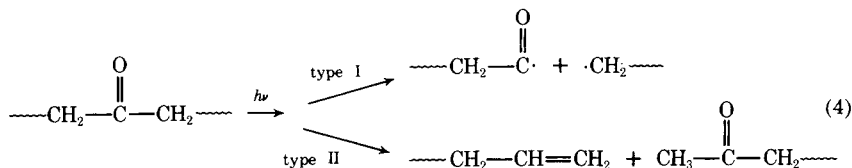
The progressive diminution of the carbonyl band due to the aromatic ketone is in agreement with the participation of this unit, not only to the photoelimination process in which an alkyl aryl ketone is formed, but also to the subsequent photodegradative process in form of the free acetophenone (or the *p*-substituted derivatives) mainly through hydrogen abstraction from the polymer via the excited triplet state.

We believe that the photochemical behavior of the grafted polymer can be interpreted in terms of two consecutive photochemical processes. In a primary process according to eq. (3), the breaking down of the α-keto ether group through a Norrish type II mechanism leads to the formation of an "in chain" ketone group and of a mole of the corresponding alkyl aryl ketone:



We think that the rigid polymeric matrix would enhance the quantum yield of the photoelimination reaction versus photocyclization as compared with yields reported for low molecular weight α-keto ether in solution.¹

In the secondary photochemical process, the "in chain" ketone group undergoes photolysis by the well-known Norrish type I and type II mechanisms of polymeric ketones with the carbonyl group in the backbone according to eq. (4):



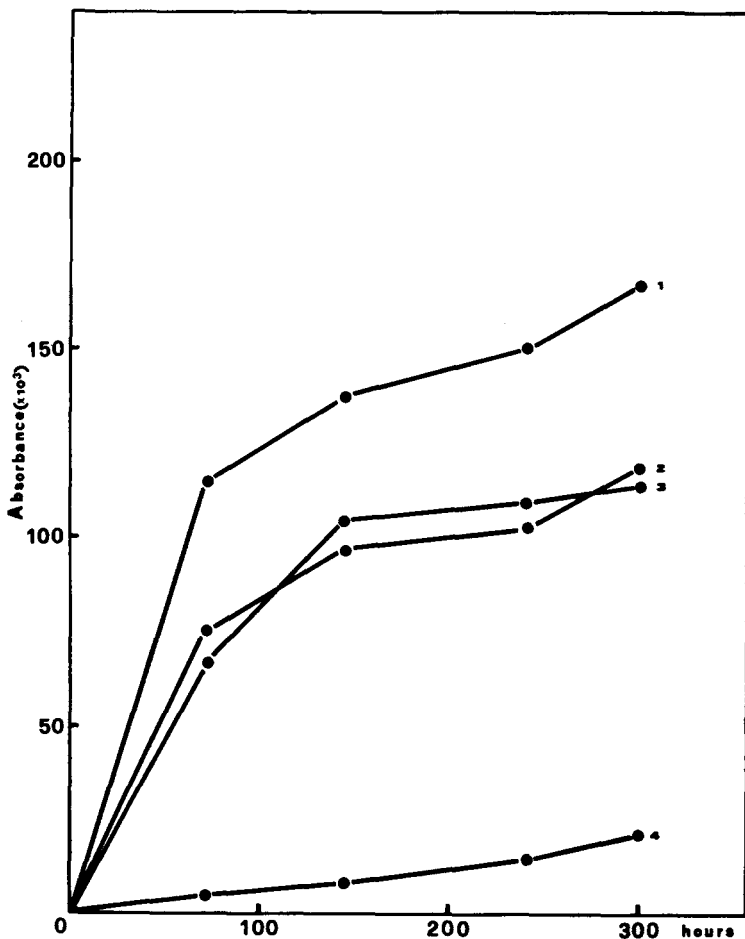
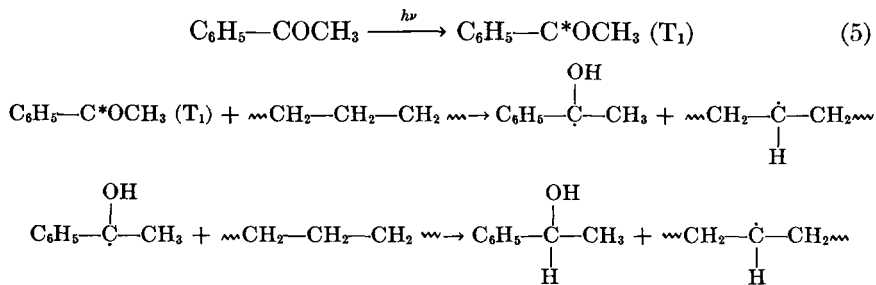


Fig. 1. Carbonyl absorption as function of irradiation time (all data corrected for background absorption): (1) *p*-nitroacetophenone; (2) *p*-chloroacetophenone; (3) acetophenone; (4) low-density polyethylene as reference.

The alkyl aryl ketone produced in the primary process could in turn contribute to the secondary photodegradation process by hydrogen abstraction via the excited triplet state⁶ according to eq. (5):



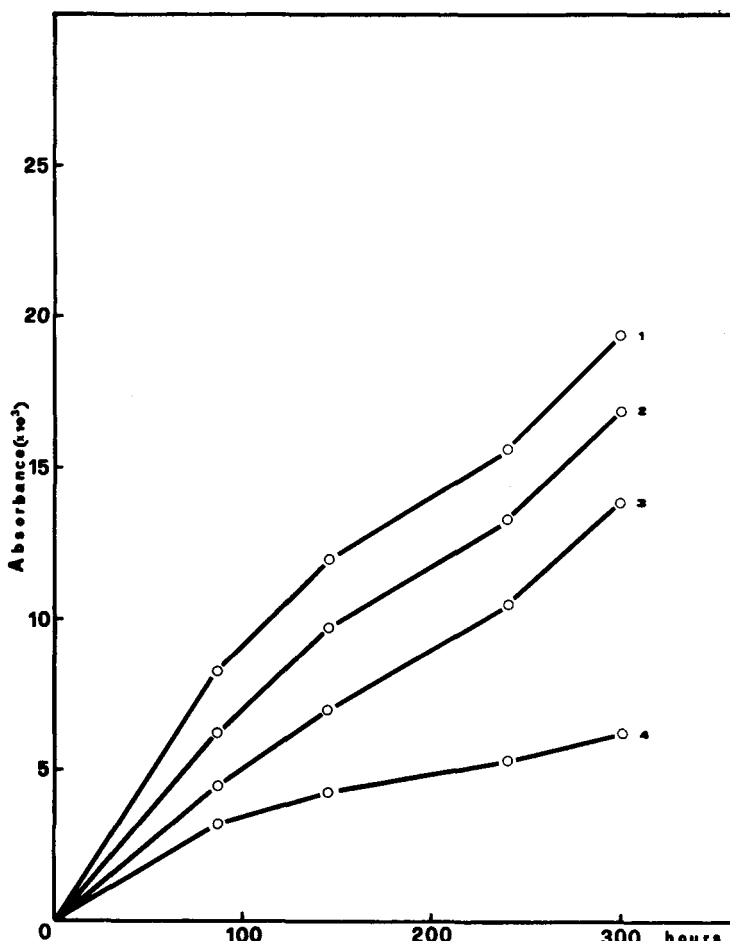


Fig. 2. Vinyl absorption as a function of irradiation time (all data are corrected for background absorption): (1) *p*-chloroacetophenone; (2) *p*-nitroacetophenone; (3) acetophenone; (4) low-density polyethylene as reference.

The alkyl radical in the polymer backbone in turn leads to crosslinks or, in the presence of oxygen, to oxidative degradation of the polymer.

The rates of carbonyl (Fig. 1) and vinyl (Fig. 2) formation do not always correlate with the per cent elongation change (Fig. 3) and with the decrease in intrinsic viscosities and molecular weight (Table II).

The initial rapid increase of the 1715 cm^{-1} band is dependent on the additive effects of the primary photoprocess in which an "in chain" carbonyl is formed for each photoelimination and of the carbonyl increase due to the evolution of the photo-oxidation in the secondary photoprocess.

As the irradiation goes on, a certain tendency to level observed in the CO absorbance-irradiation time graph seems to show a certain autoretardation effect. This has already been observed in the photodegradative behavior of

TABLE II
Variation in Intrinsic Viscosity and Molecular Weight with Irradiation Time (Polymer Grafted with *p*-Chlorodiazoacetophenone)

Irradiation time, hr	$[\eta]$	M_n	M_w	M_w/M_n
0	0.9608	34.900	260.000	7.44
70	0.820	20.000	323.000	16.15
144	0.789	17.950	280.000	15.59
327	0.592	16.250	155.010	9.53

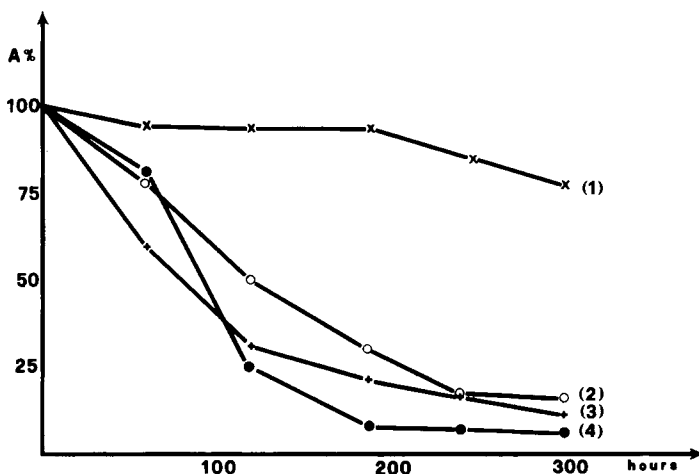


Fig. 3. Per cent elongation loss as function of irradiation time: (1) ethylene-vinyl acetate copolymer as reference; (2) diazoacetophenone; (3) *p*-nitroacetophenone; (4) *p*-chloroacetophenone.

polyethylene in the presence of aromatic ketones.⁸ Anyway, it has been observed that this is not necessarily related to a decrease in degradation rate. In fact, the increase in vinyl group formation and the continuous decrease in intrinsic viscosities (for *p*-chloroacetophenone) do not indicate a drastic reduction of degradation rate at the late stage of the irradiation.

The absence of any gel when the polymer is dissolved for measurement of intrinsic viscosities indicates furthermore a prevalence of main-chain scission with formation of methyl ketone and vinyl unsaturation versus termination by combination with formation of crosslinks. In the case of the polymer grafted with *p*-chlorodiazoacetophenone, from the intrinsic viscosity measurement a reduction of more than 50% molecular weight can be calculated at the end of 300 hr of irradiation.

Apart from the marked increase in the rate of carbonyl formation in the case of the polymer grafted with *p*-nitrodiazoacetophenone, the efficiency of the photodegradative process, as expressed by the various determinations reported in this paper, is only slightly affected by the *p*-substitution with chlorine or nitro group on the alkyl aryl ketone.

Anyway, since the extent of the Wolff rearrangement is very low for all the grafting reactions here reported, the difference observed can only be attributed to the increased efficiency of hydrogen abstraction on the part of the alkyl aryl ketone.

We believe that the reaction yields in the primary photoprocess are conditioned more by the rigidity of the matrix than by the modifications of the energy level of the excited triplet state by substitution on the aromatic ring and that the overall degradative effect is more dependent on the photochemistry of the "in chain" ketone groups generated in the primary photochemical process than on the hydrogen abstraction capacity of the alkyl aryl ketone.

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