is a rapid and satisfactory method provided that a blank control is used to correct for loss of volatile material from the support during the heat treatment.

References and Notes

(1) (a) University of Toronto; (b) Ecole Polytechnique; (c) McGill University.

(2) R. N. Lichtenthaler, R. D. Newman, and J. M. Prausnitz, *Macromolecules*, 6, 650 (1973).

(3) W. B. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, 5, 12 (1972).

(4) R. N. Lichtenthaler, J. M. Prausnitz, C. S. Su, H. P. Schreiber, and D. Patterson, *Macromolecules*, 7, 136 (1974).

(5) H. P. Schreiber, Y. B. Tewari, and D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, 11, 15 (1973).

(6) J.-M. Braun and J. E. Guillet, *Macromolecules*, 8, 882 (1975).

(7) N. D. Petsev, R. N. Nikolov, and A. Kostova, *J. Chromatogr.*, 93, 369 (1974).

(8) D. D. Deshpande, D. Patterson, H. P. Schreiber, and C. S. Su, *Macromolecules*, 7, 539 (1974).

(9) W. A. Aue, C. R. Hastings, and S. Kapila, *J. Chromatogr.*, 77, 299 (1973).

Studies of the Photocycloaddition of Benzophenone to *cis*-Polyisoprene

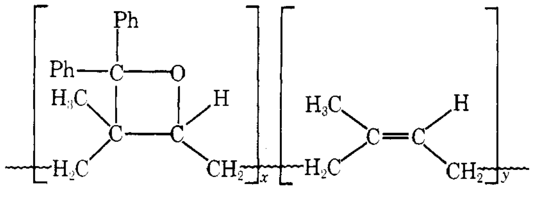
HOWARD NG and J. E. GUILLET*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.

Received February 22, 1977

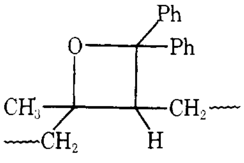
The photocycloaddition of carbonyl compounds to olefins (the Paterno–Buchi reaction) has been extensively studied for various substrates.[1,2] The general mechanism for the reaction is believed to involve the attack of the electrophilic oxygen of the n–π* triplet carbonyl on an electron-rich olefin, to generate preferentially the most stable biradical intermediate, followed by ring closure to yield an oxetane. The general requirement for this reaction is that the unsaturated system should have a higher triplet state energy level than the carbonyl n–π* triplet, so that the competing energy transfer process from the excited carbonyl triplet to the alkene is inhibited. The mechanism is further complicated when the rate of intersystem crossing from the excited singlet to the triplet is slow in comparison to the rate of addition. In this case, the n–π* singlet species initiates attack on the ethylene.[3-5] Although extensive studies of the mechanism and synthetic applications of this reaction have been carried out, it has not been generally applied to polymeric systems. This note reports the investigation of the photocycloaddition of benzophenone to *cis*-1,4-polyisoprene (natural rubber). This may serve as a probe for a deeper insight to the photochemistry of elastomers and also provides a route for the synthesis of novel polymeric structures.

A solution of benzophenone (5%, w/v, 0.17 M) and purified natural rubber (1%, w/v) in 1,2-dichloroethane was irradiated for 24 h under nitrogen with a medium pressure mercury arc in an immersion cell apparatus using a Pyrex glass filter. The rubber had an intrinsic viscosity in toluene at 25 °C of 2.21 dL g^{-1} corresponding to a viscosity molecular weight of 2.9×10^5 using values of $K = 5.02 \times 10^{-4}$ and $\alpha = 0.667$ in the Mark–Houwinck equation. The reaction mixture was then precipitated by a large excess of methanol. The coagulated precipitate was extracted by carbon tetrachloride to isolate the soluble polymer. The extracted solution after solvent evaporation and drying under vacuum for 24 h at room temperature gave a pale-yellow rubbery material (I) (14% yield), which was assigned as a copolymer of isoprene and isomeric isoprene–diphenyloxetane adducts.

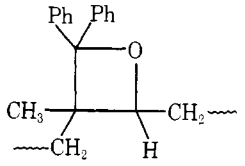


I

I showed strong absorption in the infrared at 10.1 μm, in the characteristic oxetane ring asymmetric stretching frequency range. NMR of I in CCl_4 shows the following features: δ 7.18 (phenyl proton in oxetane units), 5.08 (olefinic proton in residue isoprene units), 2.58 (small and broad, oxetane ring proton in one of the two isomeric forms Ia or Ib), 2.08, 1.98 (splitting, allylic methylene protons in isoprene units), 1.68 (methyl group in isoprene units), and 1.30 (very broad, methylene and methyl proton in the adduct segments). The expected low-field signal of another oxetane ring proton was indistinguishable from the background.

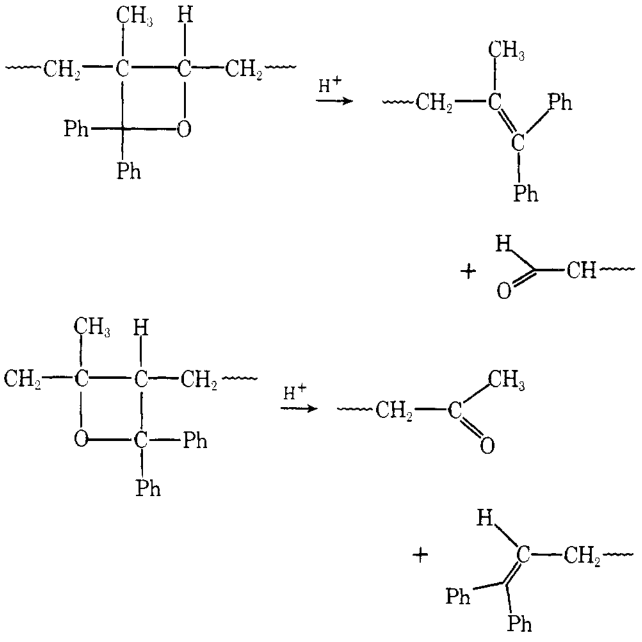


Ia



Ib

NMR analysis indicated that the polymer contained about 25 mol % oxetane rings. Treatment of I with dilute hydrochloric acid in THF and toluene gave a product (II) with a considerable decrease in molecular weight (instrinsic viscosity of I, 0.22; intrinsic viscosity of the hydrolyzed product II, 0.13). In view of the ease of acid catalyzed decomposition of oxetanes, this decrease in molecular weight may be due to chain scission resulting from the acid decomposition of oxetane in the chain skeleton as shown in the following schemes:



Infrared and NMR spectra of the hydrolyzed product II showed new peaks at IR 5.84 (strong, C=O stretching) and at NMR δ 2.20 (CH_2—C=C(PH)$_2$), 2.38 (CH_3—CO), and 6.80 (CH=C(Ph)$_2$), which is consistent with this mechanism of decomposition.

The suspension resulting from the addition of methanol to the photoreaction mixture was filtered out. It gave an orange-yellow nonrubbery oligomer (III) (31% yield, intrinsic viscosity 0.04). Infrared and NMR spectra data showed the product is an oligomer of polyisoprene with a high percentage of oxetane rings (~70%) in the chain skeleton.

The mol % of oxetane formation in the polyisoprene chain was estimated from the relative peak area of the phenyl proton and olefinic proton signals from the corresponding NMR spectra. After solvent evaporation, the filtrate from the methanol addition gave a yellowish-brown residue which was shown to be a mixture of unreacted benzophenone (33%) and the hydrogen abstraction product benzpinacol (22%).

Solid State Synthesis

The photoreaction was also carried out in the solid state with benzophenone dissolved in a thin film of natural rubber. The film was made by casting a benzene solution onto mercury and evaporating the solvent under a dry nitrogen atmosphere. The films were irradiated with a GE sunlamp at 10 cm distance using a Pyrex filter to remove wavelengths shorter than 300 nm. Thus only the carbonyl chromophore in the film was excited. After irradiation the films were brittle and transparent and insoluble in solvents such as benzene, toluene, and chloroform. The irradiated films were soaked in methanol for 2 days in order to dissolve the residual unreacted benzophenone and then dried under vacuum at room temperature for another 2 days. Infrared spectra of these films after treatment showed that the amount of residual benzophenone and benzpinacol still in the film was negligible.

The IR analysis of natural rubber has been described by Golub et al.[6,7] The decrease in the 12 μm band, arising from the loss of original unsaturation, the increase in the 10.1 μm band, due to the formation of oxetane in the chain, and the decrease in the 6.0 μm band, due to consumption of isoprenic double bonds, were monitored using the 7.25 μm band (due to CH_3 groups) as an internal standard. The residual percentage of C=C unsaturation χ after irradiation was calculated according to the following equation,

$$\chi = [(A_{12u}/A_{7.25})_t/(A_{12}/A_{7.25})_0] \times 100\%$$

where A is the absorbance at the specified wavelength measured on the films using a Perkin-Elmer Model 337 IR spectrophotometer. It is known that in our experimental conditions (λ >300 nm) the cis-trans isomerization of the olefinic units in the film is negligibly low in the short time of irradiation ($\leq$2 h).[8]

Discussion

Under our reaction conditions, the photoreaction is presumably initiated by the ^{3}(n–π*) excited state of benzophenone which results from the extremely fast intersystem crossing of the ^{1}(n–π*) state ($K_{isc} > 5 \times 10^9$ s^{-1}).[9,10] The yield of the photocycloaddition product is not 100% because of several efficient competing processes that consume the triplet excited benzophenone. Hydrogen abstraction by the triplet excited benzophenone yields benzpinacol ($k = 6.6 \times 10^4$ M^{-1} s^{-1}).[11] This process is favored in the presence of active methylene hydrogens at the allylic units in the polyisoprene chain. This is reflected by the appreciable yield of benzpinacol and the extensive cross-linking of the polymer products in inert solvents (1,2-dichloroethane and benzene). Excited benzophenone can also be deactivated as a result of the radiationless decay of the benzophenone triplet ($k \sim 3 \times 10^5$ s^{-1})[9,10] and energy transfer of the excited triplet (E_T = 69 kcal/mol) to the polyisoprene chain. Recent studies by Rabek have shown that polyisoprene is photodegraded in air by visible light sensitized by benzophenone;[12] however, the detailed mechanism is unclear. The marked decrease in intrinsic viscosity of the products in the absence of oxygen may result from chain scission by energy transfer from excited benzophenone or by proton abstraction followed by radical rearrangement. However, degradation by traces of residual oxygen in the solution is also possible.

The yield of oxetane in the polymer chain is greater in the lower molecular weight products, possibly because of steric restrictions in the longer chains. This is consistent with the high oxetane content in the oligomers (~70%). The orientation of the addition of excited benzophenone to the polyisoprene chain is not strictly dictated by the formation of the most stable intermediate biradical. Appearance of the δ 2.58 signal from the cycloaddition product and δ 6.80 signal from the hydrolyzed cycloaddition product shows an appreciable yield of oxetane derived from the less stable biradical intermediate (structure Ia).

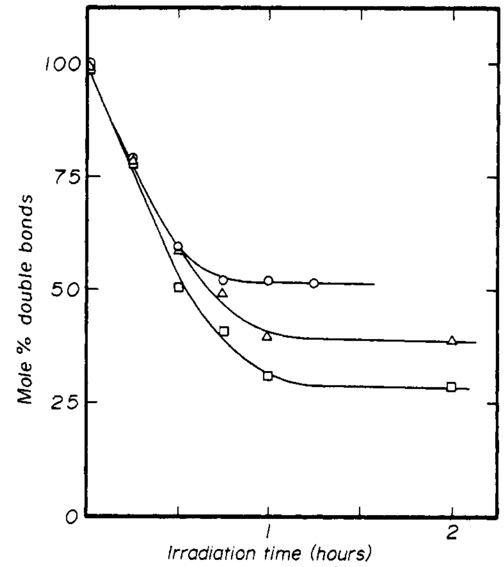


Figure 1. Variation of C–C double bond content in the polymer film as a function of irradiation time. Irradiation at 70 °C. Mole percent benzophenone: (○) 26, (△) 33, (□) 50.

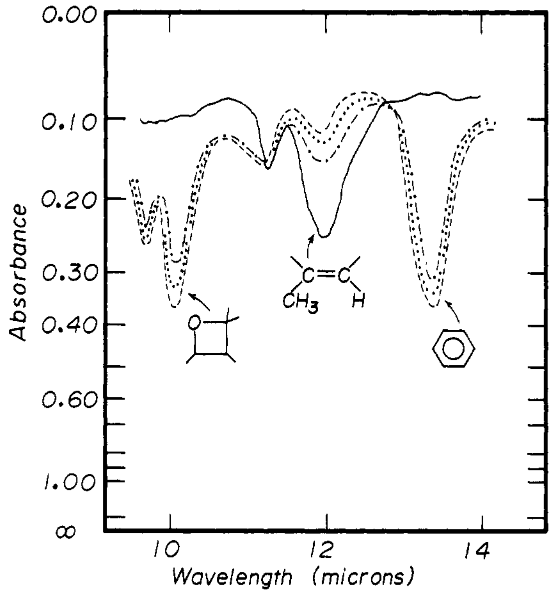


Figure 2. Infrared spectral variations of films on irradiation: (—) 0.02 mm *cis*-polyisoprene film cast on NaCl plate; 0.35 mol ratio benzophenone:isoprene at (- · -) 0.5 h irradiation, (· · ·) 0.75 h irradiation, and (- - -) 1 h irradiation.

The difficulties in solution studies caused by cross-linking of the polyisoprene were overcome by carrying out the photocycloaddition in the solid film. In this technique the benzophenone is dissolved in a polyisoprene film and after irradiation the unreacted benzophenone is removed by soaking in methanol. Using light from a GE sunlamp at 10 cm distance from the film the rate of consumption of C–C double bonds

Table I
Glass Transition Temperature of Polyisoprene and Its Photochemical Adduct with Benzophenone Determined by DSC

Irradiation time, min	Residual double bonds, mol %	T_g, °C
0	100	−64.9
15	70.4	31
30	61.8	37.8
45	58.0	37.6
60	51.5	41.2
120	42.6	45.8

is quite rapid, as shown in Figure 1. Most of the reaction takes place within 1 h after which no further radiation seems to occur. The extent of reaction increases with the initial concentration of benzophenone. Figure 2 shows the infrared spectra of the extracted films taken after various times of irradiation. They are qualitatively similar to those of the polymers made in solution and should therefore have similar structures, although it is not possible to check this by NMR because of the insolubility of the films. The maximum conversion to cyclic products, as estimated from the removal of internal double bonds in the polyisoprene, seems to level out at about 70%, as shown in Figure 1. It is not known whether this is a limit imposed by steric requirements in the chain or by the fact that the benzophenone is no longer soluble in the polymer at high degrees of conversion. Furthermore, an equimolar mixture of polyisoprene and benzophenone contains 73 wt % benzophenone, and the benzophenone tends to crystallize out at these high concentrations.

The inclusion of bulky phenyl groups into the polyisoprene chain, in addition to the "stiffening" effect of the oxetane ring, would be expected to raise the glass transition of the polymer. Measurements of T_g on a series of films made by irradiation of equimolar mixtures of benzophenone and polyisoprene for various times at 110 °C are given in Table I. The measurements were made using a Perkin-Elmer DSC IB differential scanning calorimeter. Addition of only 30 mol % benzophenone gives an increase of more than 100 °C in the glass transition, confirming the expected effect of inclusion of ring structures in the polymer chain. Increases in benzophenone units above this amount apparently do not increase T_g further, for reasons which are not obvious. It is possible that the double bond analysis overestimates the yield of cyclic products, and that toward the end of the reaction double bonds are removed by mechanisms other than cyclization, such as cross-linking.

In conclusion, these studies have shown that it is possible to add appreciable quantities of benzophenone to *cis*-polyisoprene to form novel polymer structures in which an oxetane ring replaces a double bond in the backbone of the polyisoprene chain. Presumably this reaction could be used with other polydienes and carbonyl compounds to make polymeric structures unattainable by conventional polymerization reactions. This reaction might be considered as a new type of photopolymerization in which the polydiene acts as a "template" and the rings are formed by successive addition of a photoexcited intermediate.

Acknowledgments. The authors gratefully acknowledge financial support of this work from the National Research Council of Canada and a University of Toronto Open Fellowship (to H.N.).

References and Notes

(1) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).
(2) L. L. Muller and J. Hames, "1,2-Cycloaddition Reactions", Vol. 3, Interscience, New York, N.Y., 1967.
(3) N. C. Yang and W. Eisenhardt, *J. Am. Chem. Soc.*, **43**, 1277 (1971).
(4) N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, **92**, 320 (1970).
(5) J. A. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.*, **93**, 4794 (1971).
(6) M. A. Golub and J. Danon, *Can. J. Chem.*, **43**, 2772 (1965).
(7) M. A. Golub and C. L. Stephens, *J. Polym. Sci., Part A-1*, **6**, 763 (1968).
(8) M. A. Golub and C. L. Stephens, *J. Polym. Sci., Polym. Lett. Ed.*, **4**, 959 (1966).
(9) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).
(10) For a recent review, see P. J. Wagner, *Top. Curr. Chem.*, **66**, 1, (1976).
(11) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Am. Chem. Soc.*, **91**, 5413 (1969).
(12) J. F. Rabek, *Chem. Stosow., Ser. A*, **11(1)**, 53 (1967); *Chem. Abstr.*, **68**, 79357g (1968).

Trace Element Characterization of Thin Polymer Films by Proton-Induced X-Ray Emission Spectrometry

DENNIS N. BREITER*[1a] and MARVIN L. ROUSH[1b]

Analytical Chemistry Division, National Bureau of Standards, Washington, D.C. 20234, and the Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742. *Received January 6, 1977*

Trace element levels in polymers reflect the concentrations of certain polymer constituents including catalysts, stabilizers, and fire retardants. Their characterization is of interest because these constituents affect the physical, chemical, and electrical properties of polymers. Another interest in monitoring trace constituents of polymers arises out of the medical concern that certain toxic constituents of plastics can leach out when the plastics come into contact with food or body fluids. There is also a need to know the trace element levels in selected thin plastic films which can serve as clean backing materials on which samples can be deposited for trace element analysis by x-ray and proton-induced x-ray fluorescence.

Proton-induced x-ray emission spectrometry (PIXE) is a technique which has been developed and applied to the trace element analysis of environmental samples (e.g., air particulates and trace elements in water) and biomedical samples.[2–8] The references cited in these articles provide a good guide to the literature describing PIXE and its applications. We wish to point out that this technique is particularly well-suited for the simultaneous quantitative analysis of trace elements in thin plastic films.

In PIXE, the characteristic x-ray emissions of interest accompany transitions of electrons into inner atomic shell vacancies created by bombardment by protons with energies of several MeV. These high-energy protons can be produced by Van de Graaff accelerators which exist at a number of laboratories. The energy of a characteristic x ray is determined uniquely by the atomic number of the element from which it emerges. These x rays are individually detected by a lithium-drifted silicon (Si(Li)) semiconductor detector and generate signal pulses which are linearly proportional to their energy. By counting and measuring the number and amplitude of these signal pulses with a multichannel analyzer, one obtains multielement spectra. In Figure 1 we see a typical pulse-height spectrum obtained from a Nuclepore[10] film.

The analysis procedure is calibrated by making measurements on known quantities of selected elements deposited on thin plastic films. These deposits result from solutions which contain the elements of interest at known concentrations. The uniform proton beam includes the area of the dried solution deposit so that for fixed integrated charge (known number of protons) and fixed geometrical configuration, one obtains a calibration in terms of counts per nanogram for each element of interest. Analyses of thin plastic materials are then made