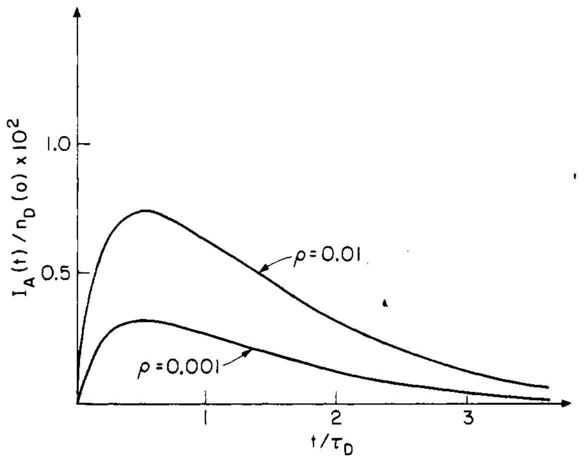

Figure 2. Time dependence of acceptor fluorescence intensity for $R_0 = 40$ Å. Gaussian distribution is assumed and $B = 115$ is used.

can be written as

$$\frac{I_D(t)}{I_0(t)} = \int g(s) \exp(-st)\, ds \tag{14}$$

where

$$s = \frac{R_0{}^6}{\tau_D R^6}, \qquad g(s) = -\frac{2\pi\tau_D R^9}{3R_0{}^6} f(R) \tag{15}$$

Since $I_D(t)/I_0(t)$ is the Laplace transformation of $g(s)$ [eq 14], we can obtain $f(R)$, in principle, by the inverse Laplace transformation of $I_D(t)/I_0(t)$. However, since this inversion is unreliable unless very precise data on $I_D(t)$ are available, the method of cumulant expansion[5] may be preferable. The cumulant expansion method can also be applied to eq 11 where inversion of $I_A(t)$ to find $f(R)$ is not possible (except in the case $\tau_A = \tau_D$) due to the complicated form of the integrand.

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Notes

On the Determination of Specific Retention Volumes of Polymer Stationary Phases

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Lichtenthaler et al.[2] have recently drawn attention to discrepancies in published retention volumes on poly(dimethylsiloxane) stationary phases.[2,3] An interlaboratory comparison[4] of retention volumes measured on seven poly(dimethylsiloxane) columns did not entirely resolve these problems, indicating the importance of packing procedure. In the present note, we wish to comment further on the accuracy of specific retention volumes determined on polymer stationary phases. Earlier studies from these laboratories[5] on polyethylene stationary phases showed a small but apparently real difference between the interactions of vapor phase probes with linear (LPE) and with branched (BPE) samples. (An average difference in the interaction parameter, χ, of 0.053 was found.)

Experimental Section

The experimental procedure and instrumentation were identical with those reported in earlier publications.[5,6] Calcinations were performed by first drying the sieved packing under vacuum for 48 h at 100 °C and then weighing and calcining at 1100 °C. Two-gram aliquots of the dried packing were calcined in porcelain crucibles for 3 h and cooled in a desiccator. All calcinations were done at least in duplicate.

Table I
Column Characteristics of Polyethylene Stationary Phases

Column[a]	Polymer	Support	Polymer in total packing, %	Polymer mass[b]
1	Branched polyethylene	Chromosorb W AW-DMCS	12.07	0.7209
2	Branched polyethylene	Chromosorb W AW-DMCS	10.67	0.7929
3	Linear polyethylene Marlex 50	Chromosorb W AW-DMCS	6.66	0.5529
4	Linear polyethylene Marlex 50	Chromosorb W AW-DMCS	5.57	0.5943
5	Linear polyethylene Marlex 6050	Chromosorb W AW-DMCS	7.42	0.3057
6	Linear polyethylene Marlex 6050	Chromosorb G AW-DMCS	6.88	0.4058

[a] Columns 1 to 4 from ref 5. [b] All packings contained 0.1% 4,4′-thiobis(3-methyl-6-*tert*-butylphenol), based on polymer mass.

Column characteristics are given in Table I. Polymers were linear polyethylene Marlex 6050 ($M_w = 92.2 \times 10^3$, $M_n = 7.4 \times 10^3$) and as earlier described.[5]

Table II
Specific Retention Volumes (V_g) on Linear (LPE) and Branched (BPE) Polyethylenes

		V_g, cm^3/g		
		BPE	LPE	
Solute	Temp, °C	Columns 1–2	Columns 3–4	Columns 5–6
n-Decane	145.1	84.37		
	145.4		78.90	85.51
	153.3		63.43	68.60
n-Dodecane	145.1	257.5		
	145.4		242.5	263.9
	153.3		187.7	203.0

Table III
Corrected Specific Retention Volumes (V_g) on Linear (LPE) and Branched (BPE) Polyethylenes

		V_g, cm^3/g		
		BPE	LPE	
Solute	Temp, °C	Columns 1–2	Columns 3–4	Columns 5–6
n-Decane	145.1	87.44		
	145.4		84.78	85.51
	153.3		68.15	68.60
n-Dodecane	145.1	266.9		
	145.4		260.6	263.9
	153.3		201.7	203.0

Results and Discussion

Table II shows a comparison of specific retention volumes obtained for *n*-decane and *n*-dodecane with those reported in ref 5 on linear and branched polyethylenes. It is seen that, apart from the difference between the linear and branched samples discussed earlier,[5] retention volumes on linear polyethylene differ by as much as 8%. On rechecking the original data it was observed, however, that in the computation of the mass of polymer, no correction had been made in the earlier data for the loss of volatiles from the inert support during calcination. Though small, the volatile content of the inert support could account for the observed discrepancy.

It was found that during drying of the (uncoated) inert support prior to calcination a weight loss of 0.2% was sustained. It has been reported[7] that weight losses of inert supports increased with increasing drying temperature. It became therefore imperative to conduct a blank in rigorously identical conditions. To prevent degradation of the polymers, drying of the support prior to calcination was conducted at 100 °C for 48 h under vacuum. It was found that upon calcination of the dry inert support, a further loss of 0.45% was recorded for both Chromosorb G, AW-DMCS treated, and Chromosorb W, AW-DMCS treated. The applicability of the calcination technique was further tested with a mixture of known composition in polyethylene to ensure complete combustion of the polymer. Treatment of the inert support with pure xylene, thereby simulating a coating procedure, did not alter the weight loss during calcination.

The previous data on linear and branched polyethylenes were recomputed, assuming a weight loss of 0.45% for the inert support, with the results shown in Table III. It is seen that now good agreement is obtained between both sets of retention volumes for LPE. Furthermore, the difference between BPE and LPE has been drastically reduced. This is to be attributed to the different loadings adopted in both sets of columns (11.62 and 10.22% vs. 6.21 and 5.12%, when corrected). The difference between BPE and LPE has been reduced from 5.4 to 1.7%, which is probably within experimental error.

Table IV
Polymer Loading for Polystyrene on Chromosorb G by Calcination and Direct Computation

Polymer in total packing, %		
Computation	Calcination	Difference, %
21.4	19.7	7.7
12.7	12.5	1.4
4.87	4.87	0
0.976	0.979	−0.31
0.359	0.387	−7.8

A comparison of Tables II and III shows that the correction of V_g and hence of any derived thermodynamic parameter such as χ depends on column loading. Thus for a low loading of 5–6% the correction is 7.5% in V_g or 0.072 in χ, whereas for the more usual loading of 10–11%, the corresponding figures are 3.6% in V_g and 0.035 in χ. Such a correction to χ does not change the thermodynamic conclusions presented in recent work[3,5] on interaction between vapor phase probes and polymers or the validity of the comparison between GLC results and those from the vapor sorption technique. This is due to the fact that the combined error of the GLC and vapor sorption techniques considerably exceeds the ~4% corrections in V_g discussed here. GLC has also been used recently[8] to characterize the interaction between polymers in a mixed stationary phase. The technique requires accurate determination of χ parameters for the interaction of vapor phase probes with the two pure polymers and with their mixture. Fortunately, if a similar loading is used for all three columns, as in ref 8, there is a cancelation of any systematic error in the interaction parameters.

It should be pointed out though that no other method has any significant advantages over calcination. Alternate techniques for determining polymer content of a packing involve either direct computation from the amounts of polymer and support originally brought together or extraction of the coated polymer with a suitable solvent. The latter method has the same drawbacks as calcination since the diatomaceous earths used as inert support have been shown to lose up to 2% in weight after repeated solvent extraction.[8] Furthermore, Aue et al.[9] found that Carbowax stationary phases could not be quantitatively recovered despite protracted solvent extraction.

Direct computation of the loading remains the method of choice for low molecular weight substances. In the case of polymers, however, large errors can be introduced owing to their film-forming properties. At high loadings and particularly for polymers requiring high coating temperatures, losses on coating vessels and particle aggregation become significant. Upon resieving to uniform size, the original proportions have probably been altered. This is illustrated in Table IV representing a comparison between calcination and direct computation for several polystyrene packings.[6] It is seen that in the range 1 to 12% agreement is excellent. At high loading, however, there is considerable loss of polymer while at very low loading the accuracy of the calcination method is questionable because of the magnitude of correction for loss of volatiles from the support.

The determination of polymer loading remains a crucial step in the derivation of specific retention volumes. It is felt that, despite some shortcomings, calcination of the chromatographic packing for the determination of polymer loading 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.

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

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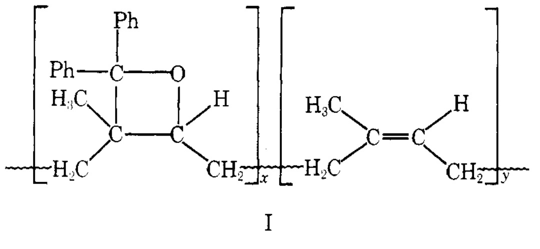
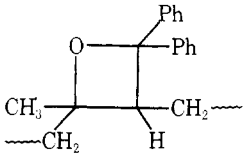
The photocycloaddition of carbonyl compounds to olefins (the Paterno–Buchi reaction) has been extensively studied for various substrates.[1,2] The general mechanism for the reaction is believed to involve the attack of the electrophilic oxygen of the n–π* triplet carbonyl on an electron-rich olefin, 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.

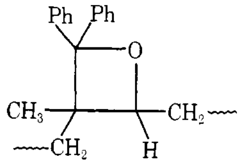


I

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.

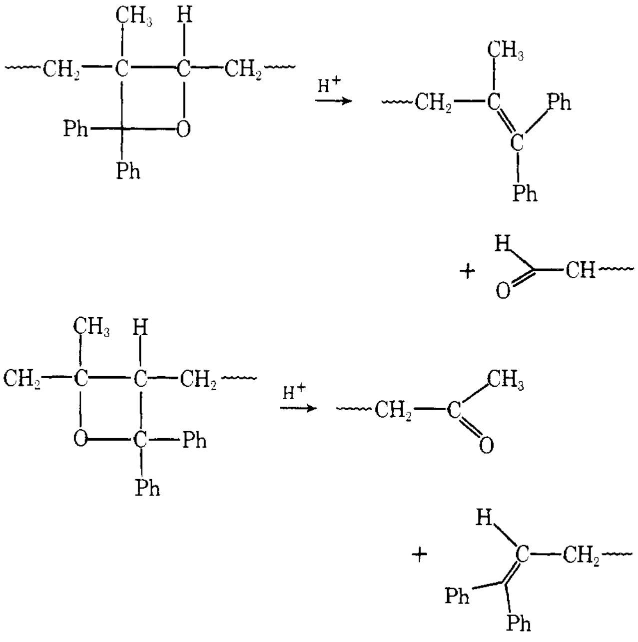


Ia



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