external lock. The use of hexachlorobutadiene, which bears quaternary carbons only, will minimize solvent signal intensities; it should therefore be preferable to trichlorobenzene. Ten-millimeter sample tubes have been used at 67.9 MHz (12 mm at 25.2 MHz), which are preferable to larger diameters at least for the normal-bore 270-MHz magnet.

The chemical shifts have been internally referenced to both the major methylene and the octamethylcyclotetrasiloxane resonances. The maximum deviation between the values of chemical shifts of a single carbon atom determined in two spectra obtained from two different copolymers amounted to 0.010 ppm. The spectrum in Figure 1 was obtained after the accumulation of 10000 scans.

Pulse widths of 90° (=24 μs) and pulse delays of 14 s were applied in order to allow for the determination of the 1-olefin concentration of the copolymer. The digital resolution amounted to 0.472 Hz/point, corresponding to a spectral width of 8000 Hz and a data length of 32 K. A data length of 16 K, however, will suffice in order to observe the splitting between the C-5 and C-8 resonances.

The ethylene–octene copolymer was prepared at 85 °C by suspension polymerization, using the catalyst system $Mg(OEt)_2$–$TiCl_4$–$AlEt_3$ and an apparatus already described.[6] The polymerization was started with ethylene and hydrogen only; octene was fed into the reaction vessel after 5 min and was held constant over the whole period.

The copolymer thus obtained was characterized by a viscosity-average molecular weight of 70000 and an ethylene/1-olefin molar ratio of 99.4:0.6.

Acknowledgment. Thanks is due Dr. L. Böhm for the synthesis of the copolymer and Professor Dr. H. Cherdron for permission to publish this paper.

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Promotion of Photo-cross-linking of Polysiloxanes by Oxygen

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Polysiloxanes are remarkably resistant to near-ultraviolet light and intense exposures may be required to detect cross-linking. Delman et al., relying on infrared analysis, reported the formation of cross-links after exposing a complex poly(dimethylsiloxane) system in air to wavelengths >281 nm.[1] Siegel et al. investigated the insolubilization of a poly(dimethyldiphenylsiloxane) of low molecular weight (480) resulting from exposure, under vacuum, to 254-nm radiation.[2]

The present report gives more extensive results on the photogelation of polysiloxanes with repeat units I–IV.

$$\underset{\text{I}}{-OSi(CH_3)_2-} \qquad \underset{\text{II}}{-OSi(CH_3)(C_6H_5)-}$$

$$\underset{\text{III}}{-OSi(C_6H_5)_2-} \qquad \underset{\text{IV}}{-OSi(H)(CH_3)-}$$

Experimental Section

Polysiloxanes were obtained from Polysciences, Inc.; the supplier's descriptions of these polymers are quoted in Table I. Two further samples of poly(dimethylsiloxane), from the same source, were analyzed by gel permeation chromatography (Springborn Laboratories) to determine number- and weight-average molecular weights, M_n and M_w, respectively. Both polymers approximated to a most-probable distribution by reference to the criterion[3] that $M_w/M_n = 2$; for one sample $M_w = 83800$ and $M_n = 47100$ ($M_w/M_n = 1.8$) and for the other $M_w = 39000$ and $M_n = 22800$ ($M_w/M_n = 1.7$).

Electronic absorption spectra were run, using cells of 1-cm path length, in a Perkin-Elmer 402 spectrophotometer.

In some experiments polymers were exposed in layers of thickness 1.0 cm, in air, directly to ultraviolet radiation. In other experiments, samples were exposed in tubes (diameter 0.4 cm.; wall thickness 0.1 cm) made of sodium glass or quartz. Samples sealed under vacuum were first rigorously degassed by freeze–thaw cycles.

Two ultraviolet sources were used, a medium-pressure Hg lamp (200 W, Hanovia) and a bank of seven low-pressure Hg lamps (each of 18 W, General Electric). The energy incident on samples or tubes was measured by two ultraviolet meters, calibrated by the National Bureau of Standards to monitor wavelengths in the short (230–270 nm) or long (300–400 nm) ranges.

The gel point was detected, approximately, by periodically tilting the samples, which were viscous fluids, until flow was no longer evident. In certain cases the depth of the gel layer (d) was measured.

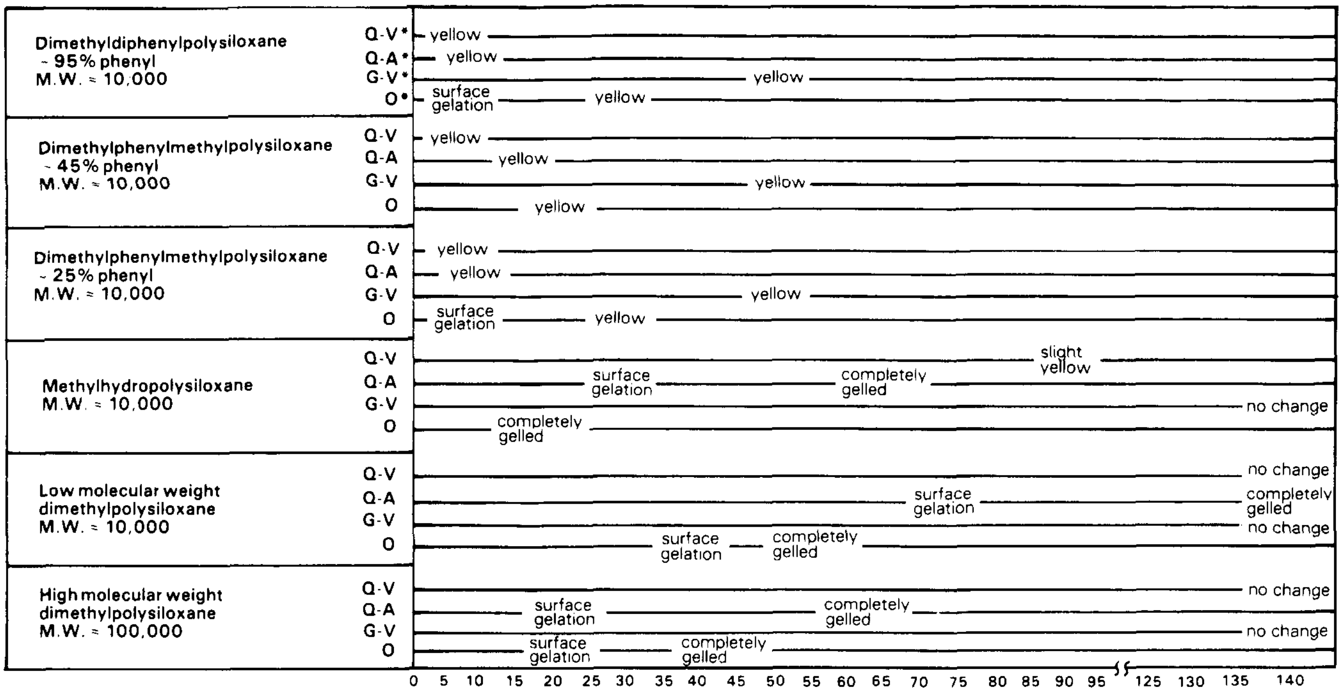
Results and Discussion

Polysiloxanes with phenyl groups eventually become yellow on exposure to the medium-pressure lamp (Table I). This observation can be rationalized by adoption of a suggestion made by Rabek and Rånby, with respect to polystyrene,[4,5] that a triplet state of the phenyl group rearranges to give a colored product such as a fulvene derivative. In extension of this view, the observed retardation of yellowing in air could be attributed to triplet-state quenching by oxygen. However, it should be mentioned that such observations about retardation by air appear to differ from previous reports on yellowing in both a poly(dimethyldiphenylsiloxane)[2] and polystyrene.[6]

The most important discovery in Table I is that photogelation is promoted by the presence of air. Therefore, despite the small sensitivity of polysiloxanes to near-ultraviolet light, it is worth compromising with difficulties inherent in estimating a quantum yield for cross-links. To this end the low-pressure lamps were selected as a rough[7] but conveniently intense source of 254-nm radiation. Polymers containing phenyl groups (cf. Figure 1) and also poly(methylhydrosiloxane) were judged inconvenient for such studies because of "skin" effects. Neither was the poly(dimethylsiloxane) of highest molecular weight studied because, in agreement with previous reports,[8,9] it was found to contain impurities which appear to be phenyl groups (cf. Figure 1A–C). Two poly(dimethylsiloxanes) of lower molecular weight were not objectionable in this extreme sense, although absorption in the range 250–300 nm still appears anomalous by reference to the dimethylsiloxane repeat unit.[10-12] Only a part of this anomalous absorption is attributable to the presence of oxygen, which was found to result in marked effects only at lower wavelengths (Figure 2). Incidentally, the influence of oxygen on ultraviolet absorption is much more pronounced than previously reported for other polymers,[13,14] presumably because of the higher solubility of oxygen in poly(dimethylsiloxanes).

The number of quanta absorbed per gram, N_q, up to the gel point was calculated from eq 1 in which t is the time to gelation, I_0 the incident intensity, k Lambert's absorp-

Table I



Sample	Container	Observations (in order of increasing exposure time)
Dimethyldiphenylpolysiloxane ~95% phenyl M.W. ≈ 10,000	Q-V*	yellow
	Q-A*	yellow
	G-V*	yellow
	O*	surface gelation — yellow
Dimethylphenylmethylpolysiloxane ~45% phenyl M.W. ≈ 10,000	Q-V	yellow
	Q-A	yellow
	G-V	yellow
	O	yellow
Dimethylphenylmethylpolysiloxane ~25% phenyl M.W. ≈ 10,000	Q-V	yellow
	Q-A	yellow
	G-V	yellow
	O	surface gelation — yellow
Methylhydropolysiloxane M.W. ≈ 10,000	Q-V	slight yellow
	Q-A	surface gelation — completely gelled
	G-V	no change
	O	completely gelled
Low molecular weight dimethylpolysiloxane M.W. ≈ 10,000	Q-V	no change
	Q-A	surface gelation — completely gelled
	G-V	no change
	O	surface gelation — completely gelled
High molecular weight dimethylpolysiloxane M.W. ≈ 100,000	Q-V	no change
	Q-A	surface gelation — completely gelled
	G-V	no change
	O	surface gelation — completely gelled

Hours exposed to a Hanovia Mercury Vapor Lamp†

* Q-V: quartz container sealed under vacuum
Q-A: quartz container open to air
G-V: sodium glass container sealed under vacuum
O: open to air

Note: Samples under vacuum were degassed by 6 freeze-thaw cycles at − 30 psi.
Transmission through vial > 3%; quartz λ > 190 nm; sodium glass λ > 280 nm.

† (~ 2 mW/cm² at long wavelength; ~ 1 mW/cm² at short wavelengths)

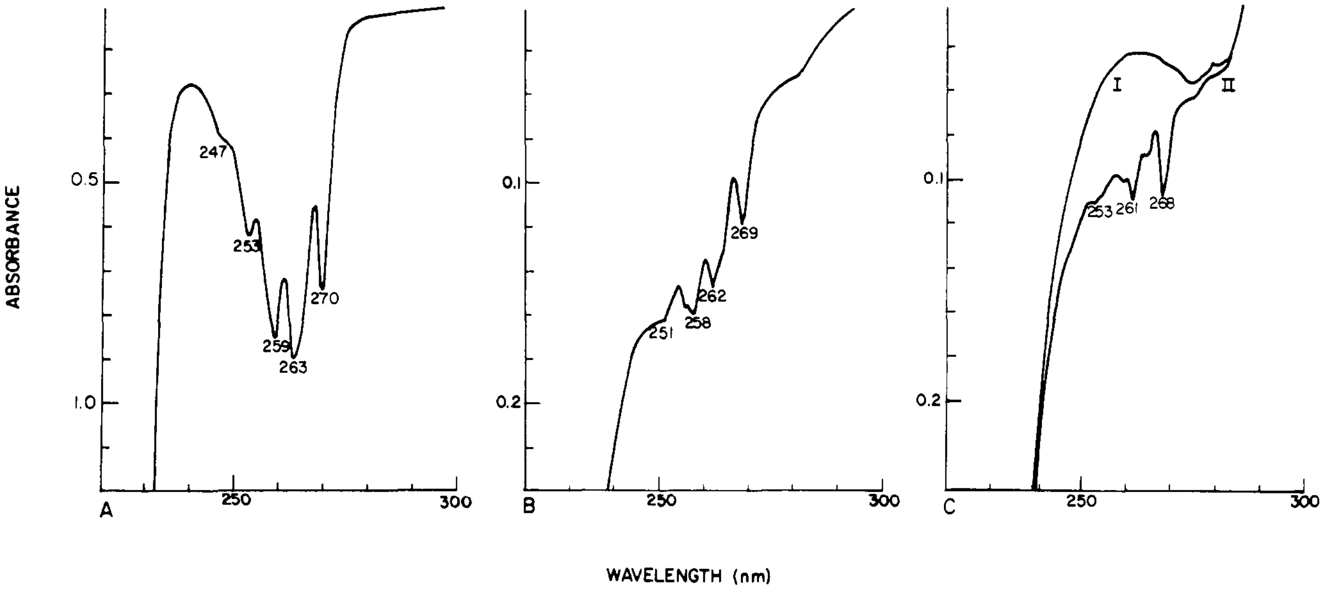


Figure 1. Ultraviolet absorption spectra: (A) poly(phenylmethylsiloxane) (in isooctane); (B) poly(dimethylsiloxane) (M = 100 000); (C) (I) poly(dimethylsiloxane) (M_n = 22 800), (II) 0.003 wt % toluene added to I.

tion coefficient, d the depth of the gel layer, and ρ the density of the polymer.

$$N_q = tI_0(1 - e^{-kd})(d\rho)^{-1} \qquad (1)$$

The number of cross-links per gram at the gel point, N_x, was calculated on the assumption that there is one cross-link per four macromolecules.[3] In eq 2, N is Avogadro's number and M_n the number-average molecular weight prior to irradiation. An implicit assumption is that fracture of the macromolecules by irradiation is negligible. In this regard it is known that the ratio of fractures to cross-links is about 1:8 when poly(dimethylsiloxanes) are exposed to high-energy radiation;[15,16] presumably the ratio would be smaller for 254-nm photons because of a smaller cage effect.[17,18]

$$N_x = 0.25NM_n^{-1} \qquad (2)$$

The quantum yield for cross-links, $\phi(x) = N_xN_q^{-1}$, was calculated for an intensity of $I_0 = 1.54 \times 10^{15}$ quanta/(cm² s), $k = 0.28$ cm^{-1} (Figure 2), $d = 0.15$ cm, and $\rho = 1.0$ g/cm³.

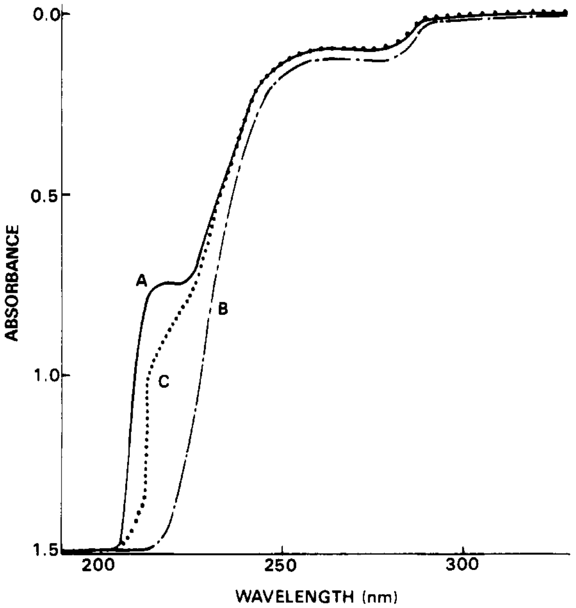


Figure 2. Influence of oxygen on ultraviolet absorption spectra: (A) poly(dimethylsiloxane) saturated with N_2; (B) poly(dimethylsiloxane) saturated with oxygen; (C) poly(dimethylsiloxane) saturated with air.

Values of ϕ(x, air) = 0.02 were obtained for both polymers studied, i.e., of M_n = 47 100 and M_n = 22 800.

In order to estimate a value of ϕ(x) for polymers irradiated under vacuum, we used a relative method in which samples were placed in quartz tubes. Because of the large dose required to cause gelation under vacuum, samples were exposed to the more intense medium-pressure lamp. It took longer to gel these samples, relative to ones in quartz tubes open to the atmosphere, by factors of 13 (M_n = 47 100) and 15 (M_n = 22 800). Adopting a value of ϕ(x, air) = 0.02 gives an estimate of ϕ(x, vacuum) = 0.0015. No other data for poly(dimethylsiloxanes) are known for direct comparison with these values but reference may be made to quantum yields for total gas ($H_2 + CH_4 + C_2H_6$) reported by Siegel and Stewart[19] for wavelengths in the vacuum-ultraviolet region: ϕ(at 124 nm) = 0.136; ϕ(at 147 nm) = 0.062. Now for ionizing radiation Miller[15] established the stoichiometric relationship that, approximately, one molecule of gas is formed per cross-link.[20] If this same stoichiometry held also for ultraviolet irradiation, then the present values of ϕ(x, vacuum) would appear to be remarkably low. Possibly there is a cage effect[17,18] such that, under vacuum, the quantum yields of both cross-links and total gas decrease with increasing wavelength in the order ϕ(at 124 nm) > ϕ(at 147 nm) $\gg$ ϕ(at 254 nm).

In conclusion, from the findings described above and also from other evidence[21] it is inferred that the presence of oxygen during ultraviolet irradiation promotes network formation in polysiloxanes. This is in striking contrast to a retarding effect generally observed in studies of other organic polymers.[22] It is suggested that polysiloxanes are exceptional because of the insensitivity of the backbone to oxidative scission; this brings into predominance cross-link reactions. Further work is needed to elucidate the role of oxygen[23-28] and to identify the chemical structure of the cross-links.[1,29]

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Cross-Linking Mechanism in the Reactions of Poly(difluorophosphazene) with Alkyllithium Reagents[1]

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Continuing interest exists in the synthesis of poly(organophosphazenes) of formula $(NPR_2)_n$ that contain alkyl or aryl groups linked to skeletal phosphorus via carbon–phosphorus bonds. Such compounds would be analogues of alkyl- or arylsiloxane polymers. Well-developed methods are now available for the synthesis of poly(organophosphazenes) that contain alkoxy, aryloxy, or amino side groups based on the nucleophilic replacement of chlorine in poly(dichlorophosphazene), $(NPCl_2)_n$, by organic residues.[2-6] These methods make use of poly(dichlorophosphazene) as a reactive polymeric intermediate. A logical extension of this approach for the preparation of alkyl or aryl derivatives would involve the reactions of organometallic reagents with a poly(dihalophosphazene).[7]

The reactions of organometallic reagents with halophosphazenes are complex.[8-21] Even so, these interactions are of special interest because of their potential for the synthesis of new high polymeric phosphazenes.[19-21] Earlier work with poly(dichlorophosphazene) has shown that the

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