

Studies in Optical Properties and Optical Radiation Hardness of Polyorganosiloxanes

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SYNOPSIS

A variety of polyorganosiloxanes containing dimethyl, diphenyl, and methylphenyl substituents were studied to determine transparency and optical radiation hardness. Siloxanes show superior optical radiation hardness when compared to optical thermoplastics such as PMMA. Transparency is diminished in polymers containing diphenyl units. This is attributed to the inability to remove traces of the crystalline monomer. Methylphenyl polymers are highly transparent. The maximum attainable refractive index in transparent systems is 1.53.

INTRODUCTION

Polyorganosiloxanes are versatile polymers which are used as biomedical implants, high temperature fluids, dielectric coolants, and lubricants. Purified polydimethylsiloxanes, noncrystalline polydimethyldiphenylsiloxanes, and polymethylphenylsiloxanes are transparent in the near UV and visible spectrum. Therefore, they are useful as optical polymers. We are concerned specifically with optical polymers used in high energy radiation environments. In the past, studies have been carried out on the radiation chemistry of siloxanes.¹⁻³ Radiation-induced crosslinking, side reactions, and free radical generation have been monitored. Little attention has been given to the radiation resistance of optical properties until recently.⁴⁻⁶ Ionizing radiation produces color centers in many glassy polymers such as poly(methyl methacrylate), polystyrene, polyvinyltoluene, and polycarbonate. One-centimeter-thick samples of polyvinyltoluene, for example, undergo a 30% reduction in transmission at a wavelength of 450 nm immediately after a radiation dose of 3 MRad in an inert gas environment, using ⁶⁰Co gamma rays as a radiation source. This loss of transmission slowly improves with time (annealing effect); however, a small permanent loss in trans-

mission usually occurs. Siloxane backbone polymers show far less degradation; 1-cm-thick platinum-cured polydimethylsiloxane and polydimethyldiphenylsiloxane exhibit < 1% loss in transmission at wavelengths > 450 nm after 10 Mrad.⁷

Radiation-resistant phenyl substituted siloxanes have an application in scintillating fibers used for the detection of high energy particles generated in colliding beam experiments. In the scintillation process,⁸⁻¹⁰ a radioactive particle interacts with a phenyl substitute in the polymer. Delocalized π electrons absorb energy from the particle and are excited to a higher singlet state. The electrons relax to the ground state, emitting a photon. The photon is absorbed by a fluorescent dye that has an absorption spectrum matching the polymer's emission spectrum. The dye emits at a longer wavelength, and this light travels down the fiber where it is collected by a photomultiplier or photodiode.

The detection efficiency is diminished by:

- (1) Impurities or crystalline moieties in the polymer matrix which scatter light
- (2) Any radiation-induced color center formation in the polymer base or fluorescent dye which results in the absorption in the region of the dye emission

This study represents an attempt to eliminate these problems. We report on the optical properties and radiation resistance of peroxide-cured, plati-

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num-cured, and linear siloxanes. Poly(methyl methacrylate) samples are included for comparative purposes.

EXPERIMENTAL MATERIALS

The following polymers were studied:

1. Peroxide-curable vinyl-terminated polydimethyldiphenylsiloxane gum, R42765, donated by Dow Corning STI and coded S1.
2. Peroxide curable vinyl terminated polydimethyldiphenylsiloxane gum, PS268, purchased from Hüls America in Bristol, PA and coded S2.
3. Linear polymethylphenyldiphenylsiloxane polymer, PS162, purchased from Hüls America and coded S3.
4. Platinum-curable polydimethyldiphenylsiloxane, PS2066, obtained from Hüls America and coded S4. Part A contained vinyl terminated resin and Pt catalyst. Part B contained silicon hydride groups.
5. PS441, vinyl-terminated pure polydimethylsiloxane, obtained from Petrarch Systems and coded S5.
6. DC710, pure methylphenylsiloxane, obtained from Dow Corning Corporation and coded S6.
7. Polymethylmethacrylate, CP-41, donated by Continental Polymers, Inc. and coded S7.

The peroxide, 1,1-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, was obtained from Penwalt in Buffalo, NY.

PURIFICATION

The siloxane gums were purified by dissolving them in a methylene chloride, diatomaceous earth slurry. The slurry was filtered in a 10–15 μm fritted glass filter. The solvent was evaporated from the polymer or the gum was reprecipitated in methanol and dried under vacuum.

The platinum cured siloxane, S4, was not purified. S3, the linear siloxane, was too low in molecular weight to reprecipitate. A Perkin Elmer 601 liquid chromatograph was used to determine that the polystyrene equivalent molecular weight of S3 \approx 1000.

DC710, S6, was purified by passing it through a 3 ft \times 1 in. column packed with activated charcoal. The material was then filtered through a 0.2 μm millipore filter to remove any carbon particles.

SAMPLE PREPARATION

One- and 5-cm samples of unpolymerized S1–S6 were prepared by heat devolatilization of samples encased in quartz cuvettes. Catalyzed 1-cm-thick samples of the siloxane gums S1 and S2 were prepared by kneading 0.2% by weight 1,1-bis-(*t*-butylperoxy)-3,3,5-trimethylcyclohexane in the gum stock. Disk-shaped samples were formed in a vacuum piston mold assembly lined with glass disks. Samples were evacuated for 2 h while under 2500 psi from the piston. The mold was removed from the press and placed in an oven at 100°C for 10 h. When samples were demolded, the glass disks formed an optical quality surface. PMMA was compression molded into 1 cm and 1 mm samples.

INSTRUMENTATION

Light transmission spectra were measured on a Hewlett Packard diode array spectrophotometer 8352A. Refractive indices were measured on an Abbè refractometer from Fisher Scientific illuminated with 590 nm light. X-ray diffraction patterns were recorded on 0.5 cm films of polymer using a Philips APD3720. The range was 5–85° at a rate of 3.0°/min.

Mechanical hardness was tested with a Shore Type A Durometer.

Samples were irradiated with a ^{60}Co gamma radiation source at doses up to 10 Mrad in argon. The dose rate was 1.56×10^5 rad/h.

RESULTS AND DISCUSSION

Of paramount importance to any optical information system is transparency. However, the transmission of light through several meters of plastic is an extremely demanding requirement. One of the biggest obstacles to transparency in plastic media is Rayleigh scattering, or scattering from irregularities of the electron density in the medium whose sizes are small compared to the wavelength of light. In the case of siloxanes, these irregularities appear in the form of crystalline monomers or low molecular weight material suspended in the polymer matrix. The monomers of concern here are listed in Table I along with crystalline melting points.¹¹ The diphenyl monomers and the trisiloxane form of methyl-substituted tetrasiloxane are crystalline at room temperature. The methyl-substituted siloxane has a melting point below room temperature. The methylphenyl monomer is a noncrystalline liquid.

Table I Siloxane Monomers

Monomer	T_m ($^{\circ}\text{C}$)
Octamethylcyclotetrasiloxane	17.5
Hexamethylcyclotrisiloxane	62–64
Octaphenylcyclotetrasiloxane	200
Hexaphenylcyclotrisiloxane	188–189
1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane	Liquid at room temp

Scattering was characterized from transmission spectra through 1 and 5 cm lengths of material. Rayleigh scattering losses evince a wavelength dependence of λ^{-4} . The intensity of transmitted light, I , is written as¹²

$$I = I_0 e^{-\tau l} \quad (1)$$

where I_0 is the incident intensity, τ (cm^{-1}) is the turbidity, and l (cm) is the sample length. The turbidity τ can be expressed as

$$\tau = a\lambda^{-4} + b(\lambda) \quad (2)$$

where a is the Rayleigh scattering coefficient and b represents the loss parameter associated with the ultraviolet cutoff. Since the functional form of b is unknown, eqs. (1) and (2) were fitted to transmission spectra at points far from the UV cutoff, where we assume $b = 0$. τ^{-1} , the attenuation length, is calculated for wavelengths ≥ 350 nm.

The long- and short-path length transmission spectra for the various polymers are depicted in Figures 1–6. Uncured samples were used for this study since they were poured into 1 and 5 cm quartz cuvettes. Attenuation lengths are recorded in Table

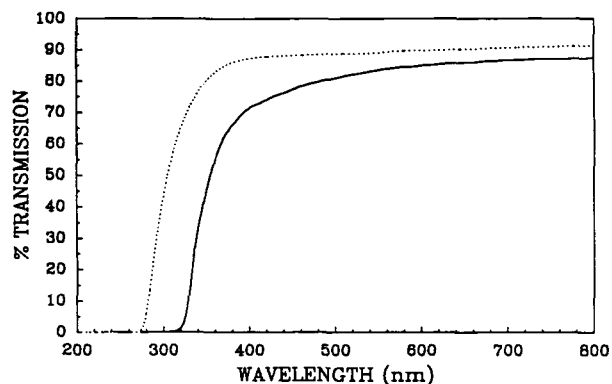


Figure 1 Transmission spectra of uncured diphenyl-containing vinyl terminated S1 sample for 1 cm (\cdots) and 5 cm (—) path lengths.

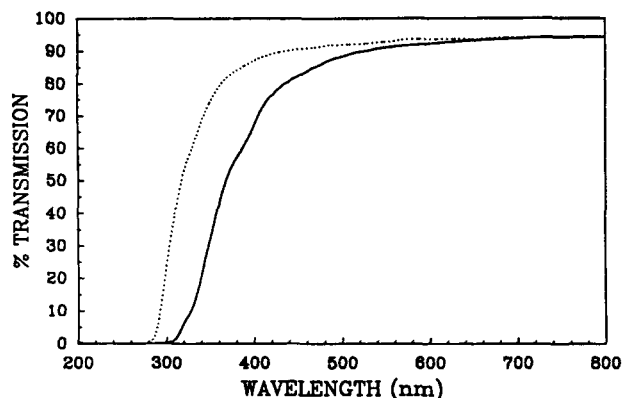


Figure 2 Transmission spectra of uncured diphenyl-containing vinyl terminated S2 sample for 1 cm (\cdots) and 5 cm (—) path lengths.

II. Samples S1–S4 all contain diphenyl units, and most likely crystalline diphenyl monomer residue. Attenuation lengths remained between a few centimeters and 3 m throughout the visible spectrum for these polymers. X-ray diffraction scans evidenced crystalline structure. This is depicted in Figure 7(a) for sample S3. Figure 7(b), in contrast, shows an X-ray scan for pure polydimethylsiloxane. No crystalline peaks are evident. The peak at $< 15^{\circ}$ is from X-rays flooding the detector due to the small angle of incidence; this peak is seen regardless of sample composition.

By contrast, samples S5 and S6, which were not synthesized from crystalline monomer, show no attenuation at wavelengths longer than 450 nm. We conclude that the best transmission is achieved when the phenyl substituents are incorporated by using methylphenyl monomers.

We note here that attempts to purify diphenyl polymers by reprecipitation in methanol or higher

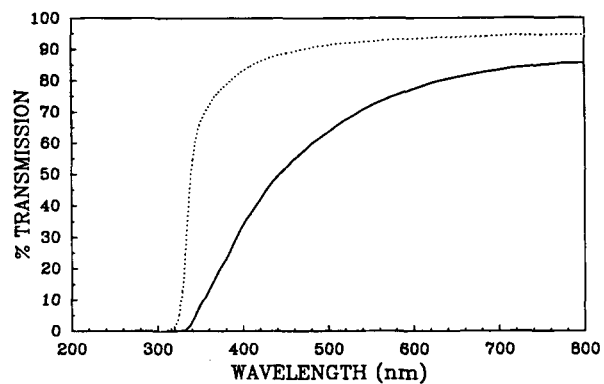


Figure 3 Transmission spectra of diphenyl-containing linear S3 sample for 1 cm (\cdots) and 5 cm (—) path lengths.

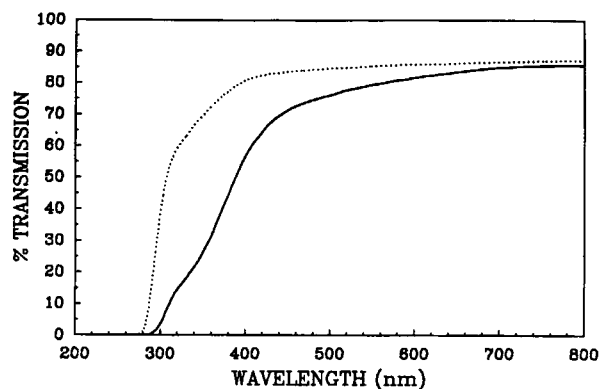


Figure 4 Transmission spectra of uncured platinum curable diphenyl containing S4 sample for 1 cm (\cdots) and 5 cm (—) path lengths.

alcohols are unsuccessful, since the diphenyl monomers are insoluble in alcohols and other solvents which precipitate the polymer. Activated charcoal, similarly, did not remove low molecular weight diphenyl moieties.

Refractive Index

The light transmitting ability of polymer fibers depends on transparency, but also on the refractive index of the polymer. Light is confined in the fiber by cladding the core of the fiber with a low refractive index material. The efficiency of light trapping is increased by increasing the numerical aperture (NA)¹²:

$$NA = (n_0^2 - n_1^2)^{1/2} \quad (3)$$

where n_0 and n_1 are the refractive indices of the core and cladding materials, respectively. Aromatic groups have a high refractive power and increase n_0

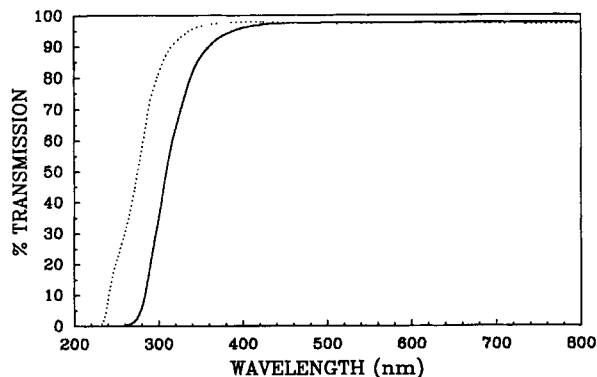


Figure 5 Uncured polydimethylsiloxane, S5, sample for 1 cm (\cdots) and 5 cm (—) path lengths.

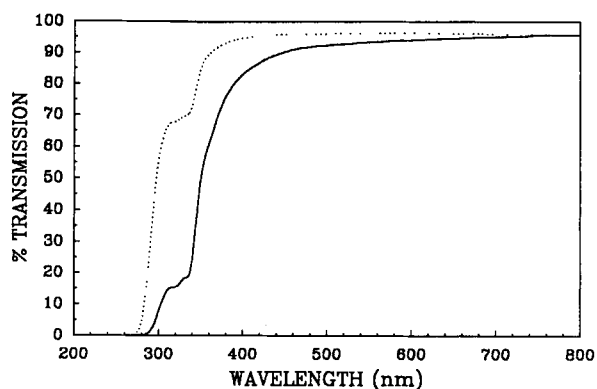


Figure 6 Purified linear polymethylphenylsiloxane, S6, sample for 1 cm (\cdots) and 5 cm (—) path lengths.

in the siloxane polymers.¹³ These results are shown in Table III. Transparent polymethylphenylsiloxane with a refractive index of 1.53 is clearly an optimal material for fiber construction.

Irradiation

Figure 8 is a transmission spectrum of S7 (PMMA) irradiated to a dose of 10 Mrad in an argon environment. Significant transmission losses occur throughout the UV/visible spectrum. This is similar to the damage noted in other thermoplastic optical polymers such as polystyrene and polyvinyltoluene.⁶ Transmission losses in these polymers slowly recover with time. During this recovery, a sharp damage boundary moves with time inward from the sample's edges, leaving a clear, recovered polymer behind. Some irrecoverable damage persists in the short wavelength portion of the spectrum.¹⁴ Scintillators which function continuously cannot compensate for such time-dependent transmission losses. Figure 9 depicts the transmission of linear polymethylphenyldiphenylsiloxanes, S3.

It is most significant to note the absence of any radiation damage at wavelengths greater than 460 nm. In addition, irradiation in argon and air produced similar results. Radiation induced absorption is confined to lower wavelengths, mostly in the UV region. This radiation induced spectral change does not recover with time. No reversion was visible after 3 months. The emission spectra of fluorescent dyes present in the scintillator are above 460 nm, where transmission losses are minimal. This means that there is little loss in transmission due to absorption from radiation induced color center formation. The reason for this marked reduction in color center formation in siloxanes may be the Si—O backbone

Table II Numbers Given are Attenuation Lengths, in cm, of the Samples^a

Material \ Wavelength	S1	S2	S3	S4	S5	S6	S7
350	6.4	4.35	2.1	0.33	34.8	14.4	—
400	18.4	14.3	5.4	9.8	647	139	—
450	27.8	37.9	11.5	21.7	4325	—	16.0
500	39.4	91.9	27.3	32.8	—	—	18.3
550	55.2	199	204	47.9	—	—	26.0
600	85.1	255	—	49.7	—	—	43.5

^a — indicates an infinitely long or infinitesimally short attenuation length.

structure of these polymers. Radiation-induced scission reactions often produce double bonds in carbon backbone polymers. These double bonds, when conjugated, form color centers which absorb visible light. Conjugated bonds are unable to form in siloxane polymer. Again, we verify radiation hardness, this time with an unpurified methylphenylsiloxane polymer, S6. This is depicted in the transmission spectrum in Figure 10. The sample was irradiated in air to 10 Mrad. Radiation-induced absorption is prevalent only at wavelengths less than 470 nm.

Such simple linear polymers are optically radiation resistant. In instances where self-supporting

matrices are required, siloxane polymers must be crosslinked. It is necessary, therefore, to characterize the effect of functional groups and catalysts on radiation-resistant polysiloxanes. Two types of cure systems were examined: platinum cure and peroxide cure.

The following reaction depicts platinum curing of siloxane prepolymers:

Block 1. Polydimethyldiphenylsiloxane, S4, was cured by this type of hydrosilation process in the presence of platinum catalyst. Figure 11 depicts transmission spectra for the cured sample before and after irradiation in argon. Damage to this platinum cure system is negligible.

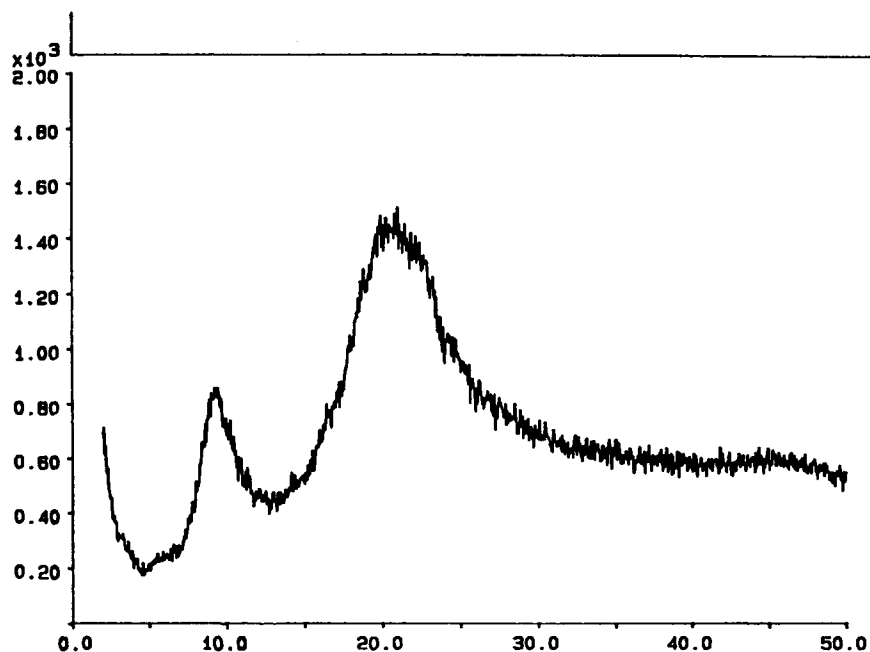


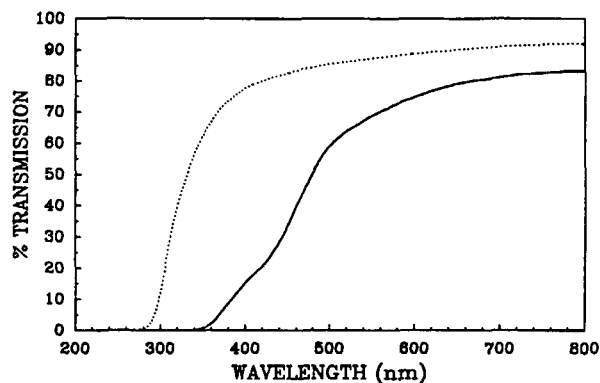
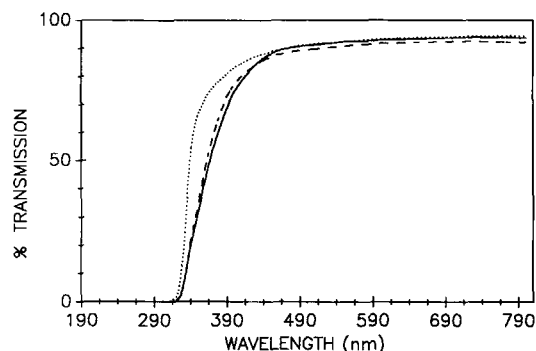
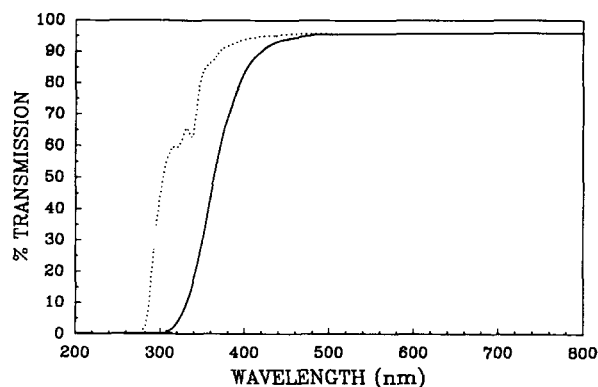
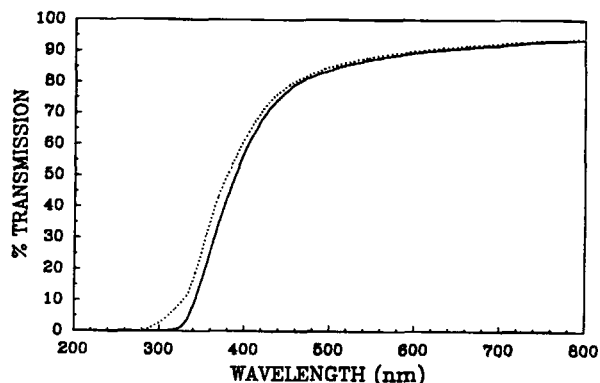
Figure 7 (a) X-ray diffraction pattern of the polymethylphenyldiphenyl siloxane, S3. (b) X-ray diffraction pattern of amorphous polydimethylsiloxane, S5.

Table III Relation between Refractive Index and Phenyl Content of Siloxane Polymers

Sample	Refractive Index	Approximate Phenyl Content (mol %*)
S1	1.43	18% diphenyl
S2	1.46	15% diphenyl
S3	1.58	50% diphenyl; 50% methylphenyl monomer
S4	1.49	20% diphenyl
S5	1.39	0%
S6	1.53	100% methylphenyl monomer

Vinyl-terminated siloxane prepolymer, S2, was cured with the following reaction:

Block 2. Figure 12 presents irradiation data on the cured sample. In Figure 13, the transmission spectra of the vinyl-terminated uncatalyzed polymer before and after irradiation are compared. The peroxide catalyst did not appear to affect optical radiation resistance. In addition, radiation-induced crosslinking and cure in the uncatalyzed gel. The gel cured to a Shore A hardness of 12. The catalyzed sample increased from 7 to 12 upon irradiation. Radiation-induced crosslinking appears not to affect the transmission. The bathochromic shift in the UV portion of the transmission spectrum after irradiation is not due to crosslinking. Both linear polymers, S3 and S6, displayed this shift. These polymers were dissolved in methylene chloride after polymerization and showed no evidence of gelation due to crosslinking.

**Figure 8** Transmission spectra of 1 cm thick sample of PMMA, S7, before (\cdots) and after (—) exposure to 10 Mrad gamma radiation in argon.**Figure 9** Transmission spectra of cured polymethylphenyldiphenylsiloxane, S3, before irradiation (\cdots). After exposure to 10 Mrad gamma radiation in air ($---$) and argon (—).**Figure 10** Linear polymethylphenylsiloxane, S6, before (\cdots) and after (—) exposure to 10 MRad gamma radiation in air.**Figure 11** Platinum cured polydimethyldiphenylsiloxane, S4, before (\cdots) and after (—) exposure to 10 Mrad gamma radiation in argon.

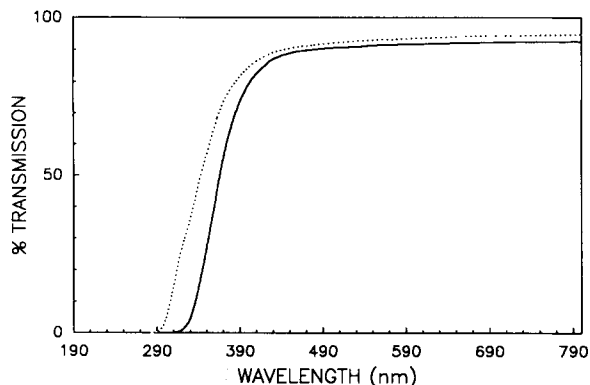


Figure 12 Peroxide cured polydimethyldiphenylsiloxane, S2, before (· · ·) and after (—) exposure to 10 Mrad gamma radiation in argon.

CONCLUSIONS

The source of Rayleigh scattering in the diphenylsiloxane polymers studied here is monomeric or low molecular weight crystalline moieties. These crystalline residues are not easily removed by conventional purification techniques. Phenyl substituents are best incorporated via the cyclic methylphenyl monomer which is a liquid and does not impart scattering centers. The maximum refractive index attainable with a pure methylphenyl monomer is 1.53. The siloxane polymers examined show superior op-

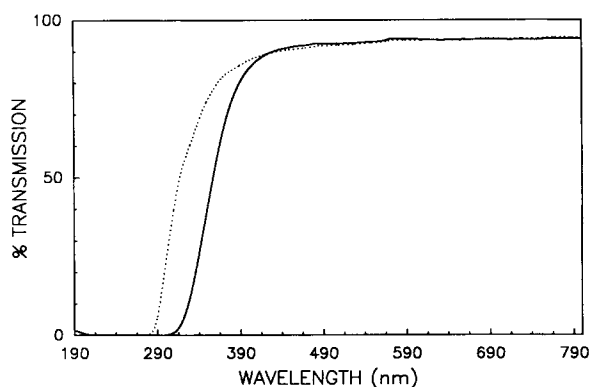


Figure 13 The same polymer as in Figure 12, uncured. Before (· · ·) and after (—) exposure to 10 Mrad gamma radiation in argon.

tical radiation resistance at wavelengths ≥ 470 nm, when compared to thermoplastic optical polymers such as PMMA. The radiation-induced absorption at these lower wavelengths is irreversible.

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