was unable to determine the stereoregularity of the AN–VA copolymers she synthesized, so our calculations explicitly included the effect of stereoregularity upon the conformational entropy.

Details of the conformational entropy calculations have been described[1–5] in detail before. In the present calculation $T = 67.5$ °C, which is midway between the T_g's of AN and VA homopolymers,[9] and a dielectric constant[9] $\epsilon = 5$ were employed.

Table I
Calculated Conformational Entropies of the Homo- and Regularly Alternating Copolymers of AN–VA

Polymer	Stereoregularity[a]	S,[b] eu/mol of backbone bonds
AN	I	1.270
VA	I	1.759
AN–VA	I	1.497
AN	S	1.298
VA	S	1.690
AN–VA	S	1.500
AN	A	1.270[c]
VA	A	1.790[c]
AN–VA	A	1.505[c]

[a] I ≡ isotactic, S ≡ syndiotactic, A ≡ atactic. [b] Calculated for chains of 500 bonds. [c] Average of 10 Monte Carlo generated chains, where the mean deviation from the average is less than 0.2%.

Table I presents the results of the entropy calculations performed on the isotactic, syndiotactic, and atactic homo- and regularly alternating copolymers of AN–VA. The entropies calculated for both the isotactic and atactic regularly alternating copolymers are less than half the sums of the isotactic and atactic homopolymers, while the syndiotactic copolymer entropy is nearly the same as half the sum of the syndiotactic homopolymer entropies.

On this basis the glass transition temperature of regularly alternating AN–VA copolymers would be expected to equal or exceed the T_g predicted by the Fox relation depending on stereoregularity. This is consistent with the observations of Chen who reports $T_g = 85$ °C for regularly alternating AN–VA copolymer of unspecified stereoregularity, though presumably atactic,[10] a value exceeding the T_g predicted by the Fox equation.

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(10) Because the AN–VA copolymers prepared by Chen[8] are amorphous, it is assumed they are stereochemically random, or atactic.

Photosensitized Degradations of Polystyrene and Poly-α-methylstyrene in Solution by Benzophenone

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Extensive studies on photochemistry of benzophenone (BP) have established that the excited BP molecule in the triplet state is capable of abstracting hydrogen atom from suitable hydrogen donor molecules (RH), which results in the formation of ketyl radical and R radical as follows:[1–8]

$$\mathrm{Ph_2CO} \xrightarrow{h\nu} {}^1\mathrm{Ph_2CO^*} \rightarrow {}^3\mathrm{Ph_2CO^*} \xrightarrow{\mathrm{RH}} \mathrm{Ph_2\dot{C}OH} + \mathrm{R}\cdot$$

In this paper, we wish to report the photosensitized degradations of polystyrene (PSt) and poly-α-methylstyrene (PMSt) in benzene solution which are initiated from hydrogen abstracted sites of polymer chains by photochemically excited BP.

PSt and PMSt were prepared at −78 °C by the use of boron trifluoride etherate as a catalyst. The polymers were purified by precipitation from benzene solution with methanol. The number-average molecular weights of PSt and PMSt thus obtained were 6.5×10^5 and 7.7×10^5, respectively. BP was purified by repeated recrystallization from ethanol solution. Spectroscopic grade benzene was used as a solvent. Irradiation of samples in quartz cells was carried out at 366 nm by using filtered light from a 500 W high-pressure mercury lamp. The flash photolysis apparatus was the same as that described by Yamamoto et al.[9] The flash excitation of samples was done with acetone-filtered light from a xenon-filled quartz flash lamp, operated at 8 kV and 3 μF. The pulse width of excitation light was about 18 μs. The molecular weights of the polymers were determined by viscometry. By GPC measurements, the polymers were shown to have most probable distributions before and after irradiation. In the present systems, therefore, we can assume that the ratio of the number-average molecular weights, $(M_0/M_t)_n$, is equal to the ratio of the viscosity-average molecular weights, $(M_0/M_t)_v$, where M_0 and M_t are the molecular weights of the polymers before and after an irradiation time of t, respectively. This relation was confirmed from the molecular weight measurements of the polymers by osmometry.

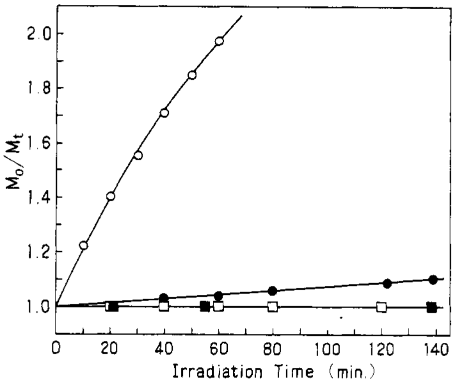

Figure 1. Photosensitized degradations of PSt (●, ■) and PMSt (○, □) by BP. [BP] = 0.5×10^{-2} M; [polymer] = 3.0×10^{-2} M (based on the monomer unit): (● and ○) under vacuum; (■ and □) in air.

The changes in the molecular weight of the polymers under various conditions are shown as a function of photoirradiation time in Figure 1. As is well known, the quantity of $(M_0/M_t) - 1$ is equal to the average number of chain scissions per original polymer molecule. The chain scission of PMSt occurs in vacuum much more rapidly than that of PSt, whereas no degradation of both polymers is observed in the presence of air.

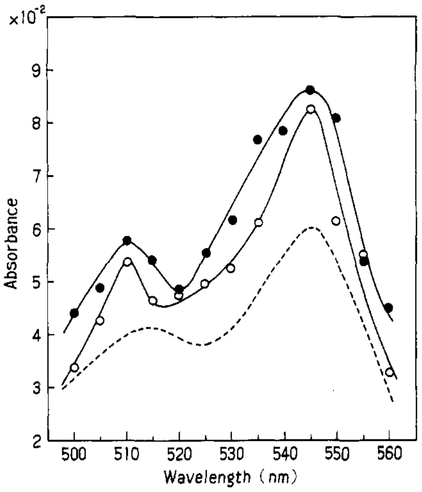

Figure 2. Absorption spectra of transient intermediates obtained after 100 μs by flash excitation. [BP] and [polymer] are the same as those in Figure 1: (●) PSt; (○) PMSt; and (- - -) reported in ref 5.

Figure 2 shows absorption spectra of transient intermediates obtained by flash photolysis experiments. The observed spectra are in good agreement with that of ketyl radical reported by Bell and Linschitz.[5] This fact implies the formation of ketyl radicals in the primary process of polymer degradation, involving hydrogen abstraction from the polymers by excited BP molecules. The random chain scission then would occur from β-position of hydrogen abstracted sites in the polymer. No formation of ketyl radical in the presence of air indicates that photoexcited BP molecules are quenched by oxygen molecules, and therefore the polymer degradation was inhibited in the presence of air.

Although an almost equivalent quantity of ketyl radical formation was observed in the case of PSt with PMSt, the average number of chain scissions for PSt was found to be much smaller than that for PMSt as described above. The different extent of chain scission is similar to the results of the thermal degradation of PSt and PMSt. The greater stability of the radical formed by abstraction of a tertiary hydrogen atom is determined by the relative rate of chain scission vs. the combined rates of other possible reactions such as hydrogen return from ketyl radical, coupling with several radicals, and hydrogen abstraction from other molecules. However, there is no information on the rate of each reaction for PSt or PMSt radicals. Further investigation is required to explain this interesting observation.

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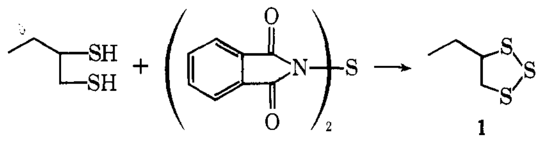
Communications to the Editor

Polymerization of a 1,2,3-Trithiane to a High Molecular Weight Polymer

Sulfur-containing polymers[1] such as alkylene[2] and arylene[3] sulfides, polydisulfides[4] and polysulfides[5] have long been of theoretical and commercial interest. It is, therefore, all the more surprising that although simple (but highly strained)[6] systems containing three contiguous sulfur atoms (1,2,3-trithiolanes) have been synthesized and, in some cases, characterized,[6] a study of polymers from these materials has been limited to that derived from tetrafluoro-1,2,3-trithiolane.[7] In most instances the polymeric nature of the nonvolatile residues obtained has only been inferred.[8]

We wish to report the conversion to polymer (presumably via a thermal and/or oxidative reaction) and the partial characterization of the polymer obtained from a simply substituted 1,2,3-trithiacyclopentane. 4-Ethyl-1,2,3-trithiacyclopentane[9] (1) was found to be a free-flowing, yellow liquid which could readily be purified by distillation.[10a] On standing in a closed flask at room temperature over 12 h this substance became a yellow, rubbery, soluble, film-forming material with $\eta_{red}^{30°}$ (c 0.84 g/dL, $CHCl_3$) of 1.02 dL/g.[10b] The polymer *as formed* (i.e., without any attempt to "cap" end groups) evolves an odorous gas above 270 °C and forms a black solid. When subjected to differential scanning calorimetry[11] the polymer undergoes an apparent endothermic transition at 250 °C, which may actually be the onset of thermal degradation. A glass transition temperature, $T_g = -15$ °C, can be readily detected.[12] Gel permeation chromatography in CH_2Cl_2 on Styragel columns (compared to polystyrene standards) gave an apparent $\bar{M}_n = 120\,000$ and an apparent $\bar{M}_w = 340\,000$.[13] These properties are in marked contrast to those observed for the perfluoro analogue which yielded a white polymer (in a polymerization catalyzed by trimethylphosphite at −80 °C) with $\eta_{inh}^{25°}$(0.1%, toluene) = 1.21. The product was pressable to an opaque, white film which clarified at 95–100 °C (T_g ?). Because of the *brittleness* of these films, the authors considered them to be of relatively low molecular weight.[7]



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A consideration of the relative bond strengths of the C–S vs. the S–S bond (65 vs. 54 kcal/mol, respectively[14]) indicates that *if* a thermal process is operative, the most probable path for initiation of polymerization could occur via S–S homolytic scission (Figure 1).

Either or both of the indicated species may then attack monomer at sulfur atoms 1, 2, or 3 possibly giving rise to a polymer composed of 2, 3, and 4 contiguous sulfur atoms, but with an average value of 3 sulfur atoms per repeat unit. Structural irregularity, taken in concert with the effect of a chiral center at C-4 and the variety of conformations attainable, undoubtedly accounts for the wide range of rubbery behavior exhibited by this unusual material.