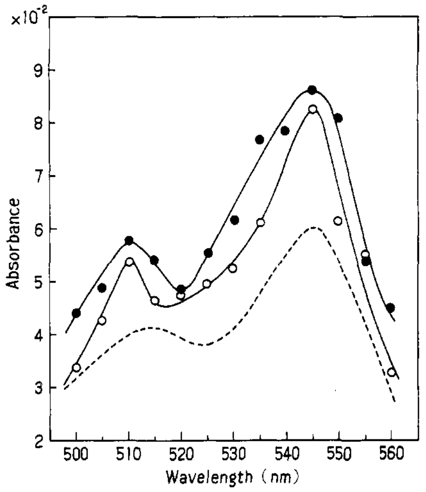

Figure 2. Absorption spectra of transient intermediates obtained after 100 μs by flash excitation. [BP] and [polymer] are the same as those in Figure 1: (●) PSt; (○) PMSt; and (- - -) reported in ref 5.

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.

Acknowledgment. The authors wish to express their thanks to Dr. M. Yamamoto and Mr. M. Ohoka for their collaboration on flash photolysis experiments.

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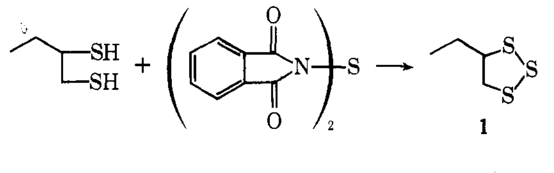
Communications to the Editor

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 $\eta_{\mathrm{red}}^{30°}$ (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 $\overline{M}_n = 120\,000$ and an apparent $\overline{M}_w = 340\,000$.[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 $\eta_{\mathrm{inh}}^{25°}$(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.

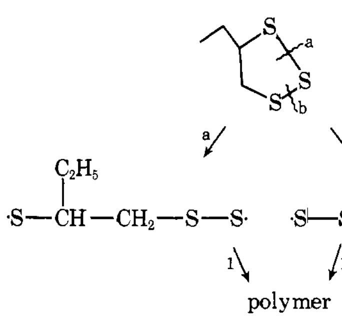

Figure 1.

We are continuing to study the physical properties of these and related compounds, as well as aspects of catalyzed polymerizations (solution and solid state). Work is also directed not only toward structure elucidation, but also toward obtaining structurally regular, as well as stereoregular polymers of this class of materials.

Acknowledgment. We thank Professor B. Wunderlich for the use of his calorimeter and D.N.H. and T.G.B. are indebted to the National Research Council of Canada for financial support of this work.

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(10) (a) A 41% yield of 1 was obtained (10 mmol scale): bp 40–44 °C (0.09 mm) (oil bath 150 °C); ms 152 (P^+). NMR: (CCl_4) δ 1.17 (t, 3 H), ~1.9 (m, 2 H), ~3.5 (m, 3 H). (b) Anal. Calcd for $C_4H_8S_3$: C, 31.5; H, 5.3; S, 63.2. Found: C, 31.5; H, 4.9; S, 63.5.
(11) A Du Pont Model 900 Thermal Analyzer was employed using a heating rate of 10 °C/min starting from 30 °C.
(12) See ref 11; the heating rate was 20 °C/min starting from −80 °C.
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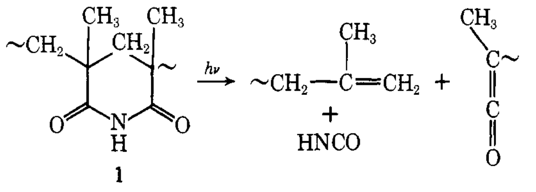
Photolysis of Poly(dimethacrylimide) and Related Polymers

Poly(acrylic anhydride) and poly(methacrylic anhydride) have been shown to undergo decarboxylation to yield olefin and ketene end groups under UV irradiation[1] and electron beam exposure.[2] Poly(dimethacrylimide) and its copolymers have been disclosed to be a useful resist under electron and x-ray irradiation.[3] We wish to report here that poly(dimethacrylimide) 1 decomposes in a similar way as poly(methacrylic anhydride) by elimination of isocyanic acid which results in main chain scission with formation of olefin and ketene end groups as shown below:



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(1)

Photochemical elimination of isocyanic acid has never been reported in the literature to our knowledge.

An ammonia treatment of poly(acrylic acid) and poly(methacrylic acid) at an ammonia pressure of 25 cm and 200 °C for 1 h yielded the structures of poly(diacrylimide) and poly(dimethacrylimide), respectively.[3] The polymer films thus obtained have identical infrared absorption spectra to the polymer obtained by the cyclopolymerization of dimethacryimide initiated by free radicals.[4] The same polyimide structures are also obtained by a similar ammonia treatment of poly(acrylic anhydride) and poly(methacrylic anhydride). Thin films of poly(dimethacrylimide) prepared on a sodium chloride plate were irradiated at low temperature (ca. −120 °C) with two medium pressure mercury lamps. When the poly(dimethacrylimide) prepared by the ammonia modification was irradiated for 5 h, an intense band at 2270 cm^{-1} (indicated by A) appeared in addition to a sharp band at 2345 cm^{-1} due to carbon dioxide, and a very weak band at 2135 cm^{-1} belonging to the ketene end group,[1] as shown in Figure 1. The band at 2270 cm^{-1} can be assigned to isocyanic acid in accordance with the data in the literature.[5] With the poly(dimethacrylimide) prepared by the cyclopolymerization of dimethacrylimide, the CO_2 band at 2345 cm^{-1} became much weaker, and the maximum peak of HNCO band shifted to 2245 cm^{-1}, while the ketene band at 2135 cm^{-1} became more intense.[6] The shift of HNCO band is probably due to the absence of the strong neighboring band in the latter case. Because the HNCO band appeared as a broad band with a half-band width of 50 cm^{-1}, the shift of the peak position from 2270 to 2245 cm^{-1} represents only the change of the absorption band shape.

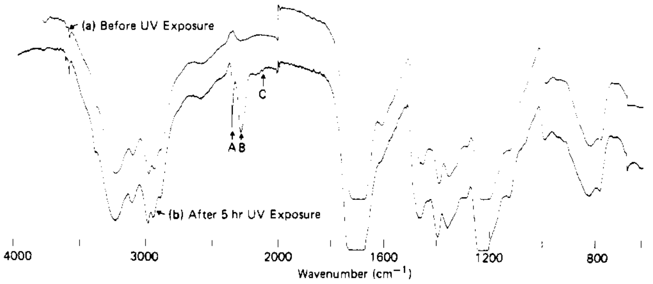

Figure 1. Low-temperature photolysis of the poly(dimethacrylimide) prepared by the ammonia modification.

The weak ketene band in comparison with the one from poly(methacrylic anhydride)[1] is due to the high reactivity of the ketene toward a labile hydrogen such as the one in the NH group, particularly in the polyimides prepared by the ammonia modification. The small but appreciable ketene band from the polyimide made by the cyclopolymerization may partially be explained by the rigid polymer structure, as revealed by a high glass transition temperature and a long lifetime of some radicals trapped in the polymer.[6] When the irradiated polymer films were warmed up, isocyanic acid and the ketene end group reacted with each other to yield carbon