Notes

Photochemistry of Glutaric Anhydride Type Polymers

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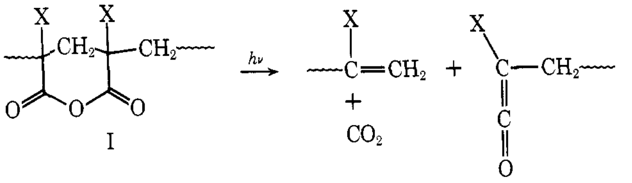
Glutaric anhydrides in both the vapor phase and the condensed phase have been shown to undergo photodecarboxylation to yield α-cleaved cyclobutanone diradicals, which result in formation of cyclobutanones as major products.[1] Although the photodecarboxylation takes place either in triplet or excited singlet states, cyclobutanones are formed only in singlet states. We wish to report here that glutaric anhydride type polymers (I) undergo photochemical degradation by decarboxylation which results in main chain scission with formation of olefin and ketene end groups as shown below:



I

X = H, CH$_3$

The difference in photochemical reactions between the above models and the polymers mainly arises from the rigid structure of the polymers.

Experimental evidence for the above conclusion has been obtained from low-temperature photolysis combined with ir and uv spectrophotometry, and from volatile photoproduct analysis. Thin polymer films of poly(acrylic acid),[2] or of poly(methacrylic acid),[2] were cast from a 2-methoxy ethanol solution on sodium chloride plates, and then baked under vacuum at 190°C for 1 hr. This treatment yielded almost exclusively[3] the glutaric anhydride type polymer structure I with new ir absorption peaks at 1805, 1750, and 1030 cm^{-1} for poly(acrylic anhydride),[4] and 1800, 1760, and 1050 cm^{-1} for poly(methacrylic anhydride),[5] respectively. Poly(methacrylic anhydride) shows strong uv absorption below 2700 Å with $\lambda_{\max}$ 2180 Å, followed by an even stronger absorption extending to 1900 Å, while poly(acrylic anhydride) shows strong uv absorption below 2800 Å, with monotonously increasing intensity down to 1900 Å. The anhydride polymer film thus obtained was irradiated with two medium pressure mercury lamps for several hours at −100°C under continuous pumping at 10^{-3} Torr. Under this condition, new peaks appeared at 2345 and 2125 cm^{-1} for poly(acrylic anhydride), and at 2345 and 2145 cm^{-1} for poly(methacrylic anhydride), as shown in Figure 1. The absorption at 2345 cm^{-1} is clearly assigned to carbon dioxide. The absorptions at 2125 and 2145 cm^{-1} are attributed to the ketene end groups, $\mathrm{HC({=}C{=}O)CH_2}\sim$ and $\mathrm{CH_3C({=}C{=}O)CH_2}\sim$, respectively.[6] When warmed up, these peaks disappeared; when reacted with methanol at −80°C, the ketene peaks disappeared, and an ester absorption appeared as a shoulder at 1730 cm^{-1} for poly(methacrylic anhydride). A residual gas analysis showed only carbon dioxide after the reaction with methanol. The formation of cyclobutanones, as found in the monomeric compounds,[1] seemed not to take place under our conditions as shown by the absence of change in ir absorption between 1760 and 1800 cm^{-1}. Under the uv irradiation at −100°C, a weak absorption band appeared between 3130 and 3220 Å, and upon warming disappeared; this uv absorption may be ascribed to the ketene end group.

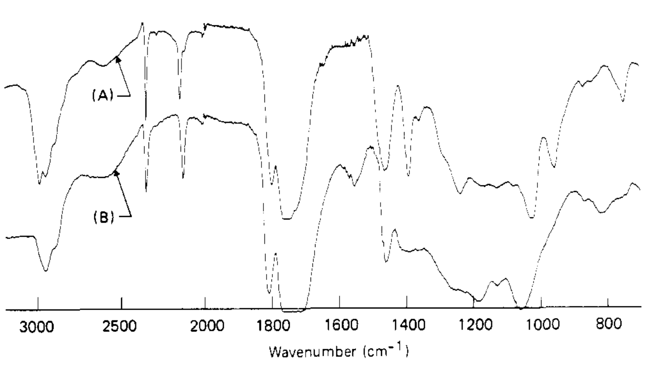


Figure 1. Ir spectra of (A) poly(methacrylic anhydride) and poly(acrylic anhydride) after several hours of uv irradiation at −100°C. Only the 2345- and 2145-cm^{-1} peaks in (A) and the 2345 and 2125 cm^{-1} peaks in (B) represent changes. No other significant changes occurred.

Table I

Volatile Photoproducts from Poly(acrylic anhydride) and Poly(methacrylic anhydride) in Uv Irradiation at 254 nm

	Photoproducts, 10^{-7} mol/min			
	CO$_2$	CO	CH$_4$	H$_2$
PAA[a]	2.1	1.4		0.1
PMA[b]	10	9.8	1.3	

[a] Poly(acrylic anhydride): as an average of three experiments, the absorbed light was estimated as 4.5×10^{-5} einstein/min, as measured as the difference in the transmitting light intensity through a polymer film coated and a noncoated quartz cell. [b] Poly(methacrylic anhydride): similarly the absorbed light was estimated to be a 2.9×10^{-5} einstein/min.

The uv irradiation at 254 nm at room temperature yielded carbon dioxide and carbon monoxide as major volatile photoproducts, and small amounts of methane and hydrogen from poly(methacrylic anhydride) and poly(acrylic anhydride), respectively. Their yields are shown in Table I. Ketenes are known to decarbonylate photochemically to yield carbenes,[7] which may give rise to olefinic end groups by hydrogen transfer. Thus, almost the same amounts of carbon dioxide and carbon monoxide were obtained from poly(methacrylic anhydride) which we interpreted to be the consequence of main chain scission. As a further evidence for this postulate the polymer films become readily soluble in methanol after uv irradiation. Poly(acrylic anhydride), however, yielded unequal amounts of carbon dioxide and carbon monoxide, and the efficiency of this photoreaction was low in comparison with poly(methacrylic anhydride). Consequently, the polymer films were virtually insoluble after the same amount of uv irradiation as for poly(methacrylic anhydride). This different behavior of poly(acrylic anhydride) is probably due to the high reactivity of tertiary hydrogen with the ketene end groups, yielding some cross-linking of the polymer chains.

Acknowledgment. The author thanks Drs. J. Bargon, E. Gipstein, and J. Pacansky for their discussion.

References and Notes

(1) H. Hiraoka, *J. Am. Chem. Soc.*, **95**, 1664 (1973).
(2) The polymer samples were obtained from Polysciences, Inc., Warrington, Pa.
(3) The ir absorption patterns of the polymer films agree with that of 2,2′,4,4′-tetramethylglutaric anhydride in which case the 1800-cm^{-1} absorption is weaker than the 1757-cm^{-1} peak, quite different from those of pivalic anhydride. This observation does not exclude the presence of several percent of the interchain anhydride linkage. An ammonia treatment of the polymer films yielded exactly the same ir absorption spectra with those of poly(dimethacrylimide) and poly(diacrylimide), reported by G. Schröder, *Makromol. Chem.*, **96**, 227 (1966).
(4) A. Eisenberg, T. Yokoyama, and E. Sambalido, *J. Polym. Sci.*, **7**, 1717 (1969).
(5) D. H. Grant, and N. Grassie, *Polymer* **1**, 125 (1960).
(6) Another possibility for these ir absorptions could be trapped carbon monoxide in the films. However, this possibility is rejected because of the following reasons: (1) the temperature of the sodium chloride plate in the low-temperature photolysis was measured to be −100°C, which was much higher for entrapment of carbon monoxide as reported by O. L. Chapman, C. L. McIntosh, and L. L. Barber, *Chem. Commun.*, 1162 (1972); (2) if they were due to carbon monoxide, its amount trapped in the films less than 10^{-2} cm thick as studied here must have been 10^{-5} mol/cm^2, exceeding the strength of the polymer films; (3) the different wave numbers, 2125 and 2145 cm^{-1}, indicate different chemical structures; (4) after the reaction with methanol no carbon monoxide was detected.
(7) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1967, pp 392.

Synthesis of Tetrathiafulvalene-Containing Polyamides

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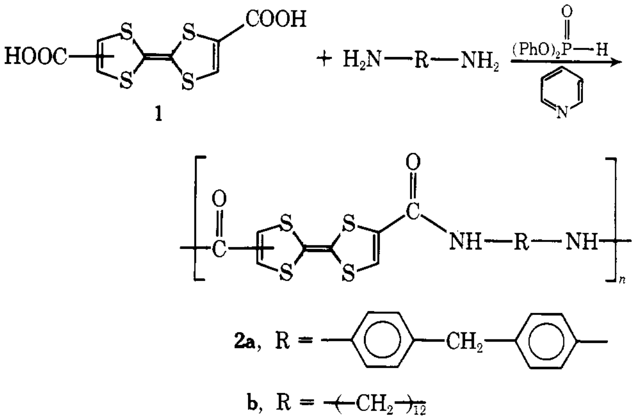
Molecular charge-transfer complexes of tetrathiafulvalene (TTF)[1-3] or its selenium analogue, tetraselenafulvalene (TSeF),[4] with tetracyanoquinodimethane behave electrically and optically like one-dimensional metals at room temperature. Recently, these "organic metals" were reviewed by Garito and Heeger.[5] Because of their high conductivity at room temperature[1,2] ($\sigma > 10^2$ ohm^{-1} cm^{-1} have been observed) and the fact that the complex of hexamethylenetetraselenafulvalene–tetracyanoquinodimethane remains a conductor down to 0.006 K,[6] derivatives of TTF and TSeF have attracted wide attention.

It was of interest to prepare polymers containing the TTF group in order to see (a) if TCNQ complexes could be made and (b) if such polymeric complexes were semiconductors. At the start of this work no polymers of TTF had been reported in the open literature.[7] One TTF polymer was since prepared in a polycoupling process by Okawara et al.[8] We have just reviewed, comprehensively, the preparative methods for TTF and TSeF derivatives.[9]

The high anisotropic conductivity of the TCNQ complexes of TTF has been attributed to the regular parallel stacking of TCNQ and TTF molecules in crystals of this complex.[1-3,5] It was not considered possible to maintain such regular stacking in polymeric complexes. However, even if the conductivity of polymeric complexes was five orders of magnitude less than TTF–TCNQ itself, this would give a useful semiconductor. The preparation of semiconducting polymers has been a continuing goal in our laboratory.[10,11]

Polycondensation of Tetrathiafulvalene-4,4′(5′)-dicarboxylic Acid (TTF-diacid), 1, with Diamines

Scheme I

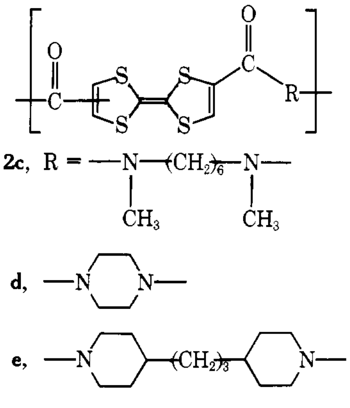


The TTF-diacid, **1**, and a diamine could be converted to a salt for pyrolytic polycondensation. However, it was reported that the pyridine salt of TTF-diacid, **1**, was thermally unstable at 240 °C where decarboxylation resulted in the formation of tetrathiafulvalene.[12] Thus the direct polycondensation of the diacid, **1**, with diamines was effected using diphenyl phosphite–pyridine as a dehyration reagent.[13]

Successful polycondensation of diacid **1** with both aryl and alkyl diamines was readily effected in *N,N*-dimethylformamide (DMF) at 70 °C using the diphenyl phosphite–pyridine reagent. Representative polymers are shown in Scheme I. The major problem encountered was the poor solubility of the resulting polymers, **2**. Trifluoroacetic acid and hexamethylphosphortriamide (HMPA) were fairly good solvents, but other solvents were unsatisfactory.

In an attempt to generate more soluble polymers, bis(secondary)amines such as *N,N*′-dimethyl-1,6-hexanediamine, 4,4′-trimethylenepiperizine, and piperazine were used. Polymerization took place to produce polymers **2c** and **2d**, but **2e** was not obtained. Instead, diacid **1** was recovered in this case. The solubility of the polymers **2c** and **2d** was still poor. The results of polycondensation reactions and the solubility of the polyamides **2** are shown in Tables I and II.

The elemental analyses of polymers **2a–d** were in good agreement with their calculated values. Ir spectra of polymers **2a** and **2b** show peaks at 1630 and 1550–1540 cm^{-1} attributed to amide I and amide II bands. Ir spectra of polymers **2c** and **2d** also showed a peak at 1650–1630 cm^{-1} due to amide groups. The spectra also contained bands at 840–820, 765–775, and 730 cm^{-1} which are characteristic of the disubstituted TTF nucleus.[8,12]



Polytransesterification has been briefly studied, but high molecular weight polymers have not yet been prepared due to thermal instability of the TTF nucleus at higher temperatures. The TTF bisanhydride, prepared from acetic anhy-