Unambiguous Proof of Nitrile Formation from Pyrazine Skeleton through Photo-Oxidative Degradation. Isolation and Structural Determination of Photodegraded Product of Amorphous Poly(2,5-distyrylpyrazine)

Yukihiko HASHIMOTO, Yutaka ADEGAWA, Masaki HASEGAWA,* Kazuyuki ONODERA,†
Hirochika SAKURAGI,† and Katsumi TOKUMARU†
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
† Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
(Received October 5, 1990)

Synopsis. In the presence of oxygen, amorphous poly(2,5-distyrylpyrazine) film was readily photodegraded, accompanied by cleavage of the pyrazine rings in the main chain. From the photodegraded film, *t*-2,*c*-4-diphenylcyclobutane-*r*-1,*t*-3-dicarbonitrile was isolated in 13% yield.

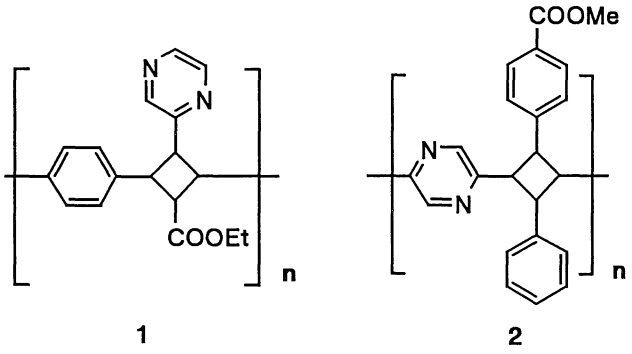
Various kinds of diolefinic compounds have been known to photopolymerize in the crystalline state into crystalline polymers having cyclobutane rings in the main chain. For example, 2,5-distyrylpyrazine (DSP) photopolymerizes in the crystalline state to give a high molecular weight liner polymer, poly(2,5-distyrylpyrazine) (poly-DSP).[1]

Thermal and photochemical behavior of poly-DSP has already been reported.[2–4] The crystalline poly-DSP is thermally depolymerized to the monomer in high yield.[2] In contrast, the photochemical reactivity of poly-DSP is affected by the matrix.[3] While poly-DSP is photodepolymerized in trifluoroacetic acid solution, it is highly stable photochemically in the crystalline state.[3] Furthermore, amorphous poly-DSP film is readily photodegraded with sunlight under air (Scheme 1). Such a high contrast in reactivity among the amorphous, crystalline, and solution states of the same polymer is quite unique in polymeric materials.

In this paper, we describe isolation and determination of one of the major degradation products of the amorphous poly-DSP film.

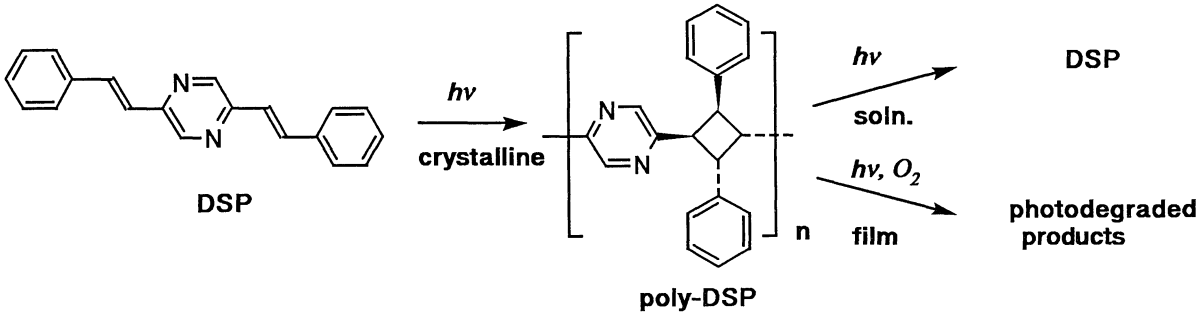
Results and Discussion

When poly-DSP film was stored in air under sunlight, absorption bands ascribable to hydroxyl, carbonyl, and cyano groups appeared in the IR spectrum.[3] Considering the structure of the polymer, the generation of nitrile compounds should be attributed to cleavage of the pyrazine rings in the main chain. On irradiation of amorphous poly[ethyl 4-[2-(2-pyrazinyl)ethenyl]cinnamate] (**1**) film, the nitrile formation was also observed in the IR spectrum.[5] A similar photodegradation was reported in the case of poly[2-(*p*-methoxycarbonylstyryl)-5-styrylpyrazine] (**2**).[6]



1 **2**

In order to confirm the generation of cyano groups and to throw light on the mechanism of photodegradation of the pyrazine ring, the photoreaction of substituted pyrazines such as 2,5-dimethylpyrazine was studied as a model of photodegradation of poly-DSP film.[3,4] In the case of low molecular weight aza-aromatics, however, few reports have described on the nitrile formation through photoreaction.[7] Recently, we studied the photoreaction of 2,3,5,6-tetraphenylpyrazine from the viewpoint of a hindered pyrazine ring. On irradiation of the tetraphenylpyrazine in dichloromethane, a trace amount of benzonitrile was formed as detected by thin layer and gas chromatog-



Scheme 1.

raphy. Nevertheless, the tetraphenylpyrazine was not suitable for a model of poly-DSP since the yield of products was not sufficient to attain our aim mentioned above.

Therefore, we tried to isolated directly degradation products of the poly-DSP film. The film was irradiated under oxygen with a super-high-pressure mercury lamp and extracted with chloroform. Evaporation of the solvent and separation with thin layer chromatography afforded a white powder as a product. This compound (**3**) was identified as 2,4-diphenylcyclobutane-1,3-dicarbonitrile by IR, ^{1}H and ^{13}C NMR, and mass spectra as follows. Namely, the IR spectrum of **3** represented the presence of cyano groups (2230 cm^{-1}) and the absence of pyrazine rings. In the ^{1}H NMR spectrum, a multiplet at ca. δ=7.5, and two double doublets at δ=4.3 and 4.0 indicated a diphenylcyclobutane skeleton for **3**. Furthermore, the ^{13}C NMR spectrum was consistent with the above formulation. The peaks at δ=135.19—127.01, 117.80, and 43.59—33.56 indicated the carbons of phenyl rings, of cyano groups, and of cyclobutane rings, respectively. The molecular weight 258 ($C_{18}H_{14}N_2$) for **3** was also confirmed by the mass spectrum. In EI-MS for **3**, a strong peak at *m/z* 129 corresponding to the fragmentation of $[M/2]^+$ (cinnamonitrile) was observed. Furthermore, CI-MS (isobutane) showed significant peaks at *m/z* 315, 259, and 130 corresponding to the fragmentation of $[M+C(CH_3)_3]^+$, $[M+H]^+$, and $[M/2+H]^+$, respectively.

The configuration of **3** was finally confirmed as shown in Fig. 1 by direct comparison of ^{1}H and ^{13}C NMR spectra with those of an authentic sample (**3'**) derived from α-truxillic acid. Consequently, the photodegradation of poly-DSP proceeds with retention of configuration around the cyclobutane rings of the starting polymer.

Although the photo-oxidative degradation mechanism and the origin of simultaneously generated carbonyl and hydroxyl groups have not been clarified yet, the present result is unambiguous proof of generation of cyano groups from pyrazine rings on irradiation under oxygen. Further interest is that a photodegradation product of polymeric material was readily isolated in a significant yield.

Experimental

Infrared spectra were recorded on a JASCO IR-810 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained by using JEOL GX-400 instruments. Melting points were determined by a Laboratory Devices MEL-TEMP and were uncorrected. DSP and poly-DSP were prepared as described in the literature.[2]

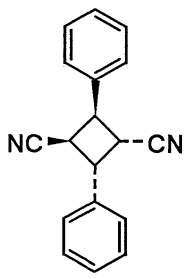


Fig. 1. Configuration of the isolated compound **3**.

Photodegradation of Amorphous Poly-DSP Film. Since crystalline poly-DSP is insoluble in usual organic solvents, trifluoroacetic acid was used as the solvent of poly-DSP. Amorphous poly-DSP film was prepared by casting its trifluoroacetic acid solution on glass plates. After the solvent was removed in vacuo, the film was washed with ethanol. The poly-DSP film (200 mg) in the flask with quartz beads was degassed by means of vacuum line and replaced by oxygen gas. The flask was sealed, and irradiated with stirring by light from a 500 W super-high-pressure mercury lamp through a water filter. After 120 h, the contents were extracted with chloroform (200 ml). The insoluble residue weighed about 40 mg. Separation of the soluble part of the products was carried out by preparative thin layer chromatography (49 : 49 : 2 $CHCl_3$/benzene/Et_2O and then 1 : 1 benzene/hexane), to give a white powder (**3**, 24 mg) as a main product, which was identified as 2,4-diphenylcyclobutane-1,3-dicarbonitrile on the basis of IR, ^{1}H and ^{13}C NMR, and mass spectra: IR (KBr) 3100—2850, 2230, 1495, 1450, 745, 700, and 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.52—7.39 (10H, m), 4.31 (2H, dd, *J*=7 and 9 Hz), and 4.03 (2H, dd, *J*=7 and 9 Hz); ^{13}C NMR ($CDCl_3$) δ=135.19, 129.31, 128.89, 127.01, 117.80, 43.59, and 33.56; MS (EI) *m/z* (rel intensity) 129 (100) and 102 (12); (CI, isobutane) *m/z* (rel intensity) 315 (35), 259 (20), and 130 (100).

Preparation of Authentic Sample of 2,4-Diphenylcyclobutane-1,3-dicarbonitrile. To a stirred suspension of α-truxillic acid (3.0 g, 10 mmol) in benzene (50 ml) was added an excess amount of thionyl chloride in the presence of DMF as a catalyst. The mixture was refluxed for 3 h. The resulting solution was concentrated in vacuo and the residual thionyl chloride was removed as the benzene azeotrope. The corresponding acid dichloride was obtained as a brown solid mass and used directly in the following step without further purification.

To 500 ml of concentrated aqueous ammonia was added dropwise, with vigorous stirring, a solution of the crude dichloride in benzene (60 ml). The reaction mixture was stirred until the precipitation was completed. Filtration followed by crystallization of the precipitate from ethanol–benzene gave the corresponding diamide (1.9 g, 65%).

To a suspension of the diamide (0.15 g, 0.50 mmol) in dichloromethane (100 ml) and DMF (8 ml) was added an excess amount of phosphoryl chloride. The mixture was refluxed for 8 h. The resulting solution was concentrated and the residual oil was poured into water. Filtration and crystallization of the precipitate from dichloromethane–hexane gave colorless plates (**3'**) (66 mg, 51%): Mp (CH_2Cl_2/hexane) 239—240 °C; IR (KBr) 3100—2850, 2230, 1490, 1460, 745, 700, and 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.50—7.39 (10H, m), 4.31 (2H, dd, *J*=7 and 9 Hz), and 4.02 (2H, dd, *J*=7 and 9 Hz); ^{13}C NMR ($CDCl_3$) δ=135.22, 129.31, 128.89, 127.03, 117.84, 43.56, and 33.56. Found: C, 83.39; H, 5.51: N, 10.95%. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84%.

The authors are pleased to acknowledge Mitsui Toatsu Chemicals, Inc., for the measurement of mass spectrometry.

References

1) M. Hasegawa, *Chem. Rev.*, **83**, 507 (1983).
2) M. Hasegawa, Y. Suzuki, F. Suzuki, and H. Nakanishi, *J. Polym. Sci., Part A-1*, **7**, 743 (1969).

3) M. Sakuragi, M. Hasegawa, and M. Nishigaki, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 521 (1976); Y. Suzuki, T. Tamaki, and M. Hasegawa, *Bull. Chem. Soc. Jpn.*, **47**, 210 (1974).

4) K. Onodera, Thesis for M. Sc., University of Tsukuba, 1980.

5) For the preparation of **1**, see, M. Hasegawa, M. Aoyama, Y. Maekawa, and Y. Ohashi, *Macromolecules*, **22**, 1568 (1989).

6) M. Hasegawa, T. Katsumata, Y. Ito, K. Saigo, and Y. Iitaka, *Macromolecules*, **21**, 3134 (1988).

7) K. L. Wierzchowski, D. Shugar, and A. R. Katritsky, *J. Am. Chem. Soc.*, **85**, 827 (1963); K. L. Wierzchowski and D. Shugar, *Photochem. Photobiol.*, **2**, 377 (1963).