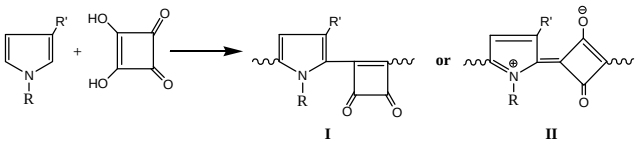
Backbone Structure of Polysquaraine Studied by Infrared Spectroscopy

Hsiao-Chi Lu (盧曉琪)[1,2], Wha-Tzong Whang (黃華宗)[1], and Bing-Ming Cheng (鄭炳銘)[2]

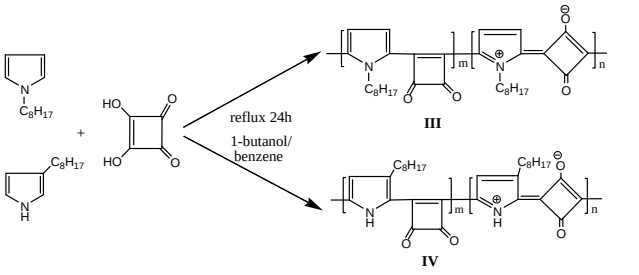
[1]Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Squaric acid might react with a pyrrole derivative by 1,2- or 1,3-addition to form poly(pyrrolyl)squaraines of two types, designated as formulae **I** and **II** as shown in Scheme 1. Condensation of these two reagents might thus generate poly(pyrrolyl)squaraine possessing both repeating units of formulae **I** and **II** in the polymer chain.



Scheme 1: Reaction of a pyrrole derivative with squaric acid in condensation forms repeating units in the structure of poly(pyrrolyl)squaraine of two types, of which formulae **I** and **II** imply the covalent and zwitterionic backbones; respectively. R and R' represent H or an alkyl group.

The general condensation of squaric acid with 1-octylpyrrole and 3-octylpyrrole is expressed in Scheme 2; the end products poly(1-octylpyrrole-co-squaric acid) and poly(3-octylpyrrole-co-squaric acid) are denoted with formulae **III** and **IV**, respectively. These poly(pyrrolyl)squaraines might contain m repeating units with a covalent backbone and n repeating units with a zwitterionic backbone in their structures; poly(1-octylpyrrole-co-squaric acid) and poly(3-octylpyrrole-co-squaric acid) as we synthesized are named poly(1-octylpyrrolyl)squaraine, abbreviated **P1**, and poly(3-octylpyrrolyl)squaraine, **P3**, respectively.



Scheme 2: In the general condensation of squaric acid with 1-octylpyrrole and 3-octylpyrrole, the end-product poly(pyrrolyl)squaraines are represented with formulae **III** and **IV**, respectively.

Infrared spectra serve to distinguish the chemical characteristics of polymers through their sensitivity to functional groups. Polysquaraines feature strong absorption in the mid-IR range, in which occurs useful information to characterize the structural composition of these polymers. Distinct IR absorption spectra of **P1** and **P3** in the spectral range 400-4000 cm^{-1} are shown in Fig. 1. Including weak absorption features, the lines in IR spectra of **P1** and **P3** number 27 and 32, respectively.

IR spectra of the **P1** and **P3** are divided into two regions. The left region, from 2700 to 3400 cm^{-1}, contains strong absorptions attributed to C-H and N-H stretching modes. The intense lines observed between 2800 and 3000 cm^{-1} are assigned to C-H stretching modes of the octyl moiety in both polymers. Unlike the octyl group linked to –N atom in **P1**, **P3** has its octyl group linked to a –C atom and shows a signal of the –NH group according to a –NH stretching mode near 3300 cm^{-1} in Fig. 1(b).

The right parts of the spectra, from 400 to 1750 cm^{-1}, serve as 'fingerprints' of other functional groups and modes. The lines associated with carbonyl (–CO) functional groups in the intrinsic structural backbone of the polymer are typically discernible in the spectra. The covalent and zwitterionic –CO functional groups in polysquaraines have characteristic absorptions near 1750 cm^{-1} and 1600 cm^{-1}, respectively. As carbonyl moieties of these two kinds are thus distinguished directly in the IR spectra, we derive information about these dissimilar components in polymers on the basis of these lines. For instance, Fig. 1 (b) shows a strong absorption at 1600 cm^{-1} and a weak one at 1742 cm^{-1}; the intensity of the latter attributed to covalent carbonyl is about 3 % as that of the former associated with zwitterionic carbonyl. This result demonstrates that **P3** possesses mostly zwitterionic repeating units in the polymer chain, so that its repeating units represented as n in Scheme 2 are about 97 %. For a similar analysis applied to the **P1**, the ratio of the intensity for the line attributed to zwitterionic carbonyl about 1622 cm^{-1} to that for the covalent one near 1736 cm^{-1} is approximately 2:1, as shown in Fig. 1(a); hence **P1** includes 1/3 covalent units in its structure.

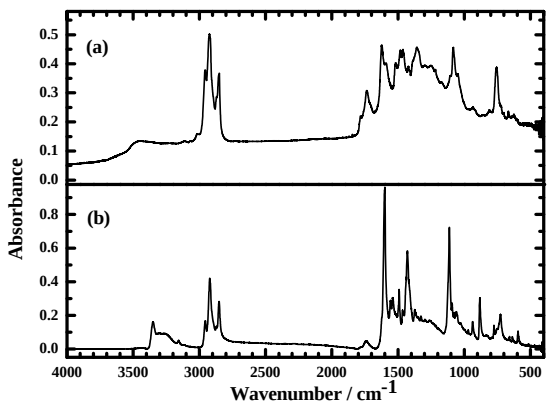


Fig. 1: IR absorption spectra of polysquaraines as synthesized, in the spectral range 400-4000 cm^{-1}: (a) **P1**; (b) **P3** .