way at present. It seems likely that the effect of deuteration on the hydrogen bonding of peptide groups is generally very subtle and would be small.[7] Owing to the complicated nature of the long side chain, the effect of hydrophobic interaction, which is mainly caused by the clustering tendency of water molecules, would be strongly operative in determining the conformation of poly[Cys(CamPrOH)]. It has been argued that D_2O can form stronger hydrogen bonding or a larger number of hydrogen bonds than H_2O. Němethy and Scheraga[8] calculated the cluster size of D_2O to be considerably larger than that of H_2O at low temperatures, and they also found that the cluster size of D_2O falls much faster with rising temperature than that of H_2O. The cluster size of D_2O becomes almost equal to that of H_2O around 60 °C or above it. The formation of the β conformation of poly[Cys(CamPrOH)] in water is closely connected with the degree of structural order of water, and its stability is largely conferred by the hydrophobic interaction. The enhancement of the β conformation in the heat-treated D_2O solution is also related to the hydrophobic interaction, and it is, in a sense, similar to the thermally induced formation of the β conformation of poly(L-lysine).[9]

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Tetsuo Tomiyama and Shoichi Ikeda*
Department of Chemistry, Faculty of Science,
Nagoya University, Nagoya, Japan

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A Novel Synthesis of Conjugated Polymers Related to the Synthesis of Ionene Polymers[1]

Conjugated polymers are in general prepared by the polymerization of acetylenes and nitriles, elimination of small molecules from saturated polymers, polycondensations, intramolecular polymerizations, ring-opening polymerizations, and so forth.[2] In this communication we wish to disclose a novel synthetic route to conjugated polymers which is closely related to the synthesis of ionene polymers. Although cross-conjugated, the polymers obtained have some properties in common with fully conjugated polymers[3] and may be potentially useful as electrical conductors.[4]

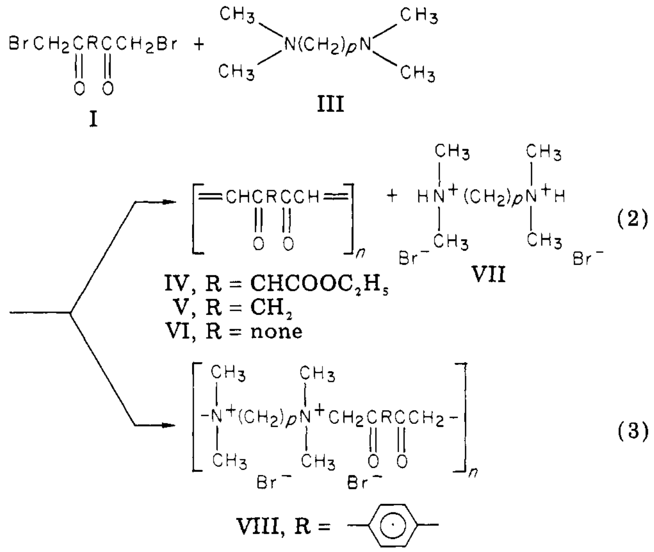
Our reaction system consists of an α,ω-dihalide (I) and a base, and the general main reaction can be shown as follows:

$$\underset{\text{I}}{\mathrm{XCH_2C(O)RC(O)CH_2X}} + \text{base} \rightarrow$$
$$\underset{\text{II}}{\mathrm{XCH_2C(O)RC(O)CH[{=}CHC(O)RC(O)CH{=}]_{\mathit{n}}\text{-}CHC(O)RC(O)CH_2X}} +$$
$$\text{product(s) from the base and HX} \quad (1)$$

$$X = \text{halogen};\ R = \text{arbitrary group}$$

Thus far, those dihalides in which group -CORCO- is conjugated within itself have been successfully polymerized by this method to obtain deeply colored polymers whose degrees of polymerization were relatively low. When an α,ω-ditertiary amine such as N,N,N',N'-tetramethyl-α,ω-diaminoalkanes (III) is used as a base, the reaction system is the same as that of the formation of an ionene oligomer or polymer[5-7] (Scheme I). Thus, the present finding in which elimination of hydrogen halide from an α,ω-dihalide predominates over quaternization also brings forward a new problem in the synthesis of polycations of ionene type.[8]

Scheme I



In a typical example, the reaction of 9.89 g (30 mmol) of ethyl γ,γ'-dibromodiacetylacetate (I, R = $CHCOOC_2H_5$; X = Br) with 3.48 g (30 mmol) of N,N,N',N'-tetramethyl-1,2-diaminoethane (III, p = 2; TMDAE) was carried out in 70 mL of acetone at −10 °C. The reaction took place instantaneously with a considerable evolution of heat. After stirring for 24 h without further cooling, the brownish yellow precipitate formed, 8.77 g, was isolated and identified as the slightly impure dihydrobromide (VII, p = 2) of TMDAE by IR and ^{1}H NMR spectroscopies as well as by elemental analyses after purification. The dark reddish brown filtrate was evaporated to dryness and the residue, 4.70 g, was purified by two reprecipitations (acetone as solvent and ether as precipitant) to give 1.80 g of a brownish yellow powder. It was easily soluble in aqueous alkaline solutions but hardly soluble in pure and acidic water. It exhibited an ability to form metal chelate compounds. Its IR spectrum (KBr disk method) showed the absorption bands due to O—H, C=O and C=C stretching vibrations at 3430, 1705, and 1605 cm^{-1}, respectively, while its electronic absorption spectrum (methanol as solvent) had absorption maxima at 219, 264, and 403 nm, the last tailing up to ca. 700 nm. In addition, the ESR spectrum of this product in the solid state consisted of a singlet with a g value of 2.0038, suggesting the presence of unpaired electrons in a delocalized state. Based on these results, we propose IV as its structure in which, however, the β-diketone structure is predominantly enolized to yield a poly-conjugated system (IX). The elemental analyses data were also in reasonably good agreement with IV, the terminal bromine content indicating that the average degree of polymerization (=n + 2) was about seven.[9]

The reaction of 1,5-dibromo-2,4-pentanedione with TMDAE yielded a similar conjugated polymer (X) but the reaction rate was remarkably smaller than that with ethyl

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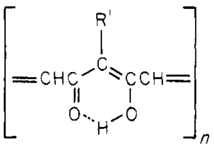

IX, R′ = $COOC_2H_5$
X, R′ = H

γ,γ′-dibromodiacetylacetate.

The base in this type of reaction is not limited to the ditertiary amines such as TMDAE. For instance, monotertiary amines such as triethylamine and potassium hydroxide also reacted with I in a more or less similar manner.

The reaction of dibromodiacetyl with TMDAE or triethylamine under the same conditions as above readily afforded a conjugated polymer (VI) of the same type. Its IR spectrum had absorption bands due to C=O and C=C stretching vibrations at 1715 and 1614 cm^{-1}, respectively. It also exhibited a singlet ESR signal at a g value of 2.0046.

In contrast, the reaction of *ω,ω′*-dibromo-*p*-diacetylbenzene with TMDAE in *p*-dioxane or *N,N*-dimethylformamide at room temperature yielded quantitatively a white powdery ionene polymer (VIII) instead of a colored conjugated polymer. In line with these results the reaction of dibromodiacetylbenzene with triethylamine in these solvents gave a diammonium salt, i.e., *ω,ω′*-bis(triethylammonio)-*p*-diacetylbenzene dibromide, in ca. 45% yield. This reaction occurred, however, with a considerably deep discoloration, particularly when carried out in dimethylformamide. Therefore, it is likely that in these cases also polymerization by the elimination of hydrogen bromide proceeded simultaneously to a small extent. In good contrast with the conjugated polymers, all the ammonium salts obtained were easily soluble in water.

The results mentioned above appear to indicate that group $-COCH_2X$ in I is one of the indispensable terminal groups for the novel polymerization reaction of *α,ω*-dihalides, and that the conjugation of group –CORCO– within itself may not necessarily be indispensable or at least is a minor factor in this type of polymerization, since dibromodiacetylbenzene, the more conjugated monomer, is more relactant to this polymerization than dibromodiacetyl. Although eq 1 appears to involve *α* elimination of hydrogen halide from *α*-halo ketone groups, the genuine mechanism of polymerization could be different.[10] Therefore, attempts to establish a detailed mechanism as well as to expand the scope of this new type of polymerization reaction are currently being carried out.

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(9) The sample prepared in a different batch and purified in the same way was triturated in water, filtered, washed with water, and dried in vacuo and then reprecipitated once as before to further remove the byproduct (VII). The analytical data for the sample thus prepared were as follows. Calcd (n = 15): C, 54.08; H, 4.61; Br, 5.29. Found: C, 54.27; H, 4.85; Br, 5.48. No nitrogen could be detected. The average degree of polymerization is therefore 17, which is higher compared with that of the less purified sample because of the loss of the lower molecular weight fraction during the purification procedure.

(10) A more likely mechanism involves (a) formation of *α*-halocarbanion, (b) nucleophilic attack of this species on a second *α*-halo ketone group to form $-C(O)CHXCH_2C(O)-$, (c) followed by *β* elimination of HX from the γ-diketone group. Incomplete *β* elimination of HX and/or occlusion of the byproduct such as VII into the isolated polymer might account for the small discrepancies between the observed and the calculated elemental compositions for the polymer.[9]

Hiromichi Noguchi,* Futao Wakui, and Yasuzo Uchida
Department of Industrial Chemistry,
Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

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