Notes

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Synthesis of Aromatic Cyclic Imine

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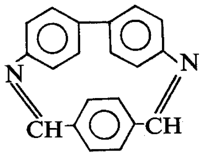
Condensation of 2,2-bis[4-(4-aminophenoxy)phenyl]propane and terephthalaldehyde in dilute solution was found to give a highly crystalline powder in 5—90% yield. The product had remarkable similarities to the linear polymer having the same repeating unit. But its non-macromolecular character was elucidated by gel permeation chromatogram and field desorption mass analyses. A dimeric ring structure is proposed.

Keywords——diamine; dialdehyde; condensation; crystalline; cyclic imine

Linear high-molecular-weight aromatic polyimines, prepared by low temperature polycondensation of diamines and dialdehydes at a concentration over 5% in *m*-cresol, are well known.[1] The polymers have potential applications in the field of high temperature plastics, medical transducers and electrical insulating materials.[2] There are, however, few reports concerning the synthesis of cyclic imines by the condensation of diamines and dialdehydes. Aliphatic cyclic imines were studied by Krässig and Grever.[3] According to the authors, the formation of the cyclic imines could be explained in terms of an equilibrium between polymerization and depolymerization. The cyclic imines are converted to linear polymer by heating in 4% benzene solution. On cooling or diluting the same solution, the equilibrium shifted in the opposite direction. However, no spectroscopic measurement of the products was carried out.

Adams and co-workers reported the formation of aromatic cyclic imines.[4] The reaction of terephthalaldehyde and benzidine was typical. They assumed a ring structure consisting of 1 mol of benzidine and 1 mol of dialdehyde with the elimination of 2 mol of water, as indicated by the formula:



However, the insolubility of the product made it impossible to determine the molecular weight. Thus, it is interesting to synthesize such an aromatic cyclic imine and identify the structre.

Experimental

Infrared (IR) and nuclear magnetic resonance (NMR) measurements were carried out on Hitachi 285 and JEOL-PS-100 (100 MHz) spectrometers respectively. X-Ray diffraction spectra were obtained by the powder method at 35 kV-100 mA and 4 deg/min. The gel permeation chromatogram (GPC) was recorded on a Japan Analytical Industry LC-8, equipped with polystyrene gel columns using $CHCl_3$ as the eluent (3.3 ml/min at 20 °C). Standard polystyrenes were used for calibration of molecular weight. The field desorption (FD) mass spectrum (MS) was measured on a JMS-01SG-2 mass spectrometer at an acceleration voltage of 8 kV. The voltage between the anode and cathode was 5 kV using a silicone emitter.

Cyclic Imine (I)——0.41 g (1 mmol) of 2,2-bis[4-(4-aminophenoxy)phenyl]propane was dissolved in 560 ml of chlorobenzene. To this solution was added 0.13 g (1 mmol) of terephthalaldehyde. The resultant homogeneous solution was concentrated by 20 ml by distillation to remove the water, cooled and left to stand at 20 °C for 264 h to precipitate yellow rhombic crystals; yield: 5%. mp: over 350 °C. *Anal.* Calcd for $(C_{35}H_{28}N_2O_2)_n$: C, 82.64; H, 5.55; N, 5.51. Found: C, 82.14; H, 5.53; N, 5.32. IR: 2870 (νCH of $-\underset{H}{C}=N-$), 1620 (νC=N), 1240 (νC–O–C). NMR: $(CDCl_3)$ δ 8.52 (2H, s, $-\underset{H}{C}=N-$), 7.99 (4H, s, benzylidene ring), 7.30—6.90 (16H, m, aromatic protons), 1.69 (6H, s, CH_3); (CF_3COOD): δ 9.40 (2H, s, $-\underset{H}{C}=N-$), 8.53 (4H, s, benzylidene ring), 7.88—7.04 (16H, m, aromatic protons), 1.78 (6H, s, CH_3).

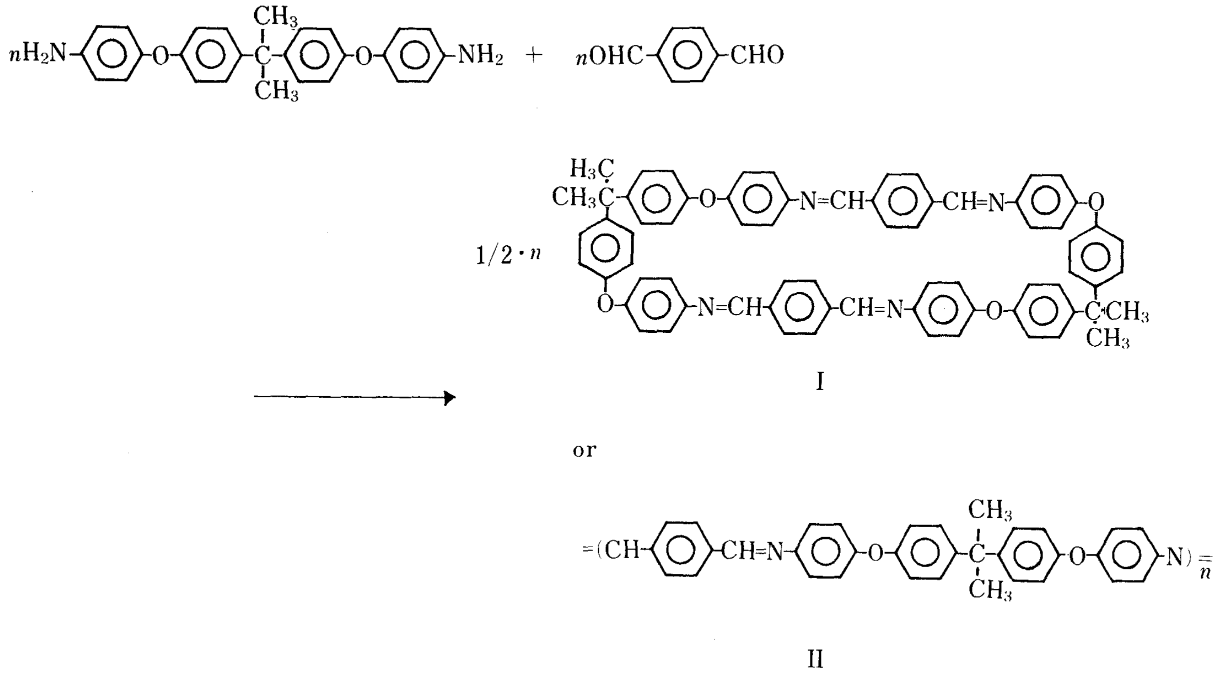


Table I. Condensation of 2,2-Bis[4-(4-aminophenoxy)phenyl]propane and Terephthalaldehyde at 20 °C

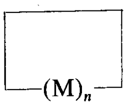
Run	Solvent	Monomer concentration (%)	Reaction time (h)	Yield of I (%)
1	Chlorobenzene	0.1	264	5
2	Chlorobenzene	0.25	48	12
3	Chlorobenzene	0.5	24	30
4	Chlorobenzene	1.6	24	48
5	Chloroform	0.5	24	56
6	TCE	1.3	264	0
7	TCE+chlorobenzene (1 : 1)	0.75	24	87
8	TCE+chlorobenzene (1 : 1)	1.6	18	90
9	Toluene	0.15	168	5

TCE; tetrachloroethane.

Results and Discussion

The results of condensation in various solvents are shown in Table I. The dilute solution reaction resulted in the precipitation of a yellow and highly crystalline solid (I), in contrast to a consentrated solution.[5] Higher yields were obtained with increased concentration in the range of 0.1 to 1.6%, although concentrations over 2% resulted in the formation of only amorphous oligomers. The mixed solvent of tetrachloroethane (TCE) and chlorobenzene gave I in excellent yield, although TCE alone did not.

It was shown earlier[6] that the condensation of compounds having bifunctional groups produces two different structures, represented by the formulas:



III

$E{-}(M)_n{-}E'$

IV

(where E and E′ are identical or different end groups, M is the repeating unit, and *n* the degree of polymerization). In the case of *n* of adequate size, structure (III) is substantially equivalent to structure (IV).

As I did not show any endo groups spectroscopically and had the expected repeating unit, it must be either the cyclic compound or the macromolecule. It has been difficult to identify the cyclic structure (I), because of the similarity to the polymer (II),[5,7] as mentioned above. In fact, the two compounds showed identical IR and NMR spectra. High melting point over 350 °C, low volatility and low solubility were also common. Both were insoluble in common solvents tried, except for $CHCl_3$ (slightly soluble), CF_3COOH (soluble) and concentrated H_2SO_4 (soluble with degradation). However, the difference of crystallinity between the two compounds was remarkable since II was always obtained in amorphous form, while I was always obtained in highly crystalline forms, as shown in Fig 1. In fact, I was obtained as rhombic single crystals from 0.1% solution (Fig. 2) or leaf-like crystals from 0.15—1.6% solution.

Its non-macromolecular character was elucidated by GPC and FD mass analyses (Figs. 3 and 4). GPC showed the peak of I near the point corresponding to the dimer (molecular weight = 1016) and FD MS showed the protonated molecular ion (MH^+) at *m*/*e* 1017. Hence, it is concluded that I has the dimeric ring structure.

The compound is expected to be useful for specialty applications, *e.g.*, as an abradant and a metal ion adsorbent. Practical investigations are in progress in our laboratories.

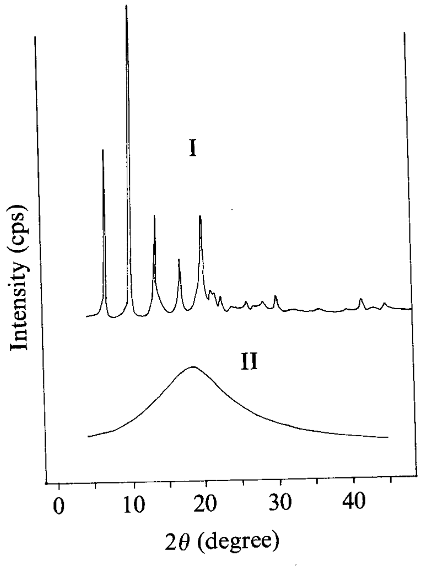


Fig. 1. X-Ray Diffraction Patterns of the Yellow Crystals (I) and the Linear Polymer (II)

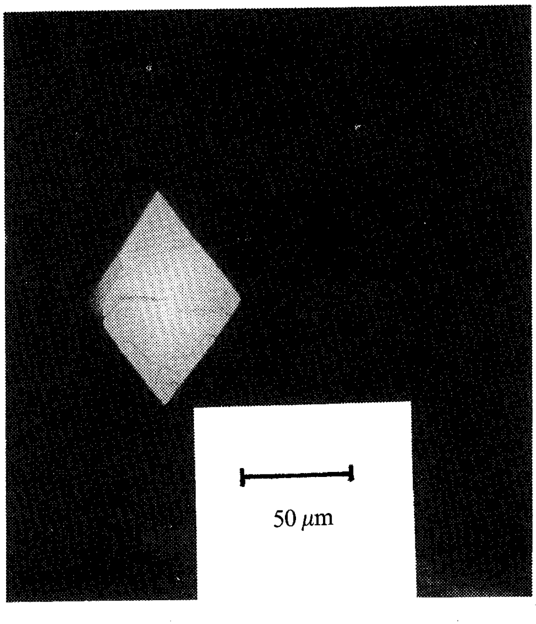


Fig. 2. Optical View of a Rhombic Crystal of I under Crossed Polarizers

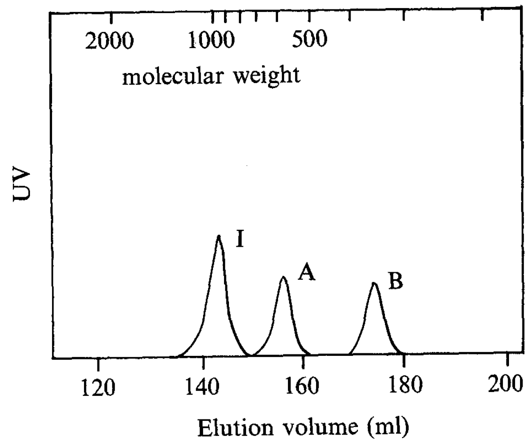
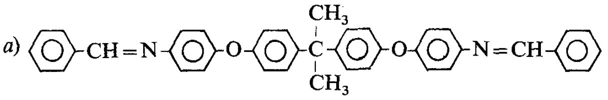


Fig. 3. GPC of I

Monomer diamine [(B), molecular weight=410] and its derivative[a] [(A), molecular weight=586] are also shown for calibration.

a)


$C_6H_5\text{-}CH{=}N\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}N{=}CH\text{-}C_6H_5$

2,2-bis[4-(4-benzylideneaminophenoxy)phenyl]-propane

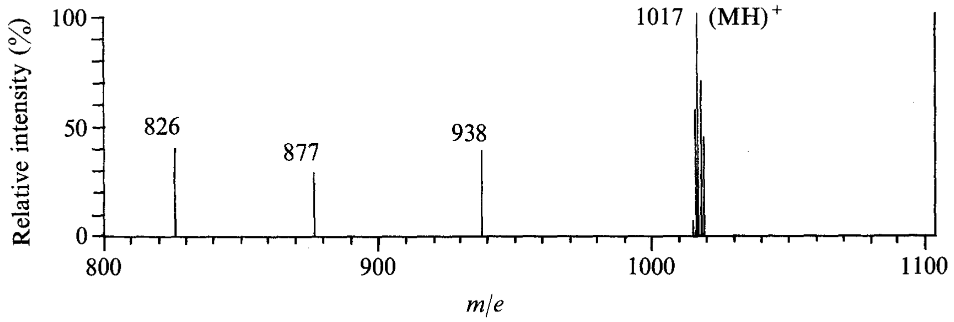


Fig. 4. FD Mass Spectrum of I

References

1) *a*) K. Suematsu and K. Nakamura, *Polym. Prep. Jpn.*, **30**, 880 (1981); *b*) K. Suematsu, K. Nakamura and J. Takeda, *Polym. J.*, **15**, 71 (1983); *c*) K. Suematsu, K. Nakamura and J. Takeda, *Coll. Polym. Sci.*, **261**(6), 493 (1983).
2) K. Suematsu, K. Nakamura and J. Takeda, *Yuki Gosei Kagaku Kyokai Shi*, **41**, 84 (1983).
3) H. Krässig and G. Grever, *Macromol. Chem.*, **17**, 131 (1955).
4) R. Adams, J. E. Bullock and W. C. Wilson, *J. Am. Chem. Soc.*, **45**, 521 (1923).
5) K. Suematsu, K. Nakamura and J. Takeda, *Yuki Gosei Kagaku Kyokai Shi*, **41**, 186 (1983).
6) H. Jakobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).
7) K. Suematsu, *Asahi Chemical Industry, Giken Monthly Report*, **12**, 1 (1976).