

## 14.5 Stability of Guest Molecules in Urea Canal Complexes by Canal Polymerization

Fumio YOSHII and Keizo MAKUUCHI  
Takasaki Radiation Chemistry Research Establishment  
Japan Atomic Energy Research Institute

• 1233 Watanuki-machi, Takasaki-shi, Gunma-ken, 370-12 Japan

**Abstract** It was found that various organic materials are attracted into urea canal by hexanediol diacrylate (HDDA) and long chain compounds. This means that materials which does not form complex by itself are induced in canal by HDDA and long chain compounds. To include with stability perfumes, insecticides, attractants and repellents in urea canal, leaf alcohol was used as a model compound for guest molecules in the canal. The leaf alcohol from the canal released gradually over many days and the release was inhibited for 15 days by long chain compounds and for 30 days by polymerized HDDA after irradiation. After releasing, the leaf alcohol in the canal remained 25 % stable for long chain compounds and 40 % for polymerized HDDA. The dose required for stabilization of leaf alcohol in the urea canal by canal polymerization of HDDA was 30 kGy.

### INTRODUCTION

It is well known that a urea (host molecule) canal complex is formed with paraffin and fatty acid (guest molecules). From x-ray analysis, the structure of this complex is hexagonal. When a urea canal complex is formed, urea undergoes crystal transition from original structure of tetragonal to hexagonal structure. The hexagonal structure of the canal complex decomposes at temperature before melting of the tetragonal urea (133°C). The polymerization (canal polymerization) of monomer in the urea canal complex gave a polymer with excellent steric regularity. For instance, canal polymerization produces isotactic polymer for acrylonitrile (Inoue Y. and Nishioka A., 1972; Matsuzaki K. et al., 1968; Minagawa M. et al., 1988; Yoshii F. et al., 1975), syndiotactic polymer for vinyl chloride (Yoshii F, Abe T. and Hayakawa N., 1975) and 1,4-trans polymer for butadiene (Chatani Y. and Kuwata S, 1975).

In the previous paper (Yoshii F. and Kaetsu I. 1978), it was found attracting effect that hexanediol diacrylate (HDDA) attracted various monomers into the canal and copolymerization occurred between HDDA and those attracted monomers by irradiation. It was expected that the urea canal complex is effective in the control of slow release of substances attracted from canal complexes, when perfumes, insecticides, attractants and repellents are included in the canal complex by the attracting effect. In this article, leaf alcohol was used as a model compound of guest molecules attracted in the canal and stabilized with long chain compound and polymerized HDDA in canal polymerization.

### EXPERIMENTAL

#### *Materials*

Urea, leaf alcohol, lauryl alcohol, cetyl alcohol, stearyl alcohol, oleic acid and stearic acid utilized were special grade. HDDA was obtained from Nippon Kayaku Co. Ltd. (Japan). These materials were used without further purification.

#### *Preparation of urea canal complex*

Solid materials of long chain compounds such as lauryl alcohol, cetyl alcohol, stearic acid, oleic acid and paraffin (melting point, 52-54 °C) attracted leaf alcohol in to the canal by grinding in a mortar with urea and leaf alcohol. The molar ratio of urea, HDDA or long chain compounds and leaf alcohol is 15 : 1 : 1.

In the case of HDDA, a mixture of HDDA and leaf alcohol was added to solid urea, then stored at room temperature. Formation of the urea canal complex attracting could be determined from the fact that those mixtures changed to a fluffy powder state from a slurry state.

### Canal polymerization and stability of leaf alcohol in the canal

The urea canal complex was irradiated to include strongly leaf alcohol in the canal by polymerization. Gamma irradiation from a Co-60 source was carried out with a dose rate of 10 kGy/hr.

The decomposition temperature of the urea canal complex including leaf alcohol was estimated using a DSC (Perkin-Elmer DSC 7). The release of leaf alcohol from the canal versus storage was determined by measuring weight reduction.

## RESULTS AND DISCUSSION

### *Stability of leaf alcohol attracted in the canal by long chain compounds*

DSC analysis is well used to elucidate formation of urea canal complexes. Figure 1 shows the change in DSC curves of urea canal complexes attracted leaf alcohol by oleic acid. Curve 1 is decomposition of single oleic acid urea canal complex. Melting of urea (peak temperature, 133 °C) appear after decomposition of canal complex. DSC curves of the canal complex including leaf alcohol are shown in curves 2 and 3. Decomposition of the canal complex shifts to higher temperatures than that of a single oleic acid canal complex. The melting point of urea after decomposition of the canal complex attracted leaf alcohol was similar to tetragonal urea, showing that the crystal lattice changes from hexagonal to tetragonal during the decomposition. From these findings, it is guessed that the peak of decomposition appears at slightly higher temperatures by the influence of leaf alcohol induced in the canal by grinding in the presence of long chain compounds.

To confirm the stability of leaf alcohol in the canal complex, weight reduction of canal complex versus storage time was estimated (Figure 2). The release of leaf alcohol from the canal continued up to 17 days and then was inhibited, while in the mixture of urea and leaf alcohol, almost all leaf alcohol (95 %) is released after the same period. In the case of oleic acid, the release of leaf alcohol from the canal is slower than that of the mixture of urea and leaf alcohol. After release, the leaf alcohol remains 20 % for stearyl alcohol and 25 % for oleic acid in the canal as shown in Figure 2. The leaf alcohol remains stable in the canal even after 45 days. The release rate for leaf alcohol attracted with cetyl alcohol and paraffin was examined. Release rate of leaf alcohol from these canal complexes was almost the same as that of the canal complex attracted with stearyl alcohol. Accordingly, it is concluded that approximately 20 - 25 % of the leaf alcohol attracted with long chain compounds in the canal remains after release.

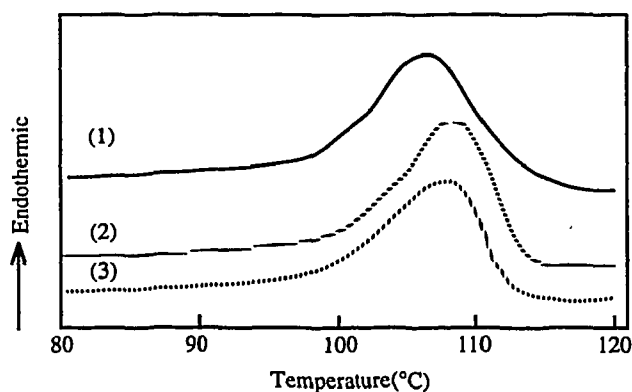


Fig.1 DSC curves of urea canal complex attracted leaf alcohol by oleic acid.

Molar ratio of Urea/Oleic acid/Leaf alcohol,

(1) Urea/Oleic acid=15/1

(2) Urea/Oleic acid/Leaf alcohol=15/1/0.5,

(3) Urea/Oleic acid/Leaf alcohol=15/1/1.

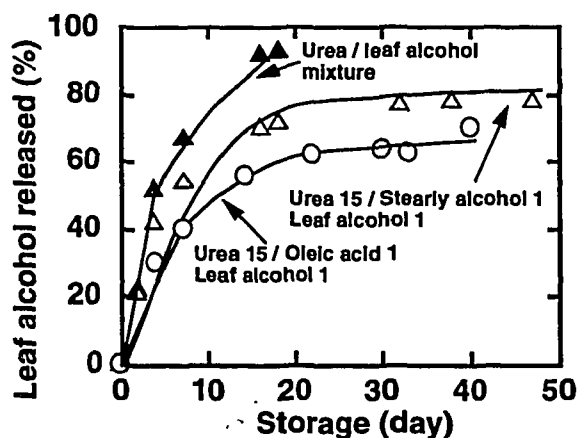


Fig.2 Release curves of leaf alcohol attracted in canal by long chain compounds

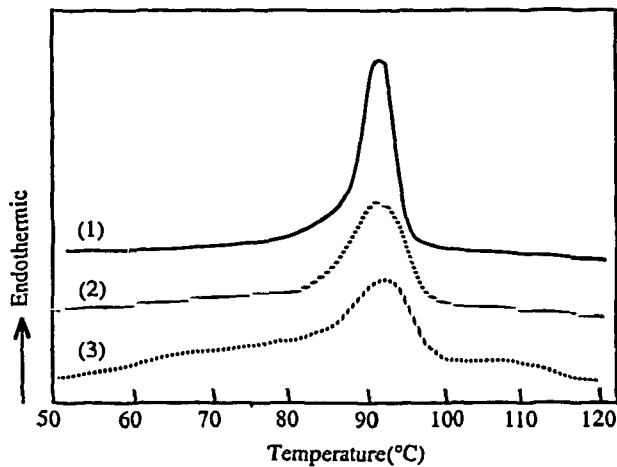


Fig.3 DSC curves of urea canal complex attracted leaf alcohol by HDDA.

Molar ratio of Urea/HDDA/Leaf alcohol,  
 (1) Urea/HDDA=15/1  
 (2) Urea/HDDA/Leaf alcohol=15/1/0.5,  
 (3) Urea/HDDA/Leaf alcohol=15/1/1.

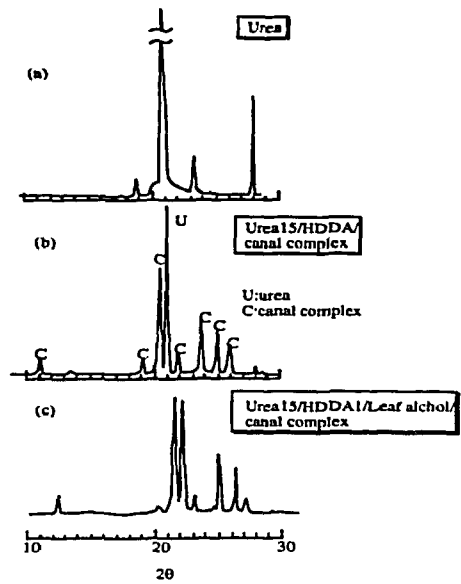


Fig.4 X-ray powder patterns of urea canal complex attracted leaf alcohol by HDDA.

**Stability of leaf alcohol by canal polymerization**

Figure 3 shows DSC curves of the urea canal complex attracted leaf alcohol in the canal by HDDA. Decomposition of the canal complex is affected by attracted leaf alcohol. The endothermic curve of the decomposition become broader and shifts to slightly higher temperature than that of the single HDDA canal complex as well as attracting of long chain compounds. The reflections of 2q in X-ray powder patterns of canal complex attracted leaf alcohol by HDDA are shown in Figure 4. Profile (a) is reflection of tetragonal urea. The HDDA urea canal complexes showed new large reflection peak due to HDDA at 12.2°, 21.4°, 23°, 25°, 26° and 24.2°. The urea canal complex of single HDDA is hexagonal analogous to well-known n-paraffin-urea canal complexes. In canal complex attracted leaf alcohol by HDDA, reflection at 22.5° of urea decrease remarkably with respect to the single HDDA urea canal complex, suggesting that leaf

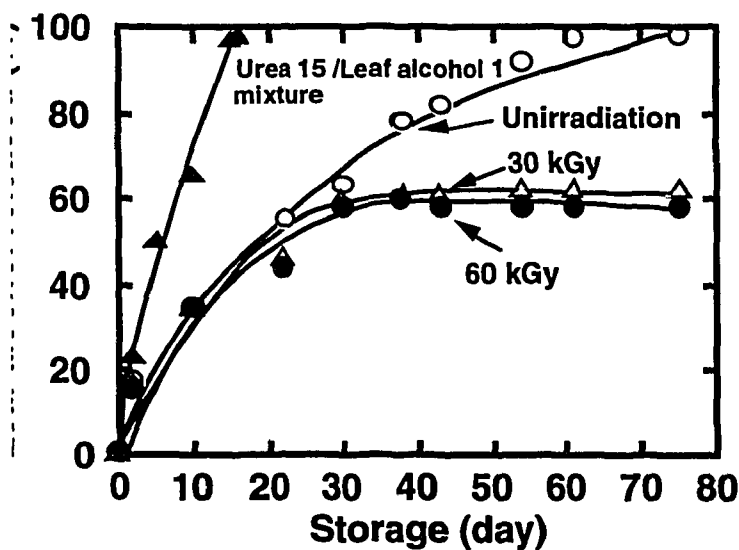


Fig. 5 Release curves of leaf alcohol in canal after canal polymerization of HDDA.

Urea 15 / HDDA 1 / Leaf alcohol 1

alcohol is attracted into canal.

In order to elucidate the stability of leaf alcohol in the urea canal complex, reduction of leaf alcohol released from the canal at 20°C was measured. Figure 5 shows stability of the leaf alcohol attracted in the canal. The leaf alcohol of nearly 100 % in the urea mixture is released for 17 days. The leaf alcohol in the unirradiated canal is released gradually over days and leaf alcohol of 95 % is released for 75 days. The release rate of leaf alcohol from the canal in the unirradiated sample is slower in HDDA canals than for long chain compounds canal complex. On the other hand, the leaf alcohol in the irradiated canal complex is gradually released over 35 days, then the release of leaf alcohol ceases. After 35 days, no leaf alcohol is released from the canal and 40 % leaf alcohol remained in the canal. In the previous paper (Yoshii F. and Kaetsu I., 1978), HDDA in the canal by irradiation began to polymerize at 80 kGy. As shown in Figure 5, the dose for stabilization of leaf alcohol in the canal is sufficient at 30 kGy. Thus, solid polymer of HDDA is not produced at this dose. However, after irradiation, when leaf alcohol urea canal complex with HDDA is added into methanol, the solution became turbid. From this finding, lower molecular weight polymer (oligomer) dissolved in methanol results from a lower dose of 30 kGy. Reduction of HDDA released from the canal versus storage and radiolysis of leaf alcohol during irradiation were not observed. Hence, it is assumed that 40 % leaf alcohol retains between HDDA oligomer in the canal after release. In Figure 2, approximately 20 % of the leaf alcohol included in the canal by stearyl alcohol remained stable in the canal after release. Accordingly, it is apparent that polymerized HDDA kept stable more leaf alcohol in the canal compared with that for long chain compounds.

#### CONCLUSION

It was found that HDDA or long chain compounds attract various organic compounds into urea canal. Stability of leaf alcohol attracted in urea canal complex by these materials were examined. After releasing in canal, leaf alcohol were stably trapped 25 % between long chain compounds and 40 % between polymerized HDDA in canal.

#### REFERENCES

- Chatani Y., and Kuwata S. (1975) Structural investigation of radiation- induced urea canal polymerization of 1,3-butadiene. *Macromolecules* **8**, 12
- Inoue Y., and Nishioka A. (1972) Nuclear magnetic resonance spectroscopy of polyacrylonitrile. *Polymer J.* **3**, 149
- Matsuzaki K., Uryu J., Okada M. and Shiroki H. (1968) The stereoregularity of polyacrylonitrile and its dependence on polymerization temperature. *J. Polym. Sci.* **6**, 1475
- Minagawa M., Miyano K., Takahashi M. and Yoshii F. (1988) Infrared characteristic absorption bands of highly isotactic poly(acrylonitrile). *Macromolecules* **21**, 2387
- Yoshii F., Abe T. and Yoda O. (1975) Radiation-induced post polymerization of acrylonitrile in urea canal complex. *Kobunshi Ronbunshu* **32**, 399
- Yoshii F., Abe T. and Hayakawa N. (1975) Radiation-induced polymerization of vinyl chloride in urea canal complex as studied by broad line NMR. *Kobunshi Ronbunshu* **32**, 429
- Yoshii F. and Kaetsu I. (1978) Trailing effect and copolymerization of long chain monomers and various monomers trailed in canal irradiated by gamma ray in urea canal complex. *Angew. Makromol. Chem.* **69**, 15
- Yoshii F. and Kaetsu I. (1978) In-source and post-polymerization of long chain monomers gamma-irradiated in urea canal complexes. *Angew. Makromol. Chem.* **69**, 1