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# Solid State Characterization and the Thermal Properties of Stereoregular Poly(vinyl chloride) Prepared by Urea Clathrate Polymerization

## Minagawa M\*

NPO: Dream Create Laboratories, 992-1446 Naoe-Sekite 3800-1, Yonezawa, Yamagata, Japan

#### Abstract

The solid state characterization of stereoregular poly vinyl chloride (PVC) prepared by urea clathrate polymerization was carried out in comparison with free radically prepared sample by using various instrumental analyses. The principle of urea clathrate polymerization by inclusion phenomenon was described from a purely experimental point of view. The stereo-chemical difference of the resulting PVC appeared in discoloration, solubility into solvents, IR, DSC, and TG curves. Solid state <sup>13</sup>C NMR spectra also clearly indicate the structural difference of this polymer. In FT-IR spectra, particularly, Krimm's novel results were confirmed in the 700-600 cm<sup>-1</sup> region. A new characteristic band (at 2933 cm<sup>-1</sup>) appeared which was explained in terms of Fermi resonance, *the enhanced intermolecular hydrogen bonding* in highly ordered syndiotactic sequences. In the dynamic ESR measurements in the solid state, signal intensity of the bulk PVC increased rapidly, which was directly connected with TG curve under the linear heating conditions (~10°C/min).

**Keywords:** Stereoregular PVC; Urea canal polymerization; Inclusion phenomenon; IR spectra; Solid state <sup>13</sup>C NMR; ESR measurements

#### Introduction

Solid state polymerization is a unique synthetic method in the field of Polymer Science. This is because ordinary free radical polymerization of vinyl monomers is generally carried out in a solution state because of the safely and economical points of view. How to add one free monomer to a propagating chain end is determined statistically (*free radical process*) or in a combined manner (*ionic process*), which defines the type of stereoregularity through the stereochemical sequences along the main chain. More structurally regular polymer is obtained by the latter method. In one hand, solid state polymerization is quite specific. The most famous example is a urea clathrate polymerization of vinyl chloride (VC) [1]. Namely, VC monomers are packed regularly in onedimensional narrow urea canal, and then strong  $\gamma$ -rays are irradiated, polymerization takes place and highly stereoregular poly(vinyl chloride) (PVC) is obtained.

The 1<sup>st</sup> research in this area was carried out by Brown and White, researchers of GE Company (USA) [2,3]. The 1<sup>st</sup> Infrared (IR) study on stereoregular PVC by S. Krimm was only one page, but its IR spectra were published in all the textbooks and professional ones in the World (Figure 1) [4,5]. In IR spectra, structural difference appeared in the 700-600 cm<sup>-1</sup> region. One can notice that two peaks are clearly observed in the urea canal PVC in contrast with three peaks in the free radical one. Lack of the left-hand peak (690 cm<sup>-1</sup>, assigned to be isotactic) strongly suggests that stereoregular PVC is highly syndiotactic.

The reason why we took up this polymer is that [1] the first synthetic



fiber was PVC, which was prepared in Germany (IG) in 1931 and called PeCe Fiber [6]. Later it was manufactured in France (Rhovyl) and also in Japan (Tebiron, *Teijin Co. Ltd.*). Of course, in industrial production, PVC was prepared by ordinary free radical method.

On the other hand, there are very few studies on the solid state synthesis of stereoregular PVC except a few cases [7,8]. In particular, this method has a wide range of fascinating topics relating to *inclusion phenomenon* in Physical Chemistry. We would like to introduce here to many Fiber scientists and Textile engineers in the World.

# **Theoretical Consideration**

Figure 2 shows the principle of urea clathrate polymerization [9]. When various organic monomers are mixed with fine urea at low temperatures (-78°C) and the mixture is kept at it, a canal complex is formed spontaneously. This is a typical *inclusion phenomenon*, and resulting canal complex is called *"inclusion complex*". It must be noted that inclusion complex is formed by the transformation of tetragonal lattice of urea toward other type of structure with the involvement of monomers in the central position. Such inclusion caused by *"phase transition"* invariably occurs, when urea was mixed with lower organic molecules and temperature was kept at such low temperatures.

The geometrical type and size of the complex is quite different according to the type of monomers [1,9]. An ideal complex is n-paraffin/ urea system (Figure 2). From ethylene/urea system, linear polyethylene (PE) with no branching is obtained. In the case of polar vinyl monomers, inclusion structure is quite different according to the type of monomers, e.g., monoclinic (VC/urea) and hexagonal (AN/urea)

\*Corresponding author: Minagawa M, NPO: Dream Create Laboratories, 992-1446 Naoe-Sekite 3800-1, Yonezawa, Yamagata, Japan, Tel: +81-(0)238-38-7360; Fax: +81-(0)238-38-7361; E-mail: gakusai-minagawa@memoad.jp

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Page 2 of 5



**Figure 2:** Schematic representation of urea clathrate polymerization [9]. (Left) Principle of  $\gamma$ -irradiation canal polymerization.Note that chain end radicals are *living*. (Right) Cross sectional view of an ideal canal complex of urea/n-paraffin.



(Figure 3). That is, slurry of initial mixture (Urea/liquid monomers) turned to be dry white flake-like substance eventually under such low temperatures [7,8]. The  $\gamma$ -irradiation toward the inclusion complex must be carried out under sufficiently cooled conditions (below -78°C), this is because if temperature is increased the canal complex is destroyed and un-reacted monomers are permitted to be free from the inclusion matrix. In spite of the fact that these monomers (VC/AN) are equally electronegative polar monomers, the reason why quite different micro-structures are produced ? has neither been clarified experimentally nor theoretically.

# Experimental

Various measurements were carried out by using instrumental analyses including solid state <sup>13</sup>C-NMR, FT-IR (KBr method), DSC, TG and Solid state ESR, etc. These measurements were carried out under carefully controlled experimental conditions. Details of the experiments are given in [8]. It is important to point out that Sample A means urea canal PVC prepared as described in the text here, while Sample B does free radical one (commercial PVC (JAPAN); Zeon 103, EP-8, straight type/ homo-polymer).

# Results and Discussion

Resulting stereoregular PVC was fine white powder. It was totally insoluble to organic polar solvents such as N,N-dimethylformamide (DMF), tetrahydrofuran (THF) and the like. Therefore, microtacticity could not be determined. In order to carry out the determination of microtacticity of a given polymer by high resolution NMR (<sup>1</sup>H), preparation of polymer solution is by all means necessary [10].

Figure 4 shows solid state <sup>13</sup>C NMR spectra. In the comparison with that of free radical PVC (Sample B), there was a distinct difference in the NMR spectra. PVC shows two <sup>13</sup>C peaks deriving from CH and CH<sub>2</sub> groups on a polymer backbone. Their relative height was almost equal in Sample B but it was quite different in Sample A. Peak area of CH and CH<sub>2</sub> signals in each sample was almost equal, however. From the broadness of NMR spectra, it is possible to consider that 3 peaks (mm, mr, rr) are separated to some extent widely and CH peak appeared as a whole envelope of these three peaks.

Figure 5 shows IR spectra of PVC. There was a distinct difference in the band below 700 cm<sup>-1</sup> region. Only two peaks were clearly observed in Sample A. Lack of the left-hand band (690 cm<sup>-1</sup>: assigned to be isotactic, in amorphous region) suggest that urea canal PVC has syndiotactic configuration. In fact, detailed IR study on various lower model compounds support this conclusion substantially [11,12]. It is apparent that Krimm's novel finding [5] was confirmed in this way.

Small difference was also observed at about 2900 cm<sup>-1</sup> region. A small band (at 2933 cm<sup>-1</sup>) appeared in the urea canal PVC (Figure 6). This band can be correlated with *Fermi-resonance*, which appears in symmetric molecules with very strong intermolecular interaction (*enhanced intermolecular hydrogen bonding*). The existence of the IR characteristic band (2933 cm<sup>-1</sup>) has also been predicted by a computer simulation [13].

From the WAXD pattern, the existence of many crystalline regions in the urea canal PVC is apparent, since Debye-Scherrer rings were observed and the 6<sup>th</sup> reflection rings were counted. The presence of sixth ring has already been confirmed for fractionated canal PVC specimen by Sakurada et al. [14].

Thermal properties were studied. Figures 7 and 8 showed DSC (Tg)



#### Page 3 of 5

Figure 5: Comparison of IR absorption spectra of 2 kinds of PVC below 1600

**Figure 5:** Comparison of IR absorption spectra of 2 kinds of PVC below 1600 cm<sup>-1</sup> region (KBr disk method). Note that 3 peaks were clearly seen in Sample B, while only 2 peaks appeared in Sample A in the 700-600 cm<sup>-1</sup> region.



and TG (Td) curves. In the former, it is very difficult to detect a glass transition temperature (Tg) under ordinary heating conditions. Under raid heating rates, however, detection became possible as shown in Figure 7 (cf. data A and B measured by 50°C/min). A small breaking point appeared. Despite the expectation of a higher Tg in the urea canal PVC (Sample A), its value was not so high as expected, the Tg value was almost equal in both samples (~90°C). Judging from the extent of the base line drift, the content of amorphous region in the urea canal PVC was estimated to be less than 1/10 of that of an ordinary free radical material (Sample B).

When sample was heated up to higher temperatures, rapid weight loss by an elimination reaction (HCl) was observed (Figure 8). If degradation temperature (Td) was defined as a cross-over point

between a base line and a tangential line, the value of sample A (288°C) was higher than that of sample B (280°C). This means that urea canal PVC is very unstable thermally (discoloration), but actual degradation is rather delayed or it occurs at higher temperatures. Further, from







Figure 8: Comparison of TG curves of two kinds of PVC.Solid line indicates weight loss curve, while dotted line does derivative one.From the latter, it is clearly seen that Sample B has only one sharp peak, while Sample A does two peaks, which are overlapped.These are connected with one step degradation and two step one, respectively.

Figures 9 shows photograph of heated PVC samples. Canal PVC turns in its color from white (RT) to pale purple (160°C), deep purple (200°C) and then black (~280°C). It is very easy in discoloration. In contrast, free radical one is very hard in its discoloration. One can understand this when compared with the color of two PVC specimens heated up to 200°C (indicated by an arrow). Canal PVC is very deep purple (left) whereas free radical one is only slightly pale orange (an arrow in the right hand side). Easy discoloration of sample A is probably inherent characteristics of urea clathrate polymer, *an absence of termination reaction*. Because of this characteristic, end radicals are living, which would act as a trigger of an elimination reaction (HCl), via a well known  $\beta$ -scission mechanism, when heated up to high temperatures.

Rather delay in substantial weight loss in Sample A is probably related to the stiffness of syndiotactic sequences of a polymer backbone. Due to low chain mobility of stereoregular sequences, an elimination reaction would proceed gradually. This is also estimated from the morphological change of PVC sample. In Sample A, powder morphology did not change inherently and only color changed from white to pale purple, deep one and then black. In contrast, in Sample B, it melted above 250°C and caused bubbling and became porous rigid material. Initial morphology was lost completely and was left hard porous black residue.

Figures 10 and 11 show solid state ESR results under the dynamic heating conditions. Pay attention to the central signal indicated by an asterisk (\*), which is derived from the original PVC powder. One can notice that signal intensity increased with the elevation of temperature. Summarized results are given in Figure 11. Signal intensification is started at about 160°C, which corresponds to the beginning of discoloration from white to pale purple toward deep one. Smooth increase of signal intensity means that elimination reaction proceeds Zipper-like (auto-catalytically), but its intensity stopped apparently in two regions (symbols 1 and 2). An ideal Zipper-like reaction started from chain ends in amorphous region was stopped due to *resonance stabilization*, and subsequent reaction may proceed in irregular form such as inter-chain elimination or at random elimination in unreacted rigid stereoregular sequence. At any rate, the presence of non-propagating stopping step is obvious. Although there may be some







Figure 10: Solid state ESR spectra of canal PVC (Sample A) under the dynamic heating conditions. Note that central peak indicated by an asterisk is a signal derived from the polymer, while other outer peaks are due to  $Mn^{2+}$  (MgO) inserted as an ESR marker.





kinds of fine structure and the like in both steps, but meaningful results could not be obtained.

## Conclusion

Highly stereoregular PVC was prepared by solid state polymerization. Its bulk characterization was carried out by using various instrumental analyses including solid state NMR and ESR, etc. In FT-IR, particularly, Krimm's novel findings were confirmed. In addition, quite specific band (at 2933 cm<sup>-1</sup>) was observed, which was connected with Fermi resonance, *enhanced intermolecular hydrogen bonding* in rigid syndiotactic sequences. Easy discoloration of urea canal PVC is probably due to the absence of termination reaction. In spite of this fact, actual weight loss rather delayed. Namely, an elimination reaction proceeded gradually in rigid syndiotactic sequences. Rigid syndiotactic sequence was estimated by WAXD, DSC (Tg), solubility into organic solvents (totally insoluble) and morphological change in heated PVC specimens. Thus, quite unique structure and properties of urea canal PVC were described. It is emphasized that canal complex is formed spontaneously by *Inclusion Phenomenon*, when liquid monomers are mixed with fine urea and temperature is lowered and kept at such low temperatures.

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Page 5 of 5