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Solubility, Discoloration, and Solid-State ^{13}C NMR Spectra of Stereoregular Poly(Vinyl Chloride) Prepared by Urea Clathrate Polymerization at Low Temperatures

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Abstract

Stereoregular poly(vinyl chloride) (PVC) was obtained by urea clathrate polymerization. The sample was a white crystalline powder. Its molecular structure was studied by appearance, FT-IR, WAXD, and NMR (solid) in comparison with those of ordinary free radical one. The sample was totally insoluble to polar solvent such as DMF in contrast with good solubility of free radical one. Prolonged heating at high temperatures ensured discoloration and elimination reaction permitted formation of trans-type double bond. This structural change was traced by FT-IR and solid-state NMR. Two non-compromise characteristics, stiff molecular chain and easy discoloration, in canal PVC are described.

Keywords: stereoregular PVC, analysis by WAXD/FT-IR/NMR/ESR, elimination reaction

1. Introduction

Solid-state polymerization is a unique polymer synthetic method in Polymer Science. The most famous example is probably a urea clathrate polymerization of vinyl chloride (VC) as described here. That is, VC monomers are packed regularly in one-dimensional narrow urea canal under low temperatures (canal complex or inclusion complex). When strong γ -irradiation or electron beam one will be made, polymerization takes place, and highly stereoregular poly(vinyl chloride) (PVC) is obtained.

The first research in this area was carried out by Brown and White, researchers of GE company (USA) [1, 2]. They showed that urea canal-polymerized polymers have a remarkable difference in its physical properties. Particularly, not only ordinary urea but also thiourea does the canal complex at low temperature, and their difference is an inner diameter of cavity (5Å or 6Å). The structures and properties

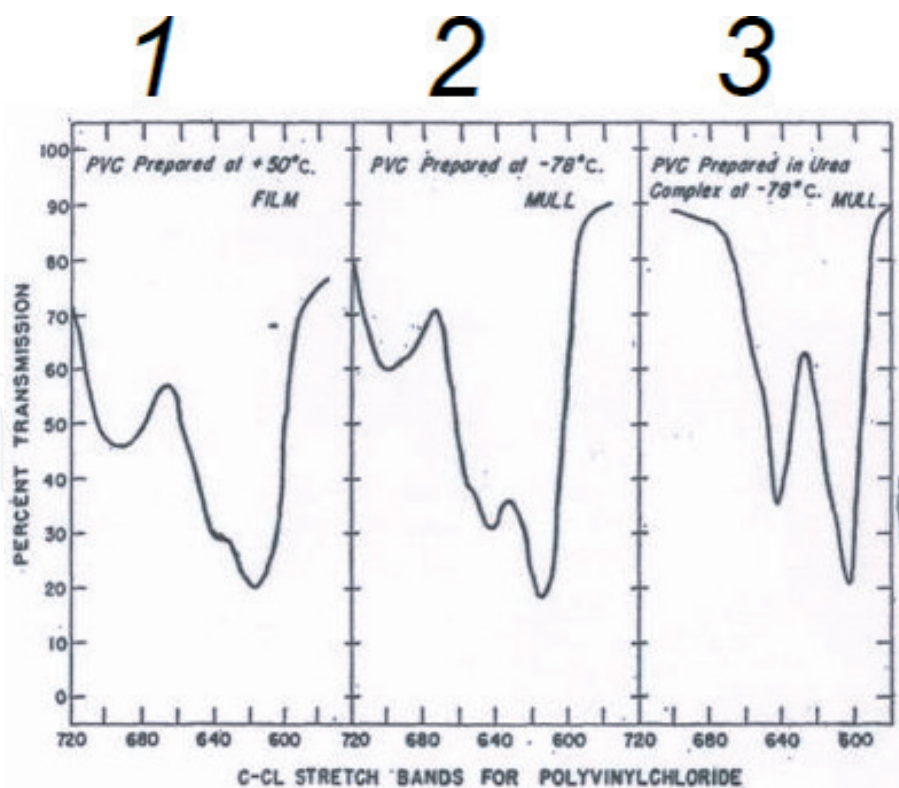


Figure 1.
Krimm's data [3, 4].

of the resulting polymers are well described by a limited number of instruments including solubility measurements, etc. Although the described time period is old, their valuable finding and observation have still a brilliant light in Polymer Science even at the present time.

Stereoregular PVC was investigated by Krimm et al. by using IR spectroscopy [3, 4]. Their first paper on stereoregular PVC was only one page, but its IR spectra were printed and published in all the textbooks and professional ones in the world (see **Figure 1**). In the IR spectra, structural difference appeared in the 700–600 cm^{-1} region. One can notice that only two peaks are clearly seen in the urea canal PVC in contrast with three peaks in free radical one. Lack of the left-hand side band (690 cm^{-1} , assigned to be isotactic) strongly suggests that stereoregular PVC is highly syndiotactic.

In Japan, a detailed IR study of PVC including stereoregular one was carried out by Shimanouchi and Tasumi in the University of Tokyo [5, 6]. Their standpoint of view was purely scientific, and direct application to industrial field appeared to be relatively small. However, their effort was greatly helpful for the improvement of commercial PVC products in Japan. They synthesized various model compounds and confirmed IR assignment of PVC, for example, the effects of C-Cl position on IR spectra and related problems are typical examples. Their collaborative work has been summarized and published in Ref. [7].

2. Theory: principle of urea clathrate polymerization

Figure 2 shows the principle of urea canal polymerization [8–10]. When organic monomers are mixed with fine urea and the mixture is kept at low temperatures (-78°C), a canal complex is formed spontaneously. This is a typical inclusion phenomenon, and the resulting canal complex is called *inclusion complex*. It must be noted that such an inclusion is caused by the *phase transition* of urea, when

urea is mixed with organic molecules and then temperature is kept at such lower temperatures.

The geometrical shape and size of the complex are quite different according to the type of monomers [9, 10]. An ideal complex is n-paraffin/urea system (Figure 2, right). A well-known fact is that started from ethylene/urea system, linear polyethylene 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) (Figure 3). That is, slurry of initial mixture (urea/liquid monomers) turned to be dry flake-like white substance eventually under such low temperatures. The γ -irradiation toward the canal complex must be carried out carefully under

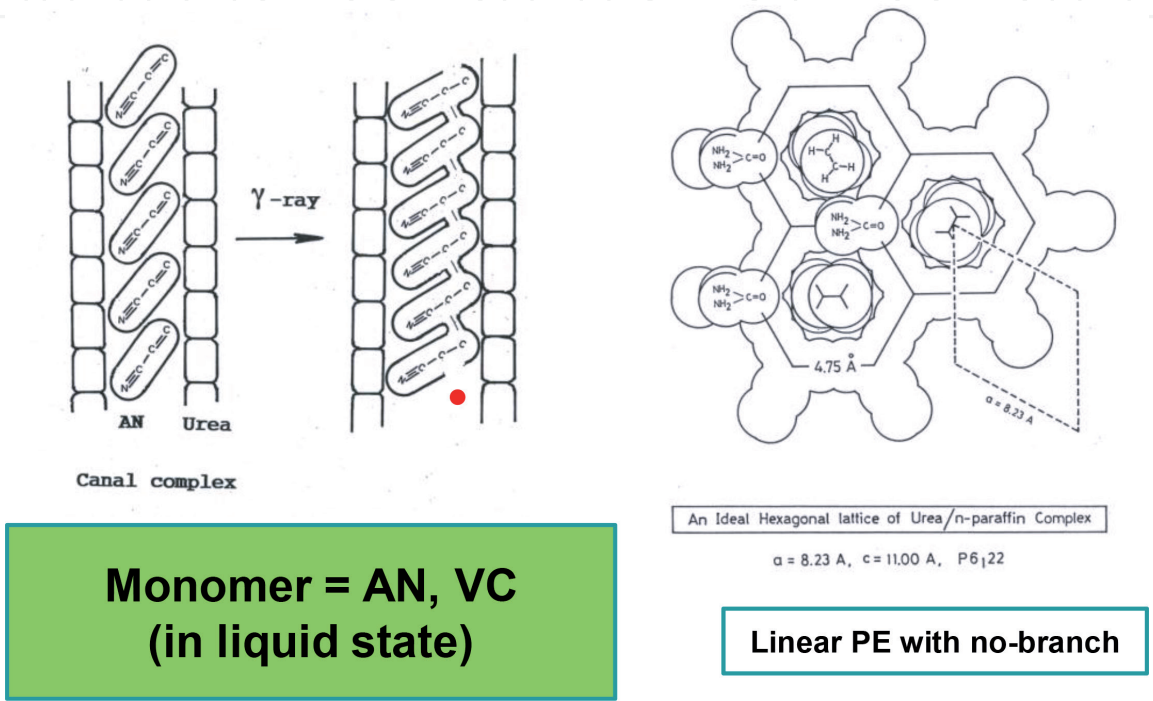


Figure 2.
Principle of urea canal polymerization.

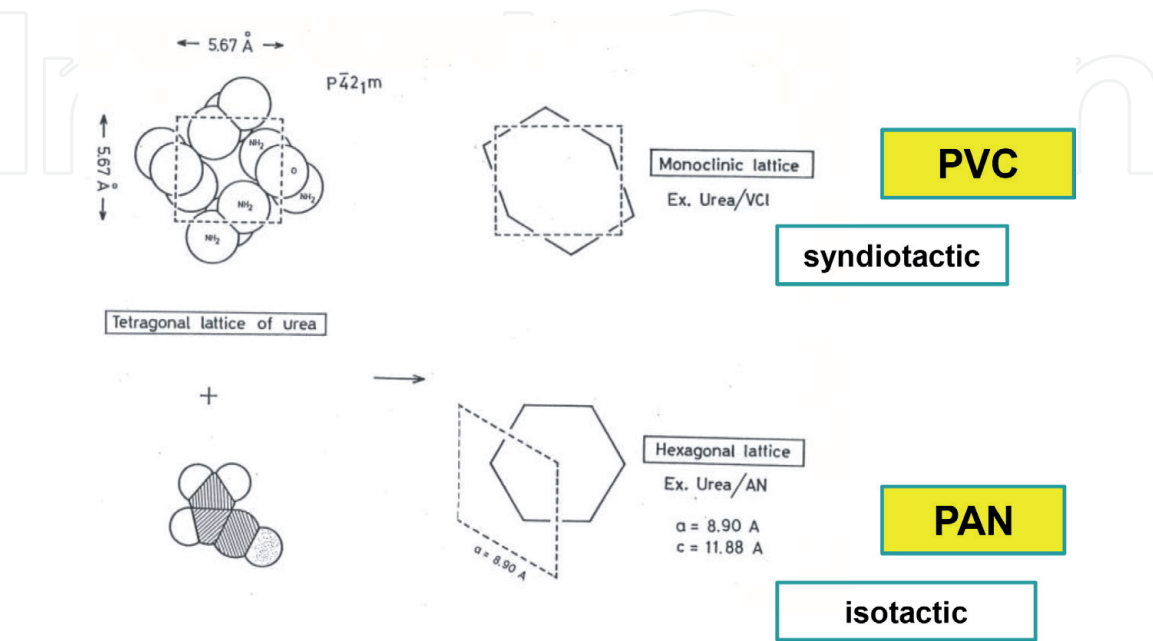


Figure 3.
The shape and size of canal complex.

sufficiently cooled conditions (below -78°C). This is because if temperature is increased, the canal complex is destroyed, then unreacted monomers will be liberated from the inclusion matrix. The liberated free monomers can be detected by broad line NMR through free rotation of liberated monomers [11, 12]. In spite of the fact that these monomers (VC/AN) are typical electronegative polar monomers equally, quite different configuration is attained (*syndiotactic*/VC and *isotactic*/AN, respectively). The reason why such different microtacticity is attained has neither been clarified experimentally nor theoretically.

3. Experimental

Canal PVC was a white powder and was totally insoluble to organic solvent such as N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). *Characterization* is given in **Table 1**. It is important to notice that *sample A* means urea canal PVC prepared as described here while *sample B* does free radical one (commercial PVC: Zeon 103, EP-8, straight type/homopolymer). *Sample C* was a standard polymer taken from 100 kinds of standard polymers (Scientific Polymer Products, Inc., USA).

Type	Symbol	Code	Form	Color	Solubility ⁴
Canal ¹	A	γ -Ray	Powder	White	×
Radical ²	B	Zeon 103	Particle	White	○
Radical ³	C	#038	Powder	White	○

¹Prepared in JAERI, Takasaki by urea canal polymerization as described in the text.
²Supplied from production company, Japan Zeon Co. Ltd. This polymer was a homopolymer.
³Supplied from the Scientific Polymer Products (USA). This was a high molecular weight homopolymer.
⁴Solubility into DMF at room temperature. (○), soluble, (×) insoluble.

Table 1.
Characterization of PVC samples.

Various measurements were carried out by using instrumental analyses such as solid-state NMR, FT-IR (KBr method), WAXD, TG, solid-state ESR, etc. under carefully controlled conditions. For example, typical NMR conditions in **Figure 7** were as follows: spectrometer, JEOL JNM GX-270; nucleus, ^{13}C ; PW2 contact time, 8 ms; PW1 pulse width (90° pulse), 4.5 μs ; PD repetition time, 5000 s; number of scans, 150,000; probe, Doty's ceramic probe (7 mm ϕ); and external reference, secondary peak of adamantane.

4. Results and discussion

4.1 Characterization of PVC powder

Figure 4 shows IR spectra [12]. There was a distinct difference in the band below 700 cm^{-1} region. Only two peaks are clearly observed in sample A. Lack of the left-hand side band (690 cm^{-1} : assigned to be isotactic in amorphous region) suggests that the urea canal PVC has syndiotactic configuration. It is apparent that Krimm's novel finding was confirmed in this way.

A small difference was also observed in 2900 cm^{-1} region. A new band (2933 cm^{-1}) appeared especially in the urea canal PVC (**Figure 5**). This band may

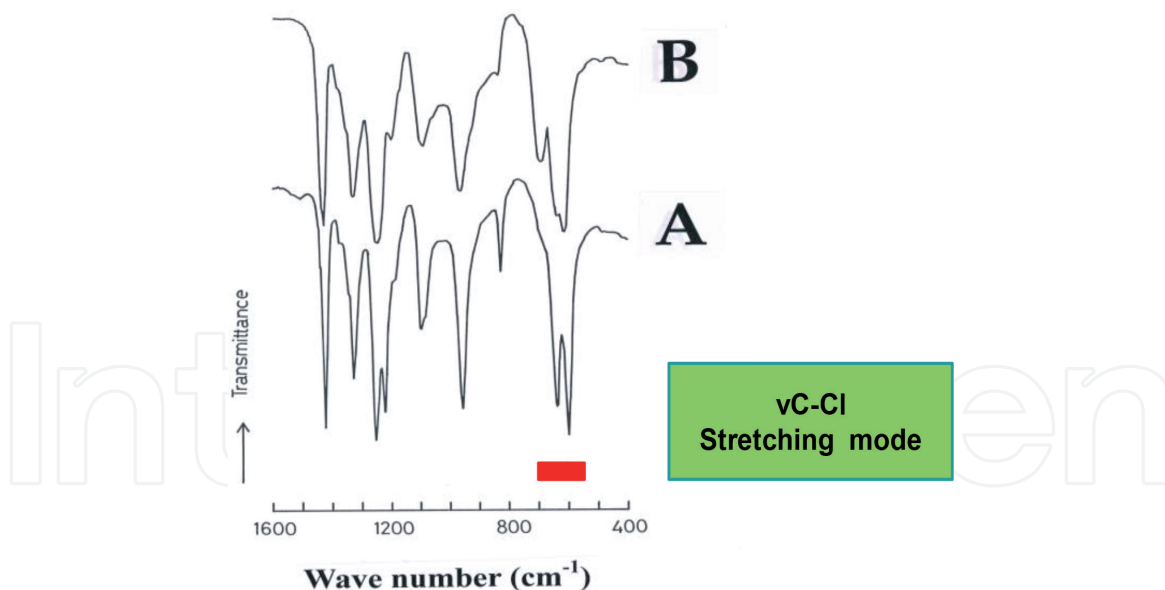


Figure 4.
 Comparison of IR spectra of two kinds of PVC.

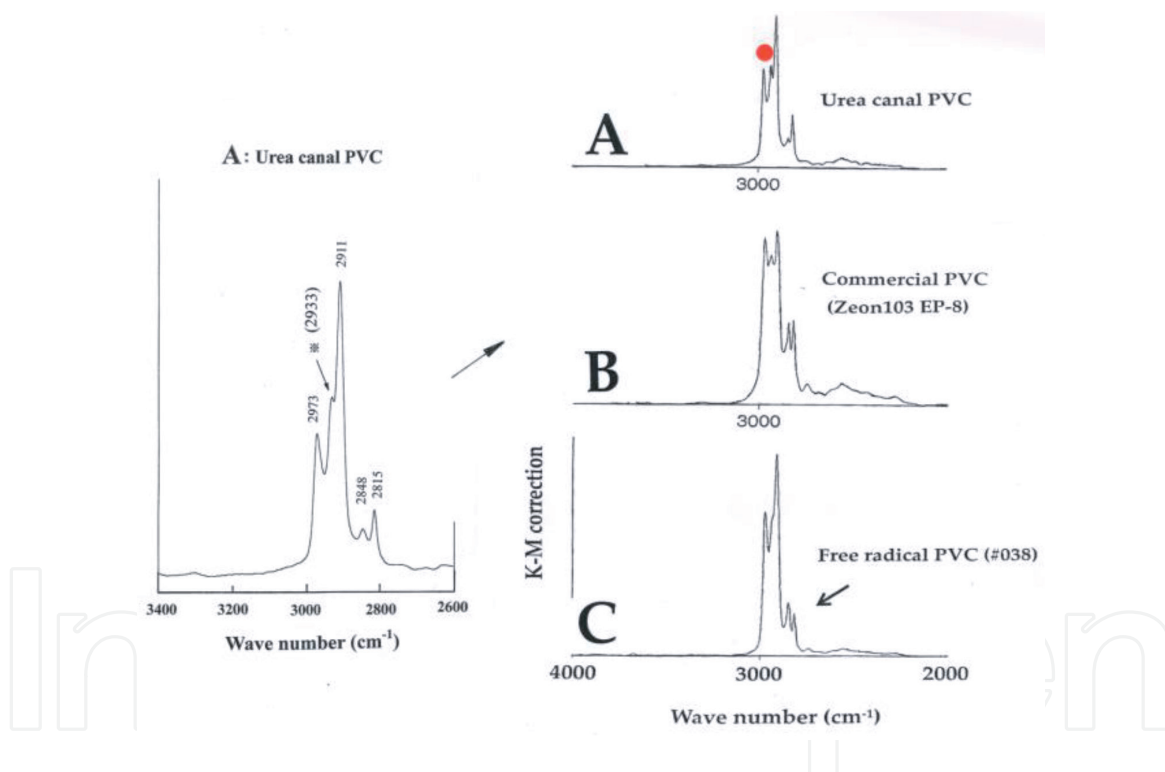


Figure 5.
 FT-IR spectra of νCH_2 region (diffuse reflection, KBr).

be correlated with some stereochemical structural factors including *Fermi resonance* and the like, which appears in highly symmetric molecules with very strong intermolecular interaction (enhanced intermolecular hydrogen bonding). The existence of such IR characteristic band has already been pointed out by Tasumi [13]. In fact, this band is directly related to the structurally well-ordered region in PVC sample, since in WAXD results, many Debye-Scherrer rings are clearly observed (see next section).

Figure 6 shows the WAXD results. The existence of many coaxial Debye-Scherrer rings in the sample A is apparent. Careful observation revealed sixth diffraction rings can be counted. With regard to WAXD measurements,

Sakurada et al. already observed sixth diffraction rings in γ -ray PVC (consists of three components indicating partial dissolution into DMF solvent) [14], but they didn't show a WAXD photograph. Even in our experiments, it was very difficult to show rings by ordinary WAXD photograph technically; therefore, we preferred to the direct observation of negative film. By this method, the number of higher order of reflected rings can be counted. Further, very thin but distinct coaxial rings in sample B (commercial one) are obvious.

Figure 7 shows the solid-state NMR spectra. (Since this polymer didn't dissolve in any organic solvent, high-resolution NMR spectra couldn't be obtained.) In comparison with that of free radical PVC (sample B), there was a distinct difference in the NMR spectra. PVC shows two ^{13}C NMR peaks deriving from CH and CH_2 groups on a polymer backbone. Their relative height was almost equal in *sample B*, but it was quite different in *sample A*. The peak area of CH and CH_2 signals in each sample was almost equal, however. From the broadness of NMR spectra, it is possible to consider that three peaks (mm, mr, rr) are separated to some extent toward

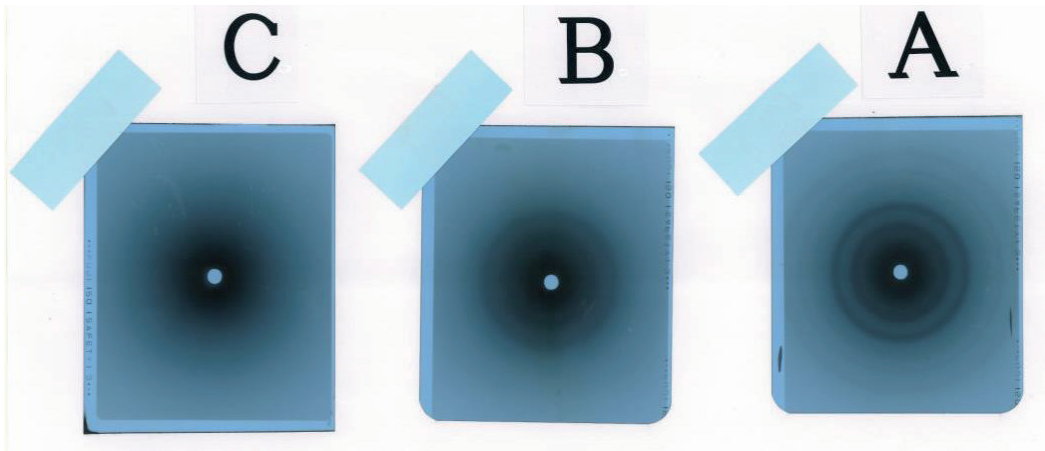


Figure 6.
Comparison of WAXD of three kinds of PVC (negative film).

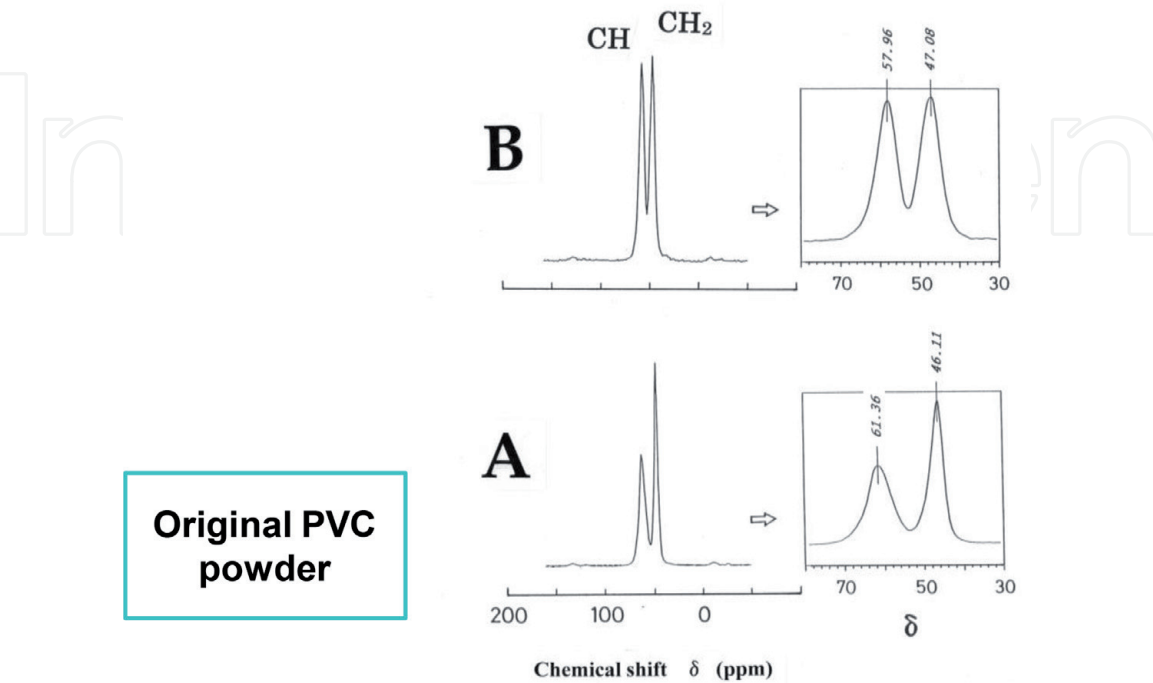


Figure 7.
Comparison of solid-state ^{13}C NMR spectra of two kinds of PVC.

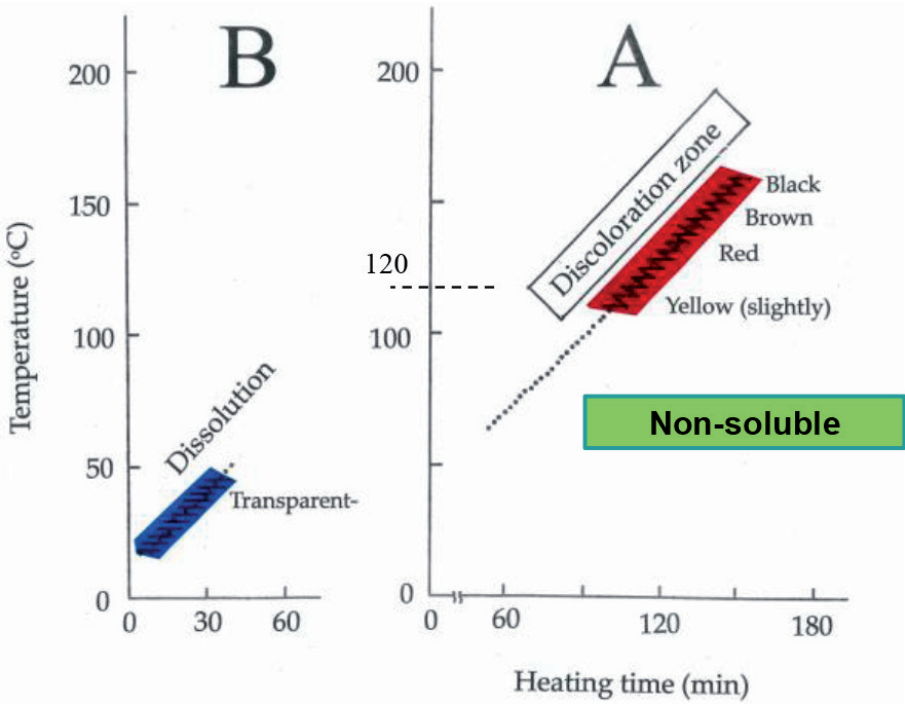


Figure 8.
Solubility of PVC in DMF solvent.

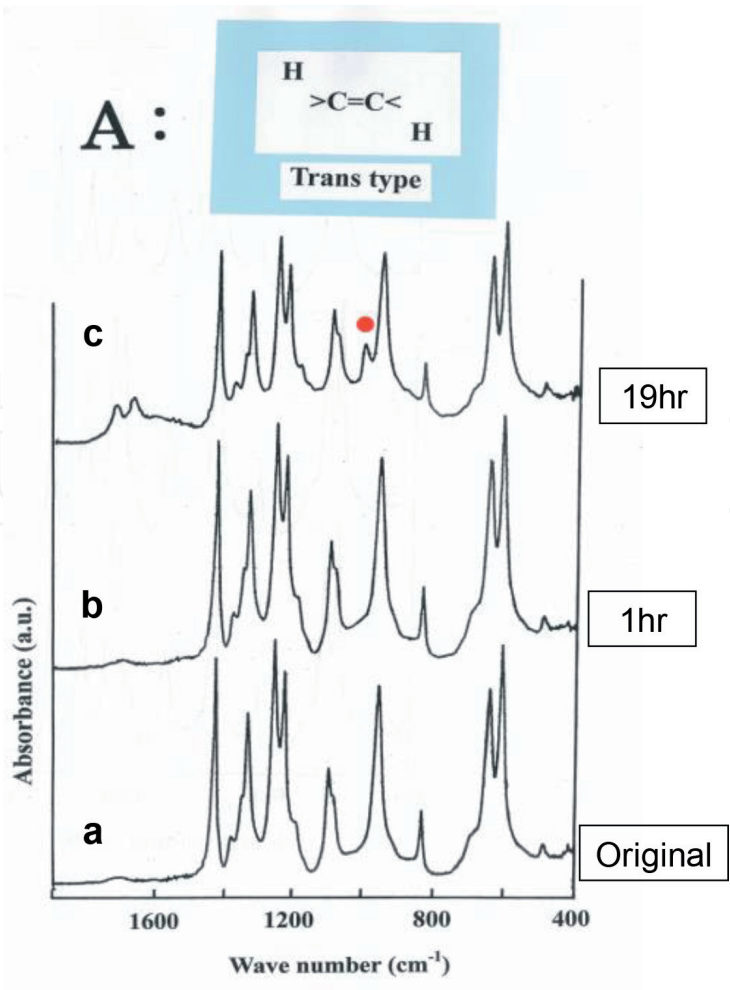


Figure 9.
FT-IR of PVC suspension heated in DMF 1080 cm^{-1} at 120 °C: a: original, b: 1 h, and c: 19 h.

the outer direction and CH peak appeared as a broad single peak with the whole envelope of these peaks [15].

Microtacticity of γ -ray PVC couldn't be determined by solid-state NMR in this way, although quite different NMR peak shape was obtained.

4.2 Solubility in DMF solvent

Figure 8 shows the solubility results of PVC. Free radical PVC (*sample B*) dissolved in DMF completely at room temperature and provided apparently transparent solution. Urea canal PVC (*sample A*), however, didn't. It did a suspension; PVC powder was dispersed in the solvent. Continuous heating up to a high temperature caused a slightly discoloration from white to pale yellow, red, brown, and black. The heated samples were recovered and FT-IR spectra were taken.

Results are given in **Figures 9** and **10**. In *sample A*, change in IR spectra is very little. Polymer backbone is retained even after heating of 19 hours. This is related to the fact that the sample is insoluble and is heated in a suspension state.

A small band appeared at 1080 cm^{-1} , which can be assigned to be trans-type of double bond [16]. In *sample B*, spectral change was large. New band appeared at 1080 cm^{-1} and became progressively large. The decrease of C-Cl band ($700\text{--}600\text{ cm}^{-1}$) is obvious. It is known that elimination reaction (HCl) accompanies the formation of trans-type of double bond. This mechanism was common in both samples. Results are summarized in **Figure 11**.

Figure 12 shows the solid-state NMR spectra [17]. In *sample A*, spectral change was small. In contrast, in *sample B*, it was large. The appearance of broad peak at about $125\text{--}130\text{ ppm}$ is probably due to the formation of double bond, $-(\text{CH}=\text{CH})_n^-$. In fact, various rubberlike materials having double bond in its molecular structure

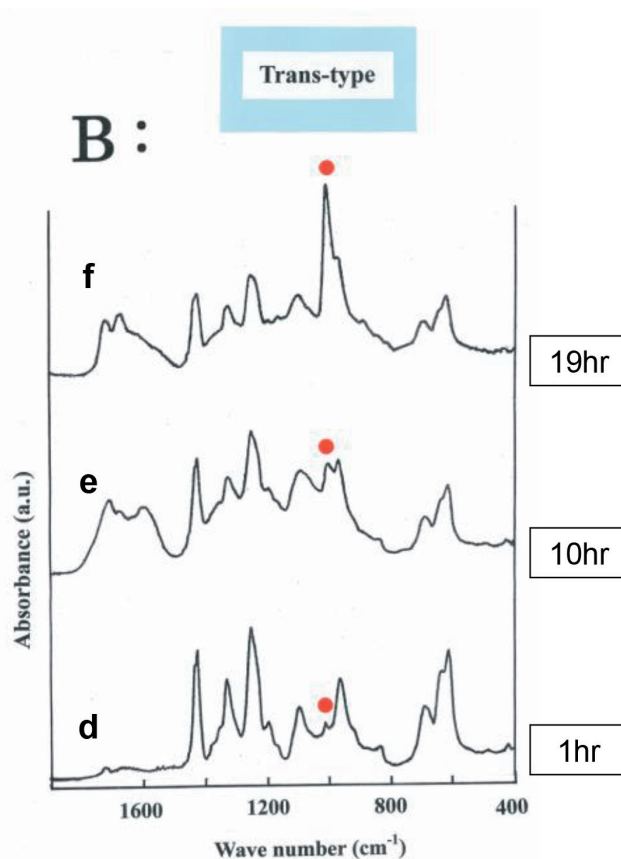


Figure 10.

FT-IR of PVC solution heated in DMF 1080 cm^{-1} at 120°C : d, 1 hour; e, 10 hours; and f, 19 hours.

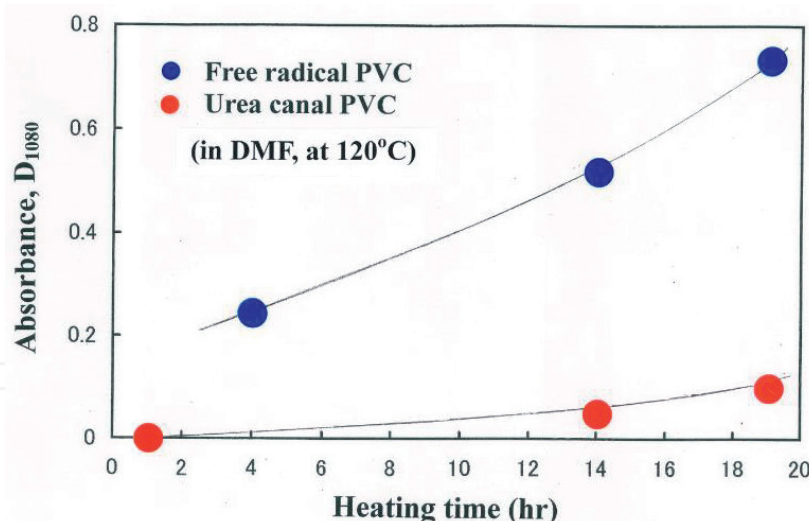


Figure 11.
 Variation of IR intensity of *trans*-type double bond.

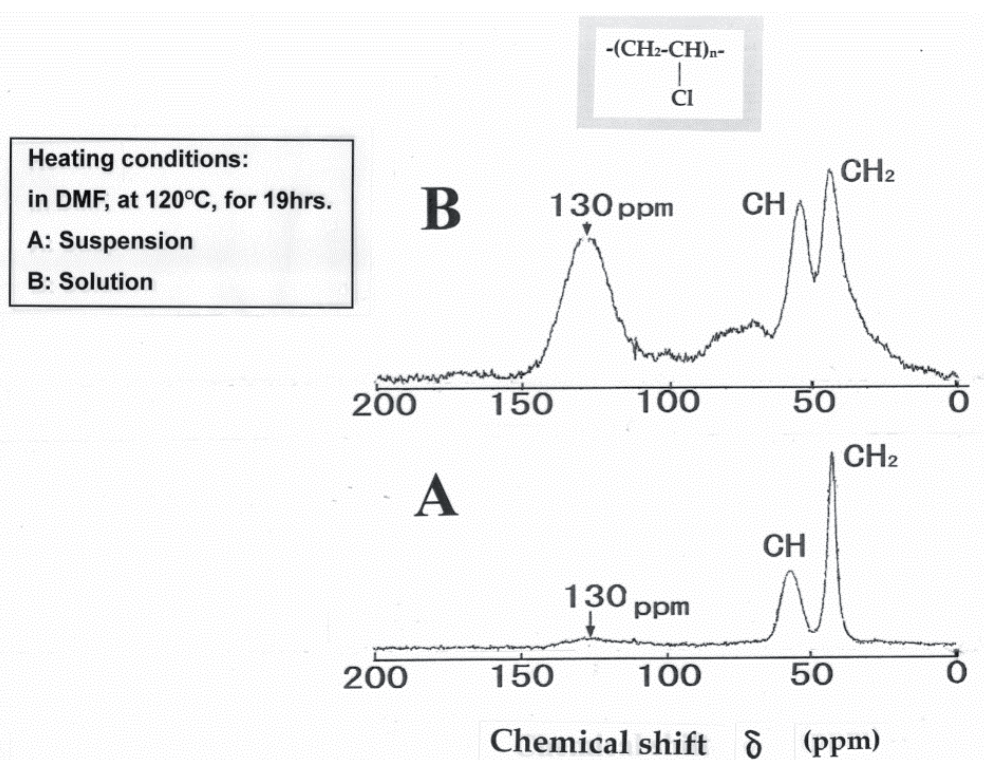


Figure 12.
 Comparison of solid-state ^{13}C NMR spectra of heated PVC.

have strong peak in this region [18]. NMR results were as a whole in good agreement with those of FT-IR (Figures 9 and 10).

4.3 Discoloration by heat treatment

Figure 13 shows a photograph of heated PVC samples [12]. 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 (right side). Easy discoloration of sample A is probably inherent characteristics of urea canal

polymer due to the absence of termination reaction. Because of these characteristics, end radicals are generally living, which would act as a trigger of an elimination reaction (HCl) via a well-known β -elimination mechanism at higher temperatures.

Figure 14 shows solid-state ESR results for sample A under the dynamic heating conditions. Pay attention to the central signal indicated by an asterisk (*), which is derived from the PVC power. Outer several peaks are due to the one from MnO^{+2} inserted as an ESR marker. One can notice that peak intensity increased with the elevation of temperature.

As summarized in **Figure 15**, signal intensification is started at about 160°C , which corresponds to the onset of color changing from white to pale purple (see a

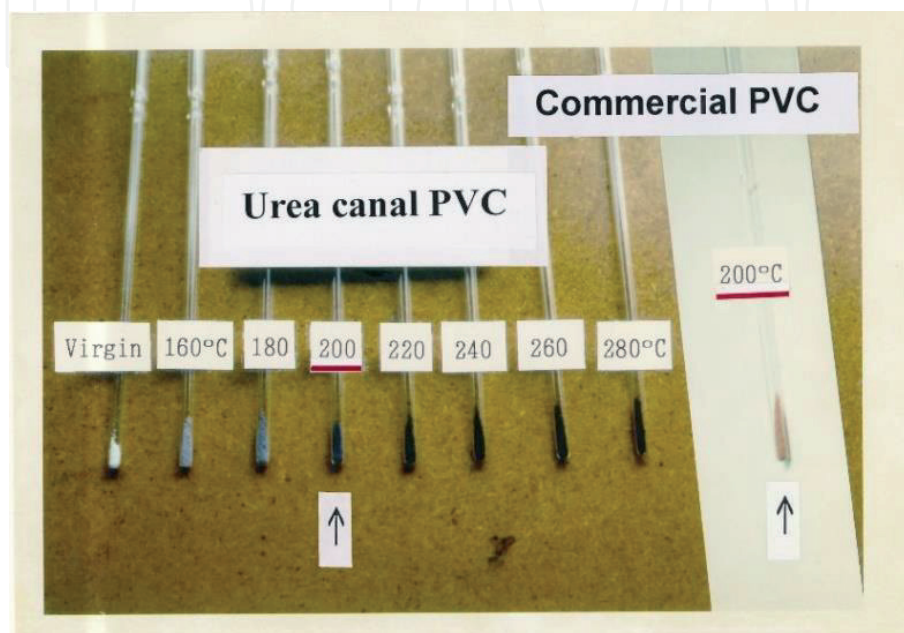


Figure 13.
Comparison of a photograph of heated PVC.

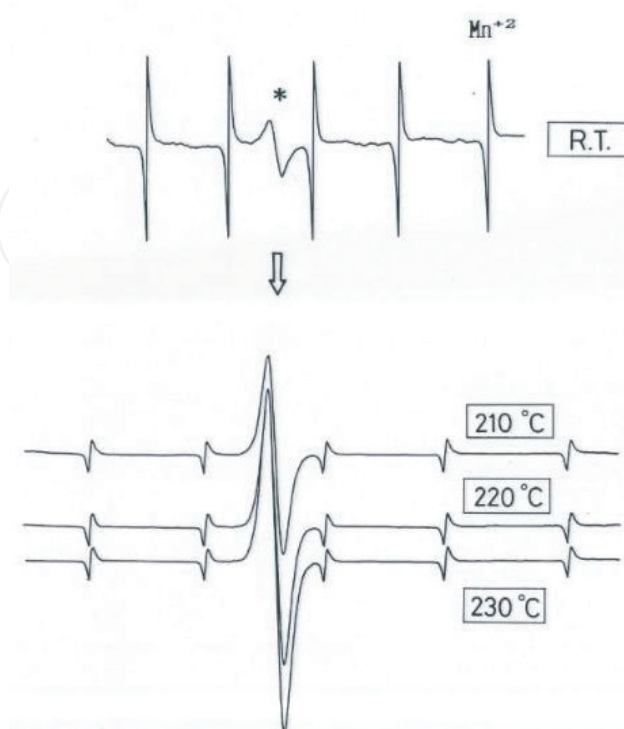


Figure 14.
Solid-state ESR spectra under dynamic heating conditions.

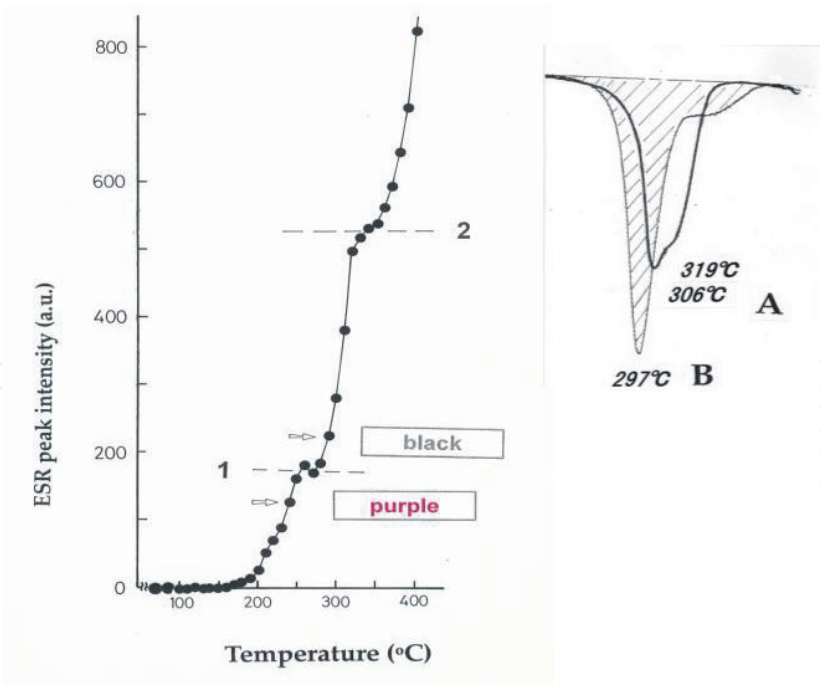


Figure 15.
ESR intensity and TG derivative curve.

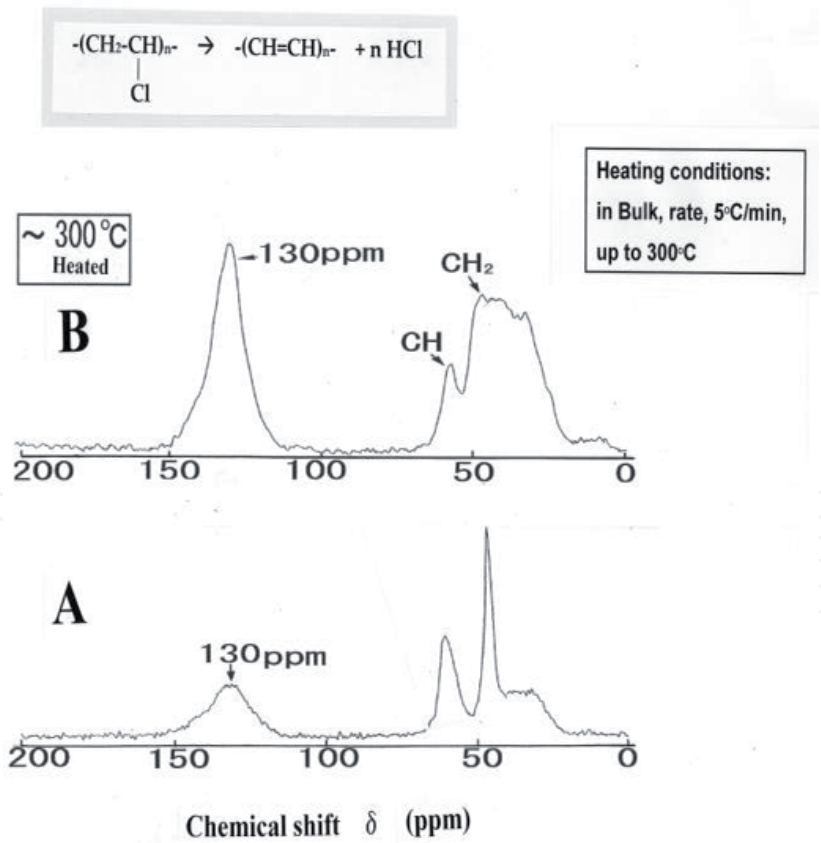


Figure 16.
Comparison of solid-state ^{13}C NMR spectra.

photograph in **Figure 13**). Smooth increase of signal intensity means that elimination reaction proceeds zipper-like (autocatalytically), 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 the like, and subsequent reaction may proceed in an irregular form such as interchain elimination or at random fashion type of elimination in unreacted rigid stereoregular sequence.

It is worth while noting that *step 2* in ESR signal agrees with the higher temperature peak of the double peak (306°C–319°C) in TG derivative curve, which were measured in other independent experiments. At any rate, the presence of non-propagating stopping mechanism is obvious. There may be some fine structure and the like in both steps, but these features could not be detected experimentally.

Figure 16 shows solid-state NMR spectra. The original structure has retained considerably in sample A, since CH₂ and CH peaks are clearly present. In contrast, in sample B, the original structural peaks have lost and new broad peak appeared at 130 ppm region. This spectral change in NMR is basically very close to those of FT-IR spectra in **Figures 9** and **10** (heat treatment in the solution or suspension state). In NMR measurements, it should be noted that the peak area is directly proportional to the concentration of functional groups in question; therefore, from both the position (chemical shift) and the peak shape (area), one can understand the mechanism wholly or intuitively.

5. Conclusion

1. The principle of urea clathrate polymerization at low temperatures was described from a purely experimental point of view. The basis lies on the canal complex formation of urea at low temperatures. Geometrical shape and size of the canal complex were described.
2. Characterization of bulk PVC sample was carried out by using FT-IR, WAXD, and solid-state NMR spectra. Lack of isotactic sequence was confirmed by IR spectra of 700–600 cm⁻¹ region. Presence of well-ordered region was suggested by FT-IR characteristic band (2933 cm⁻¹), WAXD rings, and solid-state NMR.
3. Solubility into DMF was studied. Free radical sample showed perfect solubility in DMF, while canal sample didn't. Suspension was obtained. Heat treatment caused an elimination reaction followed by formation of trans-type of double bond. The reaction rate of sample A was small.
4. Discoloration by heat treatment was described. Canal PVC showed easy discoloration but rather delay in the TG degradation. The lack of termination reaction is related to the easy discoloration (β -elimination). Slow degradation will be attributed to the stiffness of molecular chain.
5. Solid-state ESR measurements were made. Signal intensity increased exponentially with temperature, but two abrupt stopping regions appeared. The existence of some modification of the mechanism (zipper-like autocatalytic elimination) under uniform heating conditions became apparent.
6. Solid-state NMR was used in various steps such as the characterization of original PVC and thermally degraded samples. Structural change can be visually understood by the appearance of a new peak. Since the peak area is directly proportional to the amount of functional group, a whole understanding of the extent of the progress of degradation is greatly of help.

Acknowledgements

We wish to express our hearty thanks to Mr. H. Sugisawa (JEOL), Prof. Y. Nozawa (Tohoku University), and Mr. T. Katoh (Yamagata University) for NMR measurements. Thanks are also expressed to Prof. M. Matsuda, Prof. T. Miyashita, and Dr. F. Bae (Tohoku University) for many conveniences in solid-state ESR measurements. The valuable discussion on IR spectroscopic data with Prof. M. Tasumi (University of Tokyo) is also greatly acknowledged.

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