

Solid-State Characterization and the Thermal Properties of Stereoregular Poly(Vinyl Chloride) Prepared by Urea Clathrate Polymerization

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ABSTRACT: The solid-state characterization of highly stereoregular poly(vinyl chloride) (PVC) prepared by urea clathrate polymerization was carried out by using various instrumental analyses. The structural differences of PVC appeared most remarkably in solubility to organic solvents, IR, WAXD, and solid-state ¹³C-NMR spectra. The value of the glass transition temperature (T_g) was about 90°C, not as high as expected, although its detection was quite difficult. The thermal stability was poor, as evidenced by the easy discoloration of this polymer by heat treatment, which was related to the absence of a termination reaction. Dynamic ESR spectra in the solid state clearly indicate that the radical formation occurs at such a low temperature as 160°C in the initial degradation stage. The degradation characteristics of urea clathrate PVC were critically discussed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2820–2825, 1999

Key words: solid-state polymerization; stereoregular poly(vinyl chloride); thermal properties; characterization

INTRODUCTION

Stereoregular poly(vinyl chloride) (PVC) can be prepared by urea clathrate polymerization in the solid state at low temperatures.¹ The stereochemical structure of PVC prepared by such a method has been assigned to be syndiotactic in its configuration based on infrared (IR) spectroscopic measurements.^{2–8} Although there have already been many IR studies on urea clathrate PVC,^{2–6} little quantitative information on the structure and properties of this polymer has been presented. For example, Sakurada et al.⁴ reported that urea clathrate PVC is partially soluble in organic sol-

vents such as tetrahydrofuran and the like, and three components (A, B, and C) can be obtained. However, our sample was totally insoluble to these solvents.

In this article, the solid-state characterization of urea clathrate PVC is described in comparison with those of a free radically prepared sample. Emphasis is laid on the evaluation of the stereoregularity and its close relation to the thermal properties of this polymer.

EXPERIMENTAL

Sample

The stereoregular PVC was synthesized as described in ref. 9. The sample was recovered as a white powder. The particle size was controlled at

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Journal of Applied Polymer Science, Vol. 74, 2820–2825 (1999)

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CCC 0021-8995/99/122820-06

less than 20 mesh by grinding in an agate mortar and passing through a sieve. Free radical PVC was a commercial product (Geon 103, EP-8).

Solid-State ^{13}C -NMR Measurements

The JEOL NMR spectrometer, JNM GX-270, was used under the following conditions: nucleus, ^{13}C ; PW_2 contact time, 8 ms; PW_1 pulse width (90° pulse), 4.5 μs ; PD repetition time, 5000 s; number of scans, 150,000; probe, Doty's ceramic probe (7-mm diameter); external reference, secondary peak of adamantane.

IR Measurements

A Perkin-Elmer FTIR spectrometer, Paragon 1000, was used in addition to ordinary double-beam grating type of IR spectrometer, Hitachi A-285.¹⁰ Besides the KBr disk method, the diffuse reflectance (DR) method was used. Typical conditions were as follows: resolution, 4 cm^{-1} ; scanning, 32 counts; and purging gas, N_2 (flow rate, 10 L/min).

Thermo-Analytical Measurements

(A) DSC: a Perkin-Elmer DSC 7 was used under the following conditions: sample weight, 10 mg; heating rate, 10–50°C/min; atmosphere, in N_2 gas (20 mL/min). (B) TG-DTG: a Shimadzu TG instrument equipped with a derivative accessory was used under similar conditions.

Solid-State ESR Measurements

The JEOL, JES-FE3XG ERS spectrometer equipped with a high-temperature cavity (ES HTXA, No. 1-P080). This instrument enables one to directly monitor the radical formation process in the bulk sample under programmed heating conditions. The conditions were as follows: sample weight, 10 mg; heating rate, 10°C/min; atmosphere, under vacuum (10^{-2} mmHg).

RESULTS AND DISCUSSION

Solid-State Characterization by ^{13}C -NMR, IR Spectra, and Solubility

Figure 1 shows the solid-state ^{13}C -NMR spectra. In the comparison of the NMR spectra, there was a distinct difference in the peak shape and peak position, especially in the methine carbon (CH) region. In urea clathrate PVC, the peak of the CH

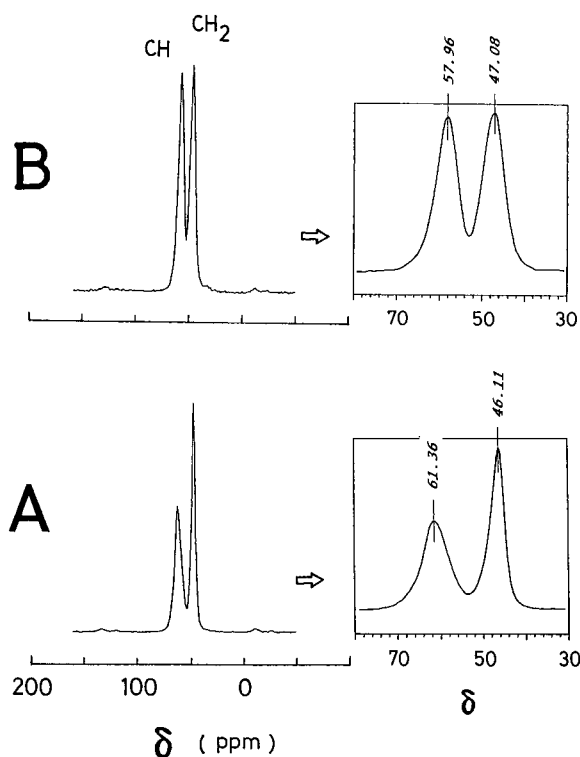


Figure 1 ^{13}C solid state NMR spectra of two kinds of PVC sample: (A) urea clathrate PVC; (B) free radical PVC.

was very broad and the value of the chemical shift (61.36) was quite different from that (57.96) of the free radical sample. Discrimination of each peak, (mm), (mr), and (rr) units, due to the difference in stereochemical configuration, was impossible in this case. Even when the measurements were carried out by use of a 400-MHz NMR spectrometer, peak separation due to the higher resolution was not attained.

Figure 2 shows the IR spectra of PVC. A structural difference appeared in the IR bands in the 1300–1200, 850, and 700–500 cm^{-1} regions.^{2–8} In particular, from the detailed analysis of IR bands appearing in the third region (700–500 cm^{-1}) comparing with those of lower model compounds,^{7,8} urea clathrate PVC has been assigned to be syndiotactic configuration. Lack of the 690 cm^{-1} band (isotactic, amorphous region) directly supports this assignment, which has been widely accepted.

Figure 3 shows FTIR spectra in the 2900 cm^{-1} region. In the comparison of both spectra, a new band appeared at 2930 cm^{-1} , and the 2816 cm^{-1} band was enhanced with the decrease of the intensity of the 2850 cm^{-1} band in urea clathrate

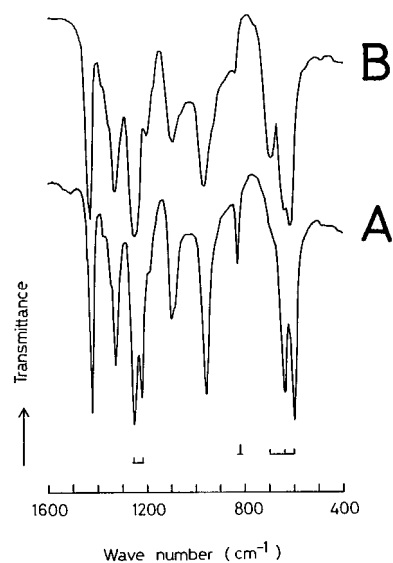


Figure 2 Comparison of IR absorption spectra of two kinds of PVC (below the 1400 cm^{-1} region). Meaning of symbols (A,B) is the same to those of Figure 1. KBr disk method.

PVC. Although detailed discussion is not made here, these results may be related to the Fermi resonance of symmetric molecules.¹¹ It is interesting to note that the difference in the stereochemical structure of PVC appeared in the IR stretching vibrational mode of the CH_2 and CH groups.

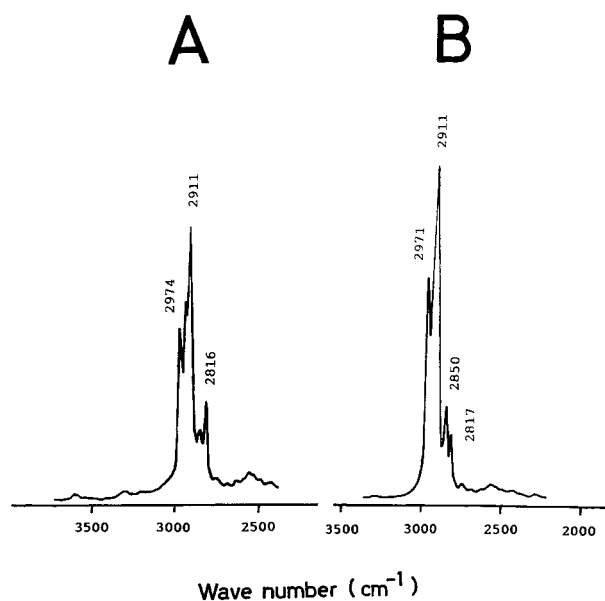


Figure 3 Comparison of FTIR spectra of the 2900 cm^{-1} region. DR method.

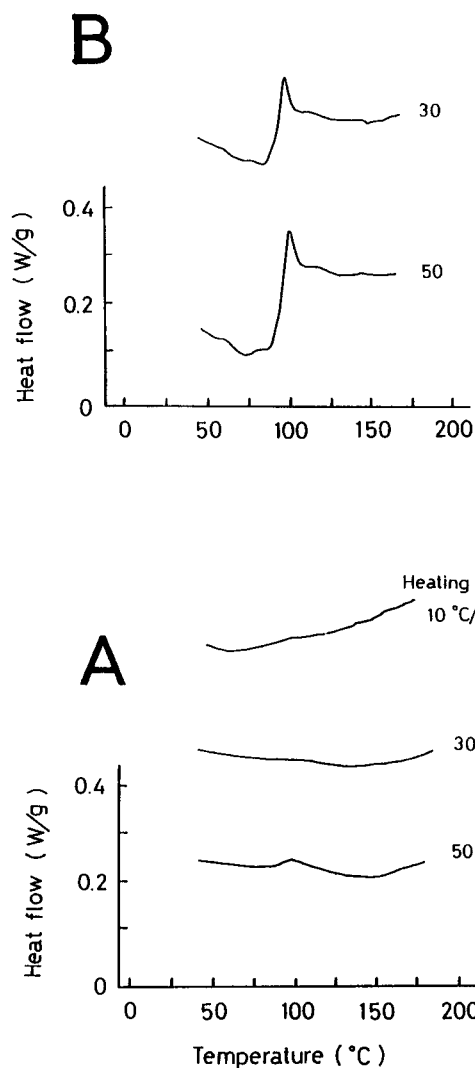


Figure 4 Comparison of DSC curves of two kinds of PVC. The meaning of symbols is the same as those of Figure 1.

The urea clathrate PVC here was totally insoluble to ordinary dipolar aprotic solvents but giving a suspension. In dimethyl sulfoxide, for example, when temperature was increased, dehydrochlorination reaction (HCl) occurred at about $130\text{--}140^\circ\text{C}$. Color changed from white to dark purple with maintaining its original powder form in a suspension state. Evolved HCl was confirmed by its characteristic odor.

Comparison of the Thermal Properties (T_g and T_d) of Two Kinds of PVC

Figure 4 shows the DSC curves. It is difficult to detect T_g by DSC under ordinary heating condi-

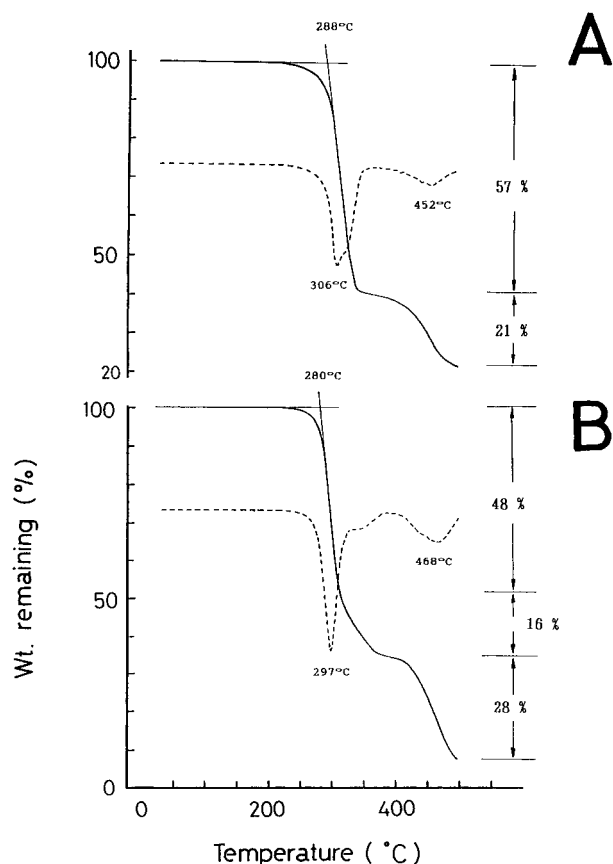


Figure 5 Comparison of TG-DTA curve of two kinds of PVC. The meaning of symbols is the same as those of Figure 1. Broken line is a TG derivative curve.

tions, even though a high-performance type of instrument is used. Under rapid heating rates, however, detection became possible as shown by Figure 4 (cf. data A and B measured by 50°C/min). Despite the expectation of a higher glass transition temperature (T_g) for urea clathrate PVC, the value of the T_g was not as high as expected; the T_g value was almost equal in both samples ($\sim 90^\circ\text{C}$). Judging from the extent of the baseline drift, the content of the amorphous region in urea clathrate PVC was estimated to be less than $\frac{1}{10}$ of that of an ordinary free radical material.

Figure 5 shows a TG curve. When the temperature was increased, a large weight loss occurred at about 280°C, and additional weight loss continued above 380°C. The TG-derivative curve clearly indicates a small difference of decomposition behavior: in the urea clathrate sample the main degradation peak is overlapped with a small minor peak, whereas in the free radical sample only one peak is observed, followed by a separated minor peak. Al-

though it is interesting to interpret the above results with sequential structure (i.e., the extent of syndiotacticity), this problem cannot be discussed here due to the difficulty in the peak separation of the NMR spectra, as shown in Figure 1.

Instability and Discoloration of Urea Clathrate PVC

Figure 6 shows the color change of the heat-treated samples. The urea clathrate PVC turned purple at 160°C, and the extent of this discoloration increased when the temperature was increased. In contrast, free radical PVC became merely orange at 200°C under the same conditions. The low instability of the former can be attributed to the presence of some kinds of labile structure, a double bond at chain ends, due to the absence of termination step in the urea clathrate polymerization.

It is important to note that a deep discoloration occurs in the temperature region, where little substantial weight loss is observed. We consider that (1) partial dehydrochlorination occurs only at chain ends, and (2) even though its concentration is small, it is sufficient to cause discoloration. From the extent of the discoloration, the sequence length of conjugated polyene, $-(\text{CH}=\text{CH})_n-$, is estimated to be relatively long. The number of sequence length (n) is presumably about 15–19 numbers based on the UV spectroscopic considerations.¹³

Figure 7 shows ESR spectra of PVC in the solid state. A trace amount of signals were observed in

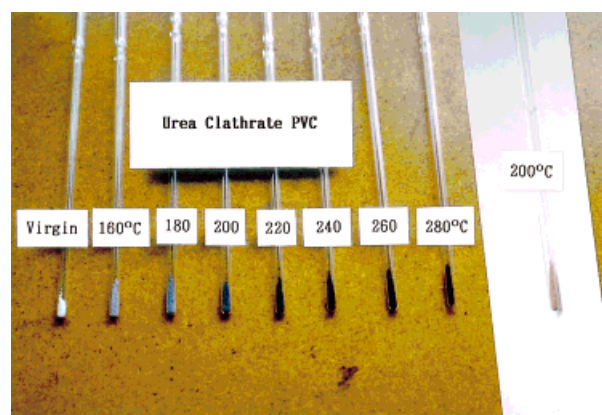


Figure 6 A photograph of heated PVC samples under linear heating conditions. The sample at the end of right-hand side is a free radical PVC heated up to 200°C. Also, it is worthwhile noting that this degradation was accompanied by little morphological change.¹² Heating conditions: sample weight, 10 mg; heating rate, 10°C/min; atmosphere, under vacuum (10^{-2} mmHg).

the original bulk sample at room temperature. There was no evidence indicating (1) the presence of a fine structure in the ESR spectra, and (2) the existence of different types of free radicals. When the temperature was increased, the signal intensity increased proportionally.

Figure 8 summarizes the ESR results. The radical formation started at about 160°C, which was in agreement with the onset of discoloration in Figure 7. There was two temperature regions, where radical propagation apparently stops at about (1) 260–280°C, and (2) 320–340°C, respectively. In the former, particularly, there was little discontinuous change in the weight loss curve. This feature may be related to the stereochemical sequential distribution in urea clathrate PVC, which has not yet been clarified.

CONCLUSIONS

1. There was a distinct difference in ^{13}C -NMR and IR spectra, but no new quantitative information was obtained regarding to the stereochemical sequences of PVC. Dissolution measurements also provided little information on this point.
2. The value of T_g was almost equal in both samples ($\sim 90^\circ\text{C}$). A small baseline drift near

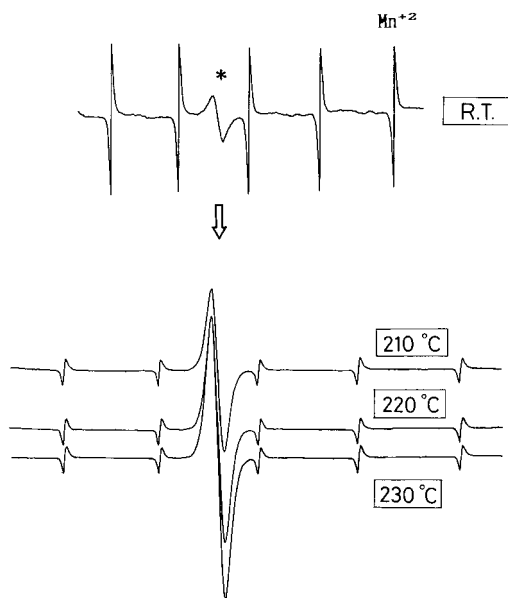


Figure 7 Typical ESR spectra of urea clathrate PVC under dynamic heating conditions. A peak indicated by an asterisk is a signal from the polymer, while other outer peaks are due to Mn^{+2} (MgO) as an ESR marker.

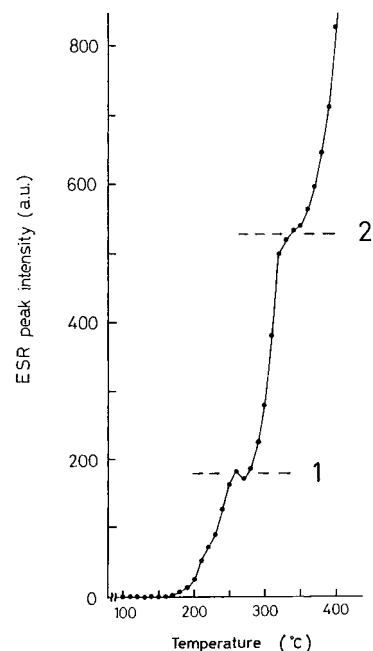


Figure 8 Change in ESR signal intensity under dynamic heating conditions. Radical concentration increased when the temperature was increased, but apparently stopped in some regions (1 and 2).

- T_g indicates that the content of the amorphous region of urea clathrate PVC is small (less than $\frac{1}{10}$ than that of free radical sample).
3. A color photograph of heated PVC clearly indicates that the instability of urea clathrate PVC is large, and a longer conjugated polyene sequence $-(\text{CH}=\text{CH})_n-$ (where, $n = 15-19$) is formed on a polymer backbone.
 4. Solid-state ESR spectra showed that radicals are formed at such a low temperature ($\sim 160^\circ\text{C}$), where little substantial weight loss is observed. The instability of urea clathrate PVC was correlated with the absence of the termination step in the canal polymerization.

We wish to express our sincere thanks to Prof. M. Tasumi (University of Tokyo) and Mr. E. Sato (Perkin Elmer, Japan) for many valuable suggestions and generous help in IR measurements. Thanks are also expressed to Profs. M. Matsuda and T. Miyashita (Tohoku University) for the dynamic ESR measurements. This work was carried out under the support of JAERI-University research cooperation.

REFERENCES

1. White, D. M. *J Am Chem Soc* 1960, 82, 5678.
2. Krimm, S.; Berens, A. R.; Folt, V. L.; Shipman, J. J. *Chem Ind* 1958, 1512.

3. Krimm, S. *Chem Ind* 1959, 433.
4. Sakurada, I.; Nambu, K. *Nippon Kagaku Zashi* 1959, 80, 307.
5. Asahina, M.; Enomoto, S. *Nippon Kagaku Zashi* 1960, 81, 1011.
6. Asahina, M.; Enomoto, S. *Nippon Kagaku Zashi* 1960, 81, 1370.
7. Shimanouchi, T.; Tasumu, M. *Bull Chem Soc Jpn* 1961, 34, 359.
8. Tasumi, M.; Shimanouchi, T. *Spectrochim Acta* 1961, 17, 731.
9. Yoshii, F.; Abe, T.; Yoda, O. *Kobunshi Ronbunshu* 1975, 32, 429.
10. Minagawa, M.; Miyano, M.; Takahashi, M.; Yoshii, F. *Macromolecules* 1988, 21, 2387.
11. Minagawa, M.; Takahashi, T.; Tasumi, M.; Sato, E.; Yoshii, F. unpublished data.
12. The urea clathrate PVC retained its original powder form even after heating up to 400°C, whereas free radical PVC did not. This strong dimensional stability was true not only for PVC but also for PAN. M. Minagawa, and F. Yoshii, unpublished data.
13. Jaffe, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; John Wiley & Sons, Inc.: New York, 1966.