

ENVIRONMENTAL STABILITY OF THE POLYENE PREPARED BY DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE)*

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Abstract A high-quality polyene can be obtained by extensive dehydrochlorination of poly(vinyl chloride) (PVC) in a liquid/solid two-phase system. The liquid phase is a tetrahydrofuran solution of PVC containing a small amount of poly(ethylene glycol) with molar mass of 400 g as a phase transfer catalyst. The solid phase is potassium hydroxide particles. The structure of the polyene is polyacetylene-like and has a long conjugated C=C sequence and a narrow dispersity of polyene sequences according to its FT-infrared and Raman spectra. The environmental stability of the polyene was also studied by IR, Raman spectra and elemental analysis. Experimental results demonstrated that the polyene was susceptible to air and could be changed into a material containing high concentrations of hydroxyl and carbonyl groups. The polyene sequences were shortened and its dispersity became broader due to the effect of dioxygen.

Keywords PVC, Two-phase dehydrochlorination, Stability, IR spectroscopy, Raman spectroscopy

INTRODUCTION

Dehydrochlorinated poly(vinyl chloride) (DPVC) contains a polyene structure similar to polyacetylene (PA). Poly(vinyl chloride) (PVC) is, therefore, a potential “precursor polymer” for PA if the degree of dehydrochlorination can reach sufficiently high levels while cross-links and other undesirable side reactions remain at an acceptable minimum degree^[1]. DPVC shows chemical and electrochemical activity and has potential applications in the fabrication of polymer rechargeable batteries with high energy density^[2]. The degradation reaction of PVC has been investigated extensively in recent years both from theoretical^[3] and practical^[4] aspects.

On the other hand, the environmental stability of DPVC is an important factor influencing its application. Although the oxidative degradation of polyacetylene was studied in detail^[5, 6], only a few publications are concerned with the environmental stability of the dehydrochlorinated PVC^[7].

In this paper, we report a high-quality DPVC prepared by dehydrochlorination of PVC in a liquid/solid two-phase system. The average number of the conjugated double bonds of DPVC ($N_{C=C}$) was measured to be as long as 33 and the polyene sequences have a narrow dispersity. The environmental stability of this polyene has been studied by elemental analysis, infrared and Raman spectroscopies.

EXPERIMENTAL

Materials

PVC with molar mass of 87600 g and dispersity of 1.96 (Shanghai Chlor-Alkali Chemical Co.) was purified by reprecipitation from THF solution by adding methanol. Poly(ethylene glycol) with molar mass of 400 g (PEG400) was purchased from Beijing Yili Fine Chemical Company and used without further treatment. Analytically pure tetrahydrofuran (THF; Beijing Chemical Factory) was distilled before use. Potassium

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hydroxide (KOH) pellets (0.5 mm in thickness) were analytically pure and powdered (< 2 mm in diameter) and then dried under vacuum at 100 °C for 24 h. Absolute methanol (Analytically Pure; Vas. Lab. Suppl. Ies.) was used as received.

Dehydrochlorination of Poly(vinyl chloride)

Dehydrochlorination of PVC was carried out in a three-necked flask equipped with a condenser, a dropping funnel and a glass inlet for nitrogen bubbling. The flask was placed in an ice-water bath for temperature control. 0.4 g PVC and 6 mL PEG400 were dissolved in 30 mL THF. After 30 mL THF and 20 g KOH were added to the flask, and the system was purged with nitrogen gas. PVC solution in THF was dropped into the flask within 15 min under stirring. The solution changed to yellow immediately and gradually to brown and finally turned dark. After 2 h, the reaction was terminated by the addition of distilled water to dissolve KOH. The product was filtered and washed with a large amount of distilled water and then with absolute methanol three times. Finally, the clean DPVCs were dried under vacuum at 60 °C for 2 h before characterization. The samples used for environmental stability studies were exposed to air at room temperature for certain time periods.

Characterization

The molar mass and dispersity of PVC were measured in THF by a GPC model Agilent 1100 series at 35 °C and calibrated by using standard polystyrene. Infrared spectra were recorded by a Spectrum GX FT-infrared spectrometer of Perkin-Elmer Company (with KBr pellets). Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 785 nm laser beam and a CCD detector with 4 cm⁻¹ resolution. The spectra were recorded by using a 20 × objective. The power supply was kept very low (0.01 mW) to avoid the destruction of samples. Elemental analysis was performed by using a Flash 1112 elemental analyzer (Italy).

RESULTS AND DISCUSSION

Structure of DPVC

Figure 1(a) shows the FT-infrared spectrum of the DPVC which is similar to that reported previously^[8]. As can be seen, the C—Cl stretching at about 600–700 cm⁻¹ largely disappeared. At the same time, the characteristic CH₂ stretching vibrations in the region of 2900 to 2800 cm⁻¹ were very weak. These implied that the reaction conversion was sufficiently high. Furthermore, this spectrum shows a strong and sharp =C—H out-of-plane deformation ($\delta_{\text{=CH}}$) band at 1000 cm⁻¹ and a strong broad conjugated C=C stretching vibration ($\nu_{\text{C=C}}$) band centered at about 1542 cm⁻¹^[9]. Moreover, the band of $\nu_{\text{=CH}}$ appears at *ca.* 3010 cm⁻¹. The spectroscopic results described above indicate that the DPVC product has long *trans* conjugated double bonds^[10]. On the other hand, the $\delta_{\text{=CH}}$ and $\nu_{\text{C=C}}$ band of DPVC prepared under two-phase conditions with ammonium or phosphonium halides as catalysts^[11–13] were found at 990 cm⁻¹ and 1670 cm⁻¹. Accordingly, the polyene sequences of the DPVC produced by the catalytic reaction of PEG400 are much longer than those prepared by ammonium or phosphonium halides, because long conjugated segments tend to have enhanced absorptions of $\nu_{\text{C=C}}$ at low frequencies and $\delta_{\text{=CH}}$ bonds at higher frequencies^[9, 14].

The 785 nm excited resonance Raman spectrum of the DPVC was shown in Fig. 1(b), which is very similar to that of *trans*-PA prepared by the Shirakawa procedure^[15]. It has excellent signal-to-noise (*S/N*) characteristics and clearly confirms the formation of polyenes although the sample is dark in color. In addition, there is nearly no “fluorescence” background in the spectrum. The 1472 cm⁻¹ band (ν_2) is assigned to the mode mainly consisting of the C=C stretching vibration. The 1292 cm⁻¹ and 1085 cm⁻¹ bands are attributed to the mixtures of C—C stretching and CH in-plane bending vibrations. The band at about 1006 cm⁻¹ belongs to that of C—C single bond stretching vibration. It was reported that the positions and shapes of the bands of C=C and C—C stretching vibrations, especially the former, were sensitive to the number of conjugated bonds ($N_{\text{C=C}}$)^[16–18]. With increasing conjugation length these bands shift to lower frequencies. According to the calculation method described by Maddams^[17], the $N_{\text{C=C}}$ of DPVC is about 33. This value is more than twice that of the DPVC formed by two-phase reaction as reported by Kise^[1, 7], and even higher than that we reported previously^[8]. The two main peaks

are strong and sharp and their width is narrow. The half bandwidth of the peak at 1472 cm^{-1} is measured to be 22 cm^{-1} and this value is very close to that of *trans*-polyacetylene obtained by the polymerization of acetylene through the catalytic reaction with Ziegler-type catalyst (about 20 cm^{-1})^[15]. In comparison, the Raman spectra of the DPVC prepared by the catalytic action of quaternary ammonium salts^[1] showed much broader Raman bands (half bandwidth of $\nu_{\text{C}=\text{C}}$ band is around 50 cm^{-1}). These results indicate that the DPVC has a structure similar to that of PA and has a narrow dispersity of polyene sequences.

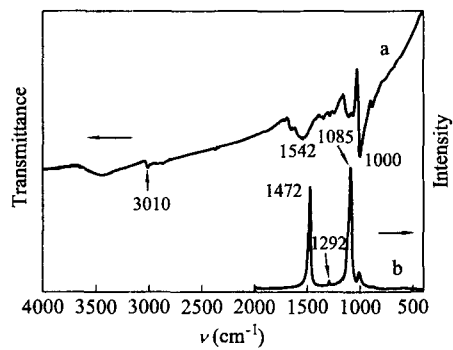


Fig. 1 FT-infrared (a) and Raman (b, accumulated for 30 s) spectra of DPVC

Elemental Analysis

Table 1 lists the oxygen contents of the DPVC samples exposed to air for various lengths of time. It is clear from this table that the oxygen content of DPVC increases with the increase of time. This indicates that dioxygen in air can react with polyene, and the oxygen atom can be chemically incorporated into the DPVC. In addition, according to its carbon/hydrogen atomic ratio, the carbon-carbon double bond content of the DPVC sample exposed to air for 5 h is estimated to be about 84%.

Table 1. Oxygen content of DPVC exposed to air for different lengths of time	
Exposure time	O ₂ (%)
5 h	14.29
24 h	20.32
1 week	29.88

Infrared Spectroscopy Study

Figure 2 clearly shows the structural change of DPVC occurring in air. The spectrum of the DPVC exposed to air for 20 min (Fig. 2a) differs from that of the original sample (Fig. 1a). The strong and broad band centered at about 1542 cm^{-1} in Fig. 1(a) shifts to 1560 cm^{-1} in Fig. 2(a). The intensity of the weak band at around 1670 cm^{-1} (Fig. 1a) is enhanced and is comparable to that of the band at 1560 cm^{-1} . Furthermore, a new $\nu_{\text{C}=\text{O}}$ band appears at 1720 cm^{-1} . These spectral changes suggest that the polyene structure has been oxidized. There is an absorption at about 3440 cm^{-1} corresponding to the hydroperoxy group (OOH)^[19] and the hydroxy moiety. The band at 1670 cm^{-1} (Fig. 2a) belongs to α,β -unsaturated ketone. The intensity of these bands (1670 , 1720 and 3440 cm^{-1}) in the DPVC spectrum increases with the length of exposure time. On the contrary, the intensity of the broad 1560 cm^{-1} band of conjugated $\text{C}=\text{C}$ bond (Fig. 2a) is decreased in comparison with those of the bands at 1725 and 1682 cm^{-1} , and its position is shifted to 1635 cm^{-1} . Furthermore, the sharp band at 1000 cm^{-1} assigned to $\text{C}-\text{H}$ out-of-plane deformation of *trans*-olefinic bonds becomes broader and shifts to about 985 cm^{-1} . Simultaneously, the sharp band at 3010 cm^{-1} (ν_{CH}) also decreases gradually with the increase of time. The infrared spectral results demonstrated that the concentration of the conjugated carbon-carbon double bonds and the average length of the polyene sequences is decreased by the reaction with air. On the other hand, oxygen is incorporated into DPVC and results in the formation of hydroxyl and carboxyl groups. Their contents are

increased with the increase of exposure time.

Raman Spectroscopy Study

Figure 3 illustrates the Raman spectra of DPVC exposed to air for different lengths of time. It is seen from these spectra that the Raman intensity decreases dramatically with the increase of time. The band originally situated at 1472 cm^{-1} (ν_2) as shown in Fig. 1(b) was shifted gradually to higher frequencies and this band for the sample exposed to air for 11 h was found at 1501 cm^{-1} (Fig. 3g). These results demonstrated that the average number of conjugated double bonds ($N_{C=C}$) decreases with the increase of time. The ν_2 positions and the corresponding $N_{C=C}$ for DPVC at different times are listed in Table 2. Furthermore, the two sharp main bands become broader and broader during the period of air exposure. This suggests that the dispersity of the polyene sequences is broadened by the reaction with air.

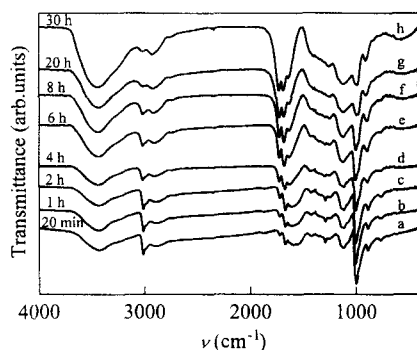


Fig. 2 Infrared spectra of DPVC exposed to air for different times

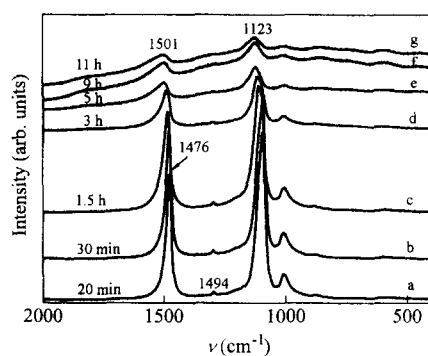


Fig. 3 Raman spectra of DPVC exposed to air for different times

(a, b and c accumulated for 30 s; d, e, f and g accumulated for 3 times and 30 s each)

Table 2. Results of Raman spectroscopic measurements on DPVC (ν_2 , $N_{C=C}$) exposed to air for different lengths of time

Exposure time	ν_2 (cm^{-1})	$N_{C=C}$
0 min	1472	33.5
20 min	1476	29.6
30 min	1477	28.7
1.5 h	1483	24.7
3 h	1487	22.5
5 h	1495	19.1
9 h	1497	18.3
11 h	1501	17.0

Influence of Water

It was reported that the polyene structures are sensitive to water or moisture in the air^[20]. However, our experimental results are contrary to this conclusion. The Raman spectrum of the DPVC sample, which has been immersed in deoxygenated water for 4 days, is the same as that of the original sample. The fine structure of the spectrum shows no perceptible changes. This implies that water or moisture could not destroy the polyene structure of DPVC in the absence of dioxygen. The structural change of DPVC exposed to air is mainly due to the effect of dioxygen.

CONCLUSIONS

A polyene structure can be obtained by dehydrochlorination of PVC in liquid/solid two-phase systems. The FT-infrared spectrum shows that PVC can be extensively dehydrochlorinated within 2 h at 0°C . The Raman spectrum indicates the product has a long polyene structure ($N_{C=C} = 33$) similar to that of *trans*-polyacetylene. The DPVC,

like PA, is susceptible to air and can be changed into a material containing high concentrations of hydroxyl and carbonyl groups, but it is stable in deoxygenated water. The long polyene structure is proven to be destroyed and shortened by the action of dioxygen in the air. Furthermore, the dispersity of polyene sequences of DPVC becomes broader.

REFERENCES

- 1 Owen, E.D., Shah, M., Everall, N.J. and Twigg, M.V., *Macromolecules*, 1994, 27: 3436
- 2 Perichaud, A. and Lemehaute, A., 1986, EU. Pat., 0.176.877
- 3 Simon, P., Gernay, P. and Valko, L., *Eur. Polym. J.*, 1989, 25: 245
- 4 Bowley, H.J., Gerrard, D.L. and Biggin, I.S., *J. Vinyl. Technol.*, 1988, 10: 50
- 5 Pochan, J.M., Pochan, D.F., Rommelmann, L. and Fibson, H.W., *Macromolecules*, 1981, 14: 110
- 6 Fibson, H.W. and Pochan, J.M., *Macromolecules*, 1982, 15: 242
- 7 Kise, H., *J. Polym. Sci. Polym. Chem. Ed.*, 1982, 20: 3189
- 8 Guo, L., Shi, G.Q., Du, X.Z., Li, C. and Liang, Y.Q., *J. Appl. Polym. Sci.*, 1998, 70: 2463
- 9 Chen, Z., Liu, M., Shi, M. and Shen, Z., *Makromol. Chem.*, 1987, 188: 2687
- 10 Shirakawa, H. and Ikeda, S., *Polym. J.*, 1971, 2: 231
- 11 Leplyanin, G.V., Salim, Gareeva, V.N. and Samikowa, N.S., *Kinet. Katal. (Russ)*, 1994, 35: 883
- 12 Weber, W.P. and Gokel, G.W., *Phase Transfer Catalysis in Organic Synthesis*, Springer, New York, 1977
- 13 Starks, C.M. and Liotta, C., *Phase Transfer Catalysis*, New York: Academic, 1978
- 14 Shindo, Y., Read, B.E. and Stein, R.S., *Makromol. Chem.*, 1968, 118: 272
- 15 Fukukawa, Y., Ohta, H., Sakamoto, A. and Tasumi, M., *Spectrochim. Acta.*, 1991, 47A: 1367
- 16 Schugerl, F.B. and Kuzmany, H.J., *Chem. Phys.*, 1981, 74: 953
- 17 Baruya, A., Berrard, D.L. and Maddams, W.F., *Macromolecules*, 1983, 16: 578
- 18 Rimai, L., Heyda, M.E. and Gill, D., *J. Am. Chem. Soc.*, 1973, 95: 4493
- 19 Folub, N.A., *Pure Appl. Chem.*, 1980, 52: 305
- 20 He, F.F. and Kise, H., *J. Polym. Sci. Polym. Chem. Ed.*, 1983, 21: 1729