# Poly(ethylene glycol)s Catalyzed Two-Phase Dehydrochlorination of Poly(vinyl chloride) with Potassium Hydroxide

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Received 2 January 1998; accepted 9 May 1998

**ABSTRACT:** Poly(ethylene glycol)s  $[HO(CH_2CH_2O)_nH$ , where n > 3] are highly active and selective in catalyzing dehydrochlorination of poly(vinyl chloride) in organic– aqueous hydroxide two-phase systems. Their catalytic activity and stability are much higher than those of widely used quaternary ammonium or phosphonium compounds. Poly(vinyl chloride) can be extensively dehydrochlorinated within half an hour at room temperature. The products are polyacetylene-like and have long polyene sequences according to their UV/visible, FT-Raman, and FT-infrared spectra. They can be doped by iodine to conductive states, with conductivities of 1-4 S cm<sup>-1</sup>. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2463–2469, 1998

**Key words:** PVC; KOH; poly(ethylene glycol); two-phase dehydrochlorination; catalyzation

## INTRODUCTION

The formation of polyene from poly(vinyl chloride) (PVC) by treatment with KOH has been known for > 60 years.<sup>1</sup> It was reported that dehydrochlorination could be proceeded with aqueous KOH, NaOH, or Ca(OH)<sub>2</sub> at very high temperatures of  $250-270^{\circ}$ C.<sup>2</sup> Unfortunately, it was found that the products produced under these conditions contained appreciable amount of aromatics and oxidized components. The technique of phase-transfer catalyzation has been successfully used for various organic–aqueous two-phase reactions.<sup>3,4</sup> Usually, the reactions were conducted under a mild condition at the interphase of aqueous solutions of necloiphiles or bases and organic PVC solutions. The phase-transfer catalysts applied in these cases usually were quaternary ammonium or phosphonium halides.<sup>3–6</sup> However, the activity and stability<sup>7,8</sup> of these catalysts are not satisfactory. It needs at least 1 day for the dehydrochlorination of PVC powders or films,<sup>9,10</sup> or in solutions<sup>10</sup> at room temperature with a conversion close to 80%.

Recently, we found poly(ethylene glycol)s (PEGs) with a repeat unit number n > 3 were extraordinary catalysts for dehydrochlorination of PVC in organic-aqueous two-phase systems. PVC could be extensively dehydrochlorinated at room temperatures within half an hour. This finding developed a new, fast, moderate, and convenient technique for making high-quality dehydrochlorinated PVCs (DPVCs).

# **EXPERIMENTAL**

#### **Materials**

PVC with a number average molar mass of 93,900 g and a dispersity of 1.77 is a product of Jinyi

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Contract grant sponsor: Chinese Science and Technology Commission and Natural Science Foundation of China; contract grant number: 29773019..

Journal of Applied Polymer Science, Vol. 70, 2463-2469 (1998)

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Electrochemical Factory (China) and had been well dried and stored under vacuum before use. Glycol and PEGs with molar masses of 200 (PEG 200), 400 (PEG 400), and 800 (PEG 800) g were purchased from Pudong Gaonan Chemical Factory (Shanghai, China). They were dried under vacuum and at 100°C for 24 h. Tetrahydrofuran (THF; Zhenxin Chemical Research Institute, Suzou of China), methanol (Shanghai First Chemical Factory, China), and KOH (Nanjing Chemical Factory, China) were analytical grade pure and used without further purification.

## **Dehydrochlorination of PVC**

In a typical experiment, 2 mL PEG and 0.2 g PVC were dissolved in 20 mL THF, and the mixture was stirred magnetically at room temperature for a few minutes. Then, 20 mL aqueous KOH solution (60%, w/w) was added. The solutions were deoxygenated by nitrogen bubbling, and reaction temperature was controlled by a water bath. Color was developed immediately in the solution, and black powders were found in several minutes. On termination of the reaction, the product was separated by filtration, washed with water and methanol three times, then successively extracted in a Soxhlet extractor with methanol for 48 h to remove PEG, base, and salt extensively. Clean product was dried under vacuum and at 60°C for 24 h before characterizations.

## **Doping of DPVCs**

The doping of DPVC was conducted by immersing the dried DPVC powders in iodine-saturated tetrachloromethane solution for 1 h, then filtered and washed with clean solvent three times. They had been dried under vacuum at 60°C for 24 h before characterizations.

# Characterizations

The molar mass and dispersity of PVC were measured in THF by a GPC model 244 (Waters Company, The United States) at 24.5°C and using polystyrene as standard. Infrared and Raman spectra were recorded on an IFS-66V Fourier transform-infrared (FT-IR) spectrometer with KBr pellets and RFS-100 FT-Raman spectrometer (Bruker Company, Germany), respectively. The electrical conductivity of iodine-doped DPVCs was measured by tow-probe technique. Elemental analysis was performed by a Perkin– Elmer 240 C elemental analyzer. The conversions of the reactions  $(f_H)$  were calculated from the atomic ratios of hydrogen and carbon (H/C) of the products according to eq. (1):

$$f_{H} = [(\text{H/C})_{o} - (\text{H/C})_{p}]/[(\text{H/C})_{0} - (\text{H/C})_{t})] \\ \times 100\% = 2[1.5 - (\text{H/C})_{p}] \times 100\% \quad (1)$$

where  $(\text{H/C})_p$  and  $(\text{H/C})_t$ , are the found and theoretical values (1.0) of hydrogen/carbon atomic ratio of DPVC, respectively.  $(\text{H/C})_o$  is that of the original PVC (equals 1.5).

UV/visible spectra were taken out on UV-240 spectrometer (Shimadzu, Columbia, MD). Three milliliters of THF solution of PVC containing a certain amount of PEG 400 (THF : PVC : PEG 400 = 1 mL : 0.1 mg : 0.1 mL), put into a 1-cm optical cell, then 1 mL of 60% (w/w) aqueous solution of KOH was dropped into the THF solution. The spectra of the organic phase during reaction were recorded at the reaction times of 0, 1, 2, 4, 6, 8, 10, and 15 min, respectively.

# **RESULTS AND DISCUSSION**

## **Catalysis of PEGs**

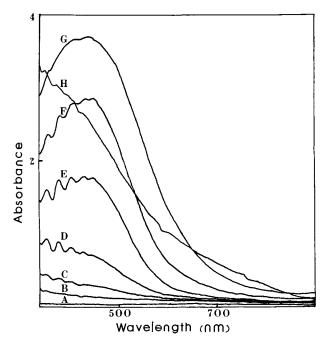
In the systems without catalyst, dehydrochlorination of PVC by hydroxide was very slow, even it was conducted at an elevated temperature. For examples, in the case of 30% aqueous KOH/PVC powders, the conversion was determined to be  $\sim 1.4\%$  as the reaction was performed at 70°C for 5 h.<sup>3</sup> In a solution reaction of 22% aqueous NaOH/ PVC in THF, the conversion was measured to be only 9.4% (70°C for 5 h).<sup>10</sup> At room temperature, this reaction was found to be even much slower, and the organic solution of the polymer was kept transparent for > 5 h, and no apparent UV/visible absorption change was monitored. On the other hand, as PEG 200, PEG 400, or PEG 800 was used as a catalyst, the reaction started immediately and was completed rapidly. Conversions of the reaction  $(f_H)$  at 30 min were measured to be 90-96% by elementary analysis, as listed in Table I. These results demonstrated that the catalytic activity of PEGs was very high and much stronger than those of ammonium or phosphonium halides. On the other hand, glycol was found to be a much weaker catalyst. PVC solution changed its color slowly and the conversion of reaction was measured to be only 19% as the reaction was conducted for 2 h.

	Time				$f_H$
Catalyst	(min)	H%	C%	H/C	(%)
PEG 800	15	6.43	72.32	1.067	86.6
PEG 800	30	6.12	70.28	1.046	90.8
PEG 800	120	7.10	77.30	1.102	79.6
PEG 400	15	6.47	74.02	1.050	90.0
PEG 400	30	6.67	78.32	1.022	95.6
PEG 400	120	6.63	75.69	1.052	89.6
PEG 200	15	6.24	64.63	1.159	68.2
PEG 200	30	6.38	74.58	1.027	94.6
PEG 200	120	6.98	73.30	1.143	71.4
Glycol	120	5.92	50.62	1.404	19.2

Table IElemental Analysis Results of DPVCsand Conversions of Reactions at DifferentTimes and Room Temperature

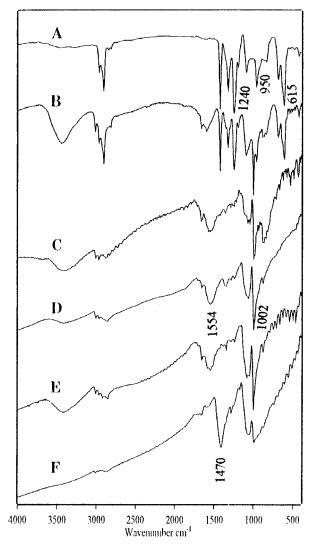
# **UV/Visible Spectra**

For an *in situ* UV/visible spectra recording, a very diluted PVC solution was used as described in the Experimental section. The spectra were recorded on a suitable absorption scale, and precipitation of the product was postponed. Figure 1 shows the spectra changes during PVC dehydrochlorination catalyzed by PEG 400. It was clear from this figure that the organic solution showed no signif-

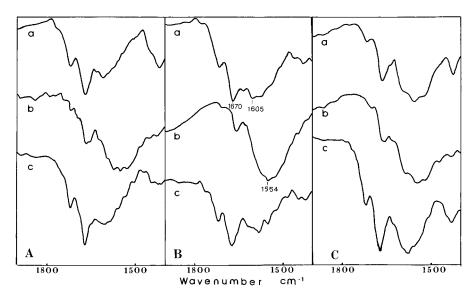


**Figure 1** UV/visible spectra of the organic phase during dehydrochlorination of PVC catalyzed by PEG 400 and recorded at the reaction time of 0 (A), 1 (B), 2 (C), 4 (D), 6 (E), 8 (f), 10 (G), and 15 (H) min.

icant absorption before reaction [Fig. 1(A)]. However, after addition of KOH solution, the spectrum changed quickly. Four main absorption peaks at 350, 378, 405, and 430 nm appeared in the spectrum recorded at the reaction time of 4 min [Fig. 1(D)], indicating that the conjugated length of the product was  $\sim 8.^{11}$  With reaction time increasing, the fine structures of the spectrum became unclear, whereas the overall absorption became stronger and broader. Simultaneously, the maximum of the spectrum shifted to a longer wavelength. Figure 1(G) is the spectrum recorded at a reaction time of 10 min. It has a very



**Figure 2** FT-IR spectra of PVC (A), DPVCs prepared by catalyzation of glycol (B; reacted for 2 h), PEG 200 (C; reacted for 30 min), PEG 400 (D; reacted for 30 min), PEG 800 (E; reacted for 30 min), and iodinedoped DPVC of the PEG 400 sample (F).



**Figure 3** Regional FT-IR spectra in the range around  $\nu_{C=C}$  bands of DPVCs obtained at reaction time of 15 (a), 30 (b), and 120 min (c), and catalyzed by PEG 200 (A), PEG 400 (B), and PEG 800 (C), respectively.

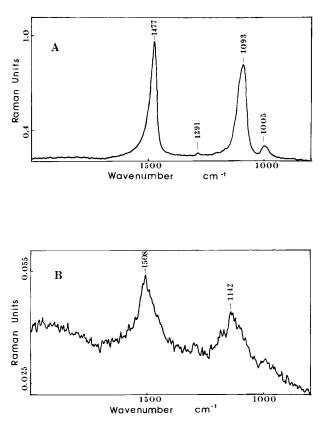
strong and broad band with maximum absorption at ~ 450 nm and tailed off to > 800 nm. The overall absorption pattern of this spectrum indicated the presence of long polyenes.<sup>12</sup> However, when the reaction was conducted for ~ 15 min, the absorption of the organic phase decreased markedly because of the precipitation of the DPVC products [Fig. 1(H)].

#### **Elemental Analysis**

Table I lists the elemental analysis results of DPVCs prepared under various conditions. This table demonstrates clearly that PVC dehydrochlorination was nearly finished within 30 min. The atomic ratio of hydrogen and carbon, H/C, of the product was decreased from 1.5 for PVC to a value close to 1.0. However, as the reaction continued to 2 h, the value of H/C increased a little, indicating a lower conversion of hydrogen whereas chlorine was extensively eliminated according to the results of infrared characterizations. This is most possibly due to side reactions resulting from aqueous base solution or catalysts changing the structures and compositions of the products. This phenomenon was observed and reported for the first time. Polyene, like polyacetylene, is sensitive to oxygen, moisture, and various other regents.<sup>10,12</sup> In a short reaction time, dehydrochlorination is the main reaction, and side reactions can be neglected. However, as PVC was extensively dehydrochlorinated, side reactions still occur and high concentrations of polyene segments strongly supported these reactions. Therefore, a suitable reaction time should be selected for making high-quality product.

# FT-IR Spectra

Figure 2 illustrates the FT-IR spectra of PVC (A) and DPVCs prepared by catalyzation of glycol (B), PEG 200 (C), PEG 400 (D), PEG 800 (E), and iodine-doped PEG 400 sample (F). As shown in Figure 2(C,E), the products exhibit characteristic stretching bands of isolated and conjugated C=C double bonds ( $\nu_{C=C}$ ) at 1670 (weak) and 1554 (medium and broad)  $cm^{-1}$ , respectively.<sup>13</sup> These indicated that the products have high concentrations of polyene sequences and a little isolated double bond. In addition, the spectra show strong absorption bands at  $1,002 \text{ cm}^{-1}$ , which assigned to C-H out-of-plane deformation of trans-olifinicbonds  $(\delta_{-CH})^{14}$ . The bands of PVC initially present at 1425, 1240, 950, and  $615 \text{ cm}^{-1}$  are very weak or disappeared, indicating an extensive elimination of chlorine and a sufficient high conversion of reaction. On the other hand, the DPVCs prepared under two-phase conditions with ammonium or phosphonium halides as catalysts showed spectra with comparable or much stronger bands at 1670  ${\rm cm^{-1}}$  than those at  $\sim 1550$ cm<sup>-1</sup>. Furthermore, their  $\delta_{=CH}$  bands were found at  $980-990 \text{ cm}^{-1}$ . According to these results, the polyene sequences of the DPVCs produced by



**Figure 4** 1064 nm excited FT-Raman spectra of neutral (A) and iodine-doped (B) DPVCs obtained at 30 min and catalyzed by PEG 400.

PEG catalyzation are much longer than those prepared by ammonium or phosphonium halides. Longer conjugated segments tend to have enhanced absorptions of  $\nu_{\rm C=C}$  at lower frequencies and  $\delta_{\rm =CH}$  bands at higher frequencies.<sup>11,14</sup> The spectrum of the DPVC prepared by the catalyzation of glycol also showed polyene bands [Fig. 2(B)]. However, the characteristic bands of undegraded sequences still present with medium strengths, indicating a low conversion.

Iodine-doped DPVC product showed a typical spectrum of Figure 2(F). This spectrum shows weak and broad  $\nu_{C=C}$  bands between 1550 and 1700 cm<sup>-1</sup>. The  $\delta_{=CH}$  band becomes broader, and its peak is shifted to ~ 990 cm<sup>-1</sup>. Furthermore, a new intense band appeared at 1470 cm<sup>-1</sup> and may be assigned to a lower frequency "ungerade" mode of  $\nu_{C=C}$ .<sup>15</sup> These findings suggest that the structure of iodine-doped DPVC is similar to that of iodine-doped all-*trans*  $\beta$ -carotene, a well-studied model compound with a fairly long polyene chain.<sup>15</sup>

The concentrations of conjugated double bonds and polyene lengths of DPVC products depend on reaction time. Figure 3 is the regional infrared spectra in the range around  $\nu_{\rm C=\!\!\!\!\!-C}$  bands of DPVC samples prepared at different reaction times. For example, note the case using the PEG 400 catalyst as an example for explanations [Fig. 3(B)]. The sample obtained at 15 min showed a medium band at 1670 cm<sup>-1</sup>, and a weaker and broader band with a maximum at 1605  $\text{cm}^{-1}$ , thus indicating that the product contains mainly short conjugated sequences. As the reaction time increases to 30 min, the maximum of the broad band shifted from 1605  $\rm cm^{-1}$  to a lower frequency of 1554  $cm^{-1}$ , and became much stronger than the 1670 cm<sup>-1</sup> band, thus implying that sufficient long conjugated sequences were formed. However, the  $1670 \text{ cm}^{-1}$  band increased and the  $1554 \text{ cm}^{-1}$ band decreased as reaction continued to 2 h. This demonstrated that the conjugated segments have been shorten as the reaction time increased from 30 min to 2 h. Similar behavior also can be found in the other two PEG systems [Fig. 3(A, and 3C) and coincides well with the results of elemental analysis.

#### **FT-Raman Spectra**

The 1064 nm excited FT-Raman spectrum of DPVC obtained by the catalyzation of PEG 400 and reacted for 30 min is illustrated in Figure 4(A). Weak "fluorescence" backgrounds and high signal-to-noise ratio are found in this spectrum. The two bands found at 1477 and 1093  $cm^{-1}$  are due to the C=C double bond stretching mode  $(\nu_2)$ and a mixed mode of CH bending and C-C single bond stretching vibrations, respectively.<sup>6,16</sup> The positions of these two bands, especially the former, are known to be sensitive to the polyene lengths of DPVCs.<sup>17</sup> The two bands of longer conjugated double bonds tend to appear at lower frequencies. On the other hand, the spectrum of the iodine-doped DPVC sample has a bad signalto-noise ratio feature, and the two main bands become much weaker and broader, thus shifting to 1508 and 1142  $\text{cm}^{-1}$ , respectively. These results indicated that iodine doping can damage the conjugated double bonds and shorten their sequence lengths. According to the calculation method reported by Maddams and colleagues,<sup>16</sup> the polyene length  $(n_{C=C})$  of neutral DPVC is  $\sim$  28 and that of doped DPVC is  $\sim$  16.

Table II lists the main FT-Raman data of a series of neutral and iodine-doped DPVC samples. It is clear from Tables I and II that the composition and polyene length of DPVC depend strongly

Catalyst	t	$f_H_{(\%)}$	$\nu_2$	$\nu_2'$		
	(min)		$(\tilde{cm}^{-1})$	$(\tilde{cm}^{-1})$	n <sub>C=C</sub>	n' <sub>C==C</sub>
PEG 800	15	86.6	1481.8	None <sup>a</sup>	25.41	None
PEG 800	30	90.8	1479.1	1507.0	27.20	15.24
PEG 800	120	79.6	1481.4	1515.1	25.66	13.24
PEG 400	15	90.0	1482.8	1500.8	24.81	17.10
PEG 400	30	95.6	1477.4	1508.5	28.45	14.83
PEG 400	120	89.6	1484.5	1501.2	23.85	16.97
PEG 200	15	68.2	1491.2	None	20.63	None
PEG 200	30	94.6	1480.3	1506.7	26.43	15.33
PEG 200	120	71.4	1492.5	None	20.09	None
Glycol	120	19.2	1483.7	1495.0	24.29	19.12

Table II Results of 1064 nm Excited FT-Raman Spectroscopic Measurements on DPVCs ( $\nu_2$ ,  $n_{C=C}$ ) and Iodine-Doped DPVCs ( $\nu'_2$ ,  $n'_{C=C}$ ) Prepared at Room Temperature

<sup>a</sup> None = poor signal-to-noise feature of the spectra and band positions cannot be accurately read.

on reaction time. For example, note the case using PEG 400 catalyst as an example. The sample obtained at 15 min has an H/C atomic ratio of 1.050 and corresponds to a hydrogen conversion,  $f_H$ , of 90% (Table I). Its  $n_{C=C}$  was measured to be  $\sim$  25 (table II). As reaction time increased to 30 min, the C/H atomic ratio of the product decreased to 1.022 ( $f_H \sim 96\%$ ), and  $n_{\rm C=C}$  increased to  $\sim$  28. However, as the reaction continued to 2 h, the product showed a little increment in its H/C atomic ratio (1.052), and  $n_{\rm C=C}$  decreased to  $\sim$  24. Similar phenomena were also found in the cases using PEG 200 and PEG 800 as catalysts. These results are in good agreement with the experimental results of FT-IR spectroscopies. The  $\nu_2$  band of doped DPVC ( $\nu'_2$ ) always appeared at a higher frequency than that of the corresponding neutral sample, thus suggesting a shorter polyene chain length ( $N'_{C=C} < n_{C=C}$ ).

The conductivity of iodine-doped extensively DPVCs ( $f_H \ge 90\%$ ) (in a pressed pellet state) was measured to be in the range of 1–4 S cm<sup>-1</sup>. This value was much higher than those of iodine-doped DPVC films formed by the catalyzation of quaternary ammonium salts (in the order of  $10^{-3}$  S cm<sup>-1</sup>).<sup>9,18</sup> This is possibly due to the fact that the DPVCs produced by PEG catalyzations have much higher conversions and longer conjugated sequences.

# CONCLUSIONS

PEGs are extraordinary phase-transfer catalysts for dehydrochlorination of PVC in organic-aqueous two-phase systems. Their catalytic activities and stabilities are much stronger than those of previously used ammonium or phosphonium halides. PVC can be extensively dehydrochlorinated within 30 min at room temperature. Reaction conversion and polyene length of DPVC depend strongly on reaction time. At the beginning, the conversion and polyene length increased with reaction time. However, they are decreased with reaction time after dehydrochlorination was nearly finished. This may be due to the fact that polyene segments of DPVCs are unstable in the reaction medium. High concentrations of conjugated double bonds and the presence of water and base-supported side reactions decreased the property of the product. The DPVCs with the highest qualities were obtained at a reaction time of 30 min, and they have a structure similar to polyacetylene, with high concentrations of long polyene sequences. Furthermore, they showed doping behavior similar to general conducting polymers, and the conductivity of doped DPVCs was in the range of 1-4 S cm<sup>-1</sup>.

The authors thank Dr. Xiaohu Yan and Zhiliu Wang for molar mass measurement of PVC.

### REFERENCES

- C. S. Marvel, J. H. Sample, and M. F. Rov, J. Am. Chem. Soc., 61, 3241 (1939).
- J. E. Campbell and W. H. Rauscher, J. Polym. Sci., 18, 461 (1955).

- H. Kise, J. Polym. Sci. Polym. Chem. Ed., 20, 3189 (1982).
- K. T. Howang, K. Iwamoto, M. Seno, and H. Kise, Makromol. Chem., 187, 611 (1986).
- G. V. Lepoyanin, N. V. Salim Gareeva, and N. S. Samikowa, *Kinet. Katal.* (Russ.), **35**, 883 (1994).
- E. D. Owen, M. Shah, N. J. Everall, and M. V. Twigg, *Macromolecules*, 27, 3436 (1994).
- Y. Kimura and S. L. Regen, J. Org. Chem., 47, 2493 (1982).
- C. M. Straks and C. Liotta, *Phase Transfer Catalysis*, Academic Press, New York, 1978, p. 126.
- F. F. He and H. Kise, *Kobunshi Ronbunshu*, **41**, 547 (1984).
- F. F. He and H. Kise, J. Polym. Sci. Polym. Chem. Ed., 21, 1729 (1983).

- Y. Shindo, B. E. Read, and R. S. Stein, *Makromol. Chem.*, **118**, 272 (1968).
- H. J. Bowley, D. L. Gerrard, W. F. Maddams, and M. R. Paton, *Makromol. Chem.*, **186**, 695 (1985).
- E. Tsuchia, C.-N. Shih, I. Shinohara, and S. Kambara, J. Polym. Sci., Part A, 2, 3347 (1964).
- 14. Z. Chen, M. Liu, M. Shi, and Z. Shen, *Makromol. Chem.*, 188, 2687 (1987).
- I. Harada, Y. Fukukawa, M. Tasumi, and S. Ikeda, J. Chem. Phys., 73, 4746 (1980).
- A. Baruya, D. L. Gerrard, and W. F. Maddams, Macromolecules, 16, 578 (1983).
- 17. I. Harada, M. Tasumi, H. Shirakawa, and S. Ikeda, Chem. Lett., 1411 (1978).
- H. Kise, M. Sugihara, and F. F. He, J. Appl. Polym. Sci., 30, 1133 (1985).