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Poly(ethylene glycol)s catalyzed homogeneous dehydrochlorination of poly(vinyl chloride) with potassium hydroxide

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Abstract

Poly(vinyl chloride) (PVC) can be extensively dehydrochlorinated by KOH at room temperature in a mixed homogeneous medium of tetrahydrofuran (THF) and poly(ethylene glycol) (PEG) with a number average molar mass greater than 200 g mol^{-1}. PEGs act as solubility promoters for the base and highly active catalyst for the reaction. The structure of dehydrochlorinated PVC (DPVC) has been studied by elemental analysis, UV/visible, FT-infrared, FT-Raman and X-ray photon electron spectroscopies. Experimental results demonstrated that the reaction was nearly finished within 1 h and had a conversion of 84–98%. DPVCs have high concentrations of long polyene sequences and can be doped by iodine. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl chloride); Dehydrochlorination; Poly(ethylene glycol)s

1. Introduction

It is well known that poly(vinyl chloride) (PVC) can be dehydrochlorinated thermally and photochemically, or by ionizing radiation or base catalysis in the solution phase [1–5]. These result in the elimination of HCl and discolor the polymer. Dehydrochlorinated poly(vinyl chloride) (DPVC) has a polyene structure similar to, while not same to polyacetylene (PA). The essential difference between polyenes in PA and those in DPVC is the former extend throughout the polymer, whereas the latter are relatively short and are isolated from each other by undegraded chain segments [6].

DPVC, like other conducting polymers, shows chemical and electrochemical activity and has potential applications in fabrication of polymer rechargeable battery with high energy density [7]. Thus, the reaction of PVC degradation has been investigated widely in these years both theoretically [8] and practically [9]. For extensive dehydrochlorination, thermal degradation is not useful because secondary reactions such as crosslinking, Diels–Alder reactions reduce the content of conjugated bonds as the reaction is carried out at high temperature [10–12]. Although low temperatures (<400 K) suppress these side reactions, the elimination is not efficient. For efficient degradation, the reaction must be initiated by radiation (UV, X-ray), or chemically by a basic agent.

Two-phase dehydrochlorination of PVC by hydroxides was usually carried out in the presence of different ammonium or phosphonium halides as phase transfer catalysts [13–15]. The dehydrochlorination proceeds following an ionic mechanism at the interphase. The catalytic activity of the quaternary ammonium compounds depends on the necleophility of the cation and on the anion compositions. The products obtained from these systems were PA-like and have large concentrations of short conjugated segments. The conjugated polyene length ranges from 1 to about 15 [16]. Furthermore, the organic ammonium salts are unstable and lose their activity quickly at an evaluated temperature [17]. This resulted in the reactions needing a long time for a high conversion. Typical side reactions during elimination are substitution reactions. In the case of PVC dehydrochlorination, the replacement of chlorine by the base should be considered [18]. Strong nucleophilic solvent such as water and low base concentrations support these side reactions. Substitutions can be suppressed completely by using homogeneous reaction in an anhydrous ether (chain or cyclic) media and by using moderately necleophilic or bulky bases [19].

Homogeneous reactions are generally carried out by the use of organic bases. Many polar solvents can dissolve both

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the base and the polymer. These reactions are suitable for extensive dehydrochlorination of PVC in a short time. For moderate dehydrochlorination up to a conversion of a few percentages, many bases including tributylamine [20], dibutyl amine and butyltrimethylammonium hydroxide [21], can be used. It was reported extensively that dehydrochlorinated DPVCs could be prepared by NH_2Na/liquid NH_3 in tetrahydrofuran (THF) [22], or by in situ formed *t*-BuOK [19,23] at moderated temperatures. Unfortunately, neither the systems produced DPVC with long conjugated chains. In this paper, we report a safer and more convenient and moderate process for making high-quality DPVCs by a homogeneous reaction of PVC and KOH in a mixture solvent of THF and PEGs with molar masses of 200–800 g under a deoxygenated environment following reaction (1)

$$\sim (CH_2CHCl)_n \sim \underset{PEG+THF}{\overset{KOH}{\rightarrow}} \sim (CH{=}CH)_n \sim \qquad (1)$$

Commercially obtainable PVCs used for dehydrochlorination are usually powders of suspension type. They are soluble in THF, cyclohexanone and dichloroethane. However, these solvents are poor media for dissolving the inorganic bases such as KOH and NaOH. On the other hand, PEG is a good solvent for various inorganic salts and bases [24]. Actually, we found PVC and KOH were soluble in a mixture solvent of PEG and THF with a volume ratio of 10 ml/200 ml. In addition, PEG oligomers with CH_2CH_2O repeat unit number, n, greater than 3 were found to be extraordinary catalysts in liquid–liquid two-phase dehydrohalogenation of organic halides to corresponding olfenes with a conversion higher than 99% and no side reactions have been detected [17]. On the basis of these considerations, we chose the mixture solvent of PEG and THF as the medium for PVC dehydrochlorination with KOH. Here, PEG acts as the solvent for the base and the catalyst for the reaction.

2. Experimental

2.1. Materials

PVC with molar mass of 93,900 g and dispersity of 1.77 is a product of Jiyi Electrochem. Fact. (China) and had been well dried and stored under vacuum and at 60°C before use. Glycol and poly(ethylene glycol)s with molar masses of 200 (PEG 200), 400 (PEG 400) and 800 g (PEG 800) were purchased from Pudong Gaonan Chem. Fact. (Shanghai, China). They were dried under vacuum and at 100°C for 24 h. Water free THF was prepared by treatment of analytical grade pure THF (Zhenxin Chem. Research Institute, Suzou of China) with metallic Na and distilled under dry condition. Methanol (Shanghai 1st Chem. Fact., China) and KOH (Nanjing Chem. Fact., China) were also analytical pure grade and used without further purification.

2.2. Dehydrochlorination of poly(vinyl chloride)

Dehydrochlorination of PVC was carried out in a flask with three necks. It consisted of one condensate tube, one dropper and one glass tube for nitrogen bubbling. The flask was dipped in a silicon oil or a salty ice bath for temperature control and set over a stirrer. 0.1 g PVC dissolved in 100 ml THF and 0.3 g KOH dissolved in 10 ml PEG, respectively. Then, the base solution of PEG dropped into the polymer solution within 2 min to form a homogenous system. The transparent solution of PVC changed into yellow immediately and gradually to brown and finally to dark. The reaction was terminated by adding a mixture solution of THF and methanol (1:1). DPVCs as black powders were deposited and filtered. The rough products were washed with a large amount of distilled water and methanol three times, then successively extracted in a soxhlet extractor with methanol for 48 h to remove PEG, base and salt extensively. The clean products were dried under vacuum at 60°C for 24 h before characterizations.

2.3. Doping of DPVCs

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

2.4. Characterizations

The molar mass and dispersity of PVC were measured in THF by a GPC model 244 of Waters company at 24.5°C and using polystyrene as standards. Infrared and Raman spectra were recorded on an IFS-66V FT-infrared spectrometer with KBr pellets and RFS-100 FT-Raman spectrometer of Bruker Company, respectively. UV/visible spectra were taken out on an UV-240 spectrometer. Elemental analysis was performed by a Perkin–Elmer 240 C elemental analyzer. The conversions of the reactions were calculated by measuring the H/C (f_H), or Cl/C (f_{Cl}) atomic ratios (with a photon electron spectrometer model VGS 5000) of the products following Eqs. (2) and (3), respectively,

$$f_H = f_H = [(H/C)_o - (H/C)_p]/[(H/C)_o - (H/C)_t] \times 100\% \\ = 2[1.5 - (H/C)_p] \times 100\% \qquad (2)$$

$$f_{Cl} = [(Cl/C)_o - (Cl/C)_p]/[(Cl/C)_o - (Cl/C)_t] \times 100\% \\ = 2[0.5 - (Cl/C)_p] \times 100\% \qquad (3)$$

where $(H/C)_p$, $(H/C)_t$, are the found and theoretical value (1.0) of hydrogen/carbon atomic ratio of DPVC, respectively. $(H/C)_o$ is that of original PVC (equals 1.5). $(Cl/C)_p$, $(Cl/C)_t$, and $(Cl/C)_o$ have the similar meaning.

UV/visible spectra measurements were carried as follows: at specific reaction time intervals 1 ml samples were withdrawn and then dissolved in 10 ml mixture solution of PEG and THF (PEG : THF = 1 : 10). After a reaction time of 4 h, some insoluble products existed in the solutions. UV spectra were carried out after removing the insoluble precipitates. It should be noted that the majority of the products still in the solutions and the content of precipitates were low before terminating the reaction and the results of the UV spectra were reliable.

3. Results and discussion

3.1. Catalysis of PEGs

Unlike organic base such as *t*-BuOK, tributylamine, etc. the inorganic base shows low base ability although they are dissolved in some general organic solvents. For example, in the case of using glycol as solvent of KOH, the reaction rate of dehydrochlorination is so low that no obvious discoloration of the reaction mixture solution could be observed after reaction of 4 h. However, when we added a certain amount of PEG 800 in glycol or used PEG 800 or PEG 400 as base solvent, the reaction rate increased rapidly and the polymer solution changed its color quickly. Table 1 lists the elemental analysis results of DPVC products prepared at various conditions. It is clear from Table 1 that in the case of PEG 800, the maximum conversion of the reaction reached up to about 98% (f_H) as the reaction was carried out to 1 h, and the product has an H/C atomic ratio (1.01) close to that of the theoretical value for PA (1.00). These indicated that PEGs with repeat unit number greater than 3 are not only the solvent of the base, but also the extensive catalyst. The chain length of PEGs influences the catalytic activity of them. In this paper, PEGs with greater repeat unit number shows higher catalytic activity (PEG 800 > PEG 400 > PEG 200), and glycol shows no catalytic activity. This may be due to the fact that PEGs cannot only dissolve inorganic base, but can also coordinate with the cations of the base (such as K^+) to form crown-like polymeric hydroxides as active agent when the chain length of PEG is optimal (in this case, PEG 800 is optimal) and increase the activity of the base [17].

It is well accepted that if dehydrohalogenation of polyhalogen-containing polymer becomes more complete and less side reaction occurs, the ratio of hydrogen to carbon of the product must be trend to equal to unit. It can be seen from Table 1 that the conversion calculated from Cl/C ratio is something higher than that from H/C. This may be due to side reactions such as substitution of –OH group on the polymer chain, which occur during the dehydrochlorination. So although the content of Cl is decreasing with the reaction time increasing, the content of H is not decreased accordingly. However, it was found that the difference between them is low and the two conversion results become almost equal in the case of PEG 800 after reaction of 1 h. These indicated that the undesirable side reactions are kept to an accepted minimum. The elemental analysis results show that the sum of carbon and hydrogen is less then 100%. This shortage may be mainly due to the incorporation of oxygen in the molecules [22]. In general, the content of the oxygen can reach to about 10–25%. On the other hand, the side reaction such as substitution of –OH and the low dehydrochlorination conversion of PVC could also decrease the sum of the carbon and hydrogen.

It can be seen from Table 1 that in the case of using PEG 800, reaction conversion reached to about 98% (f_H) as the reaction was carried out for 1 h. However, if the reaction time was as long as 4 h, f_H was decreased to about 90%. This is mainly due to the fact that in a short reaction time, dehydrochlorination is the dominant reaction and the side reactions can be neglected. However, as the main reaction was nearly finished, side reactions were still present, which result in the damaging of the polyene structures of the product and increasing the atom ratio of H/C. Although, the trend of f_H did change with reaction time in the case of using PEG 400 catalyst, its value at reaction time of 4 h (90%) was much lower than f_{Cl} (98%). This also indicated the presence of side reactions. In the case of PEG 200, the conversion of the reaction was detected to be only 46% at the reaction time of 4 h, indicating a much lower catalytic activity.

Table 1
Elemental analysis results of DPVCs and conversions of reactions

Catalyst	T [a] (°C)	t [b] (h)	%H	%C	H/C	Cl/C [c]	f_H (%)	f_{Cl} (%)
PEG 800	r.t. [d]	1	6.34	75.36	1.01	0.008	98	98
PEG 800	r.t.	4	6.30	72.11	1.05	0.004	90	99
PEG 400	r.t.	1	6.47	71.91	1.08	0.054	84	89
PEG 400	r.t.	4	5.94	67.95	1.05	0.040	90	92
PEG 200	r.t.	4	5.73	54.45	1.27	0.254	46	49
Glycol	r.t.	4	–	–	–	–	–	–
Glycol + PEG 800	r.t.	4	6.20	72.74	1.04	0.020	93	96

[a] Reaction temperature.
[b] Reaction time.
[c] Measured by an XPS technique.
[d] Room temperature.

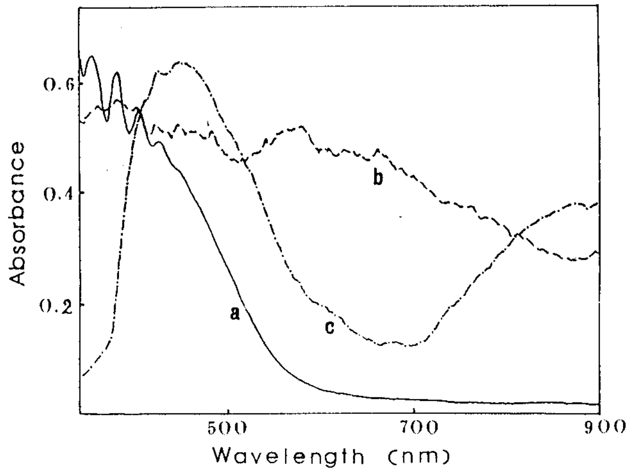

Fig. 1. UV/visible absorption spectra of poly(vinyl chloride) dehydrochlorinated in a mixture solvent of THF and PEG 800 with KOH for (a) 5 min, (b) 1 h, and (c) 4 h.

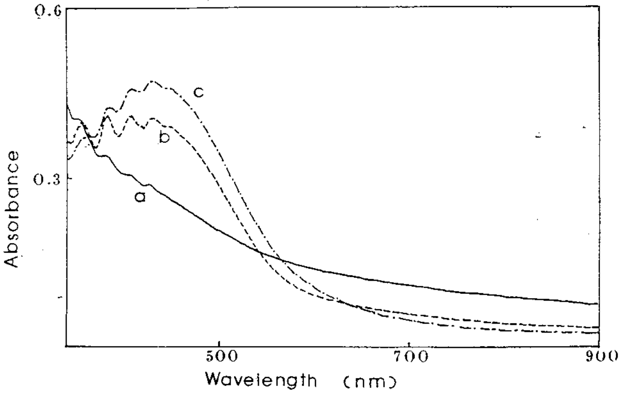

Fig. 2. UV/visible absorption spectra of poly(vinyl chloride) dehydrochlorinated in a mixture solvent of THF and PEG 200 with KOH for (a) 20 min, (b) 2 h, and (c) 4 h.

3.2. UV/visible spectra

Fig. 1 illustrates the spectra of the solution at different reaction times. At the beginning, the product exhibits a typical spectrum of a thermally degraded polymer and tailing off at long wavelength in visible position (Fig. 1a) [4]. As the reaction time increased to 1 h, an irregular absorption spectrum appeared (Fig. 1b). The absorption bands in ultraviolet were suppressed, while the broad absorption with several peaks at 383, 450, 580, 625 and 662 nm in visible region increased. These phenomena indicate that long conjugated polyene segments were formed through the elongation of the short conjugated C=C double bonds as the reaction conversion increase [25]. The longest polyene sequences of DPVC product may longer than 100 and comparable to that of PA (670 nm) [26]. However, when the reaction time was increased to 4 h, only a strong and broad band with a peak at about 450 nm was observed and a new broad band appeared at a wavelength greater than 900 nm (Fig. 1c). These results inferred that the long polyene sequences were shortened by side reactions if the reaction time was too long, and the conjugated segment lengths trend towards a narrower range. In the case of using PEG 200 as the catalyst, the solution during dehydrochlorination process showed UV/visible spectra of Fig. 2. These spectra have various fine structures of polyene sequences similar to those of DPVC by chemical reactions described previously [19,27], indicating relative short polyene segments. In the case of glycol, the reaction rate is so low that the color of the mixture solution is not changed after a reaction time of 4 h and no precipitated product could be obtained. At the same time, UV/visible spectra show no obvious absorption peak within the experimental region.

For a homogenous reaction, the content of KOH and PEG in the mixture solvent should be considered. It found that if the amount of KOH is exceeded, the reaction rate may be higher and dehydrochlorination of PVC may become more completely. However, if the amount of KOH were too large, the side reaction such as substitution of –OH would occur. At the same time, if the amount of PEG was sufficiently small, KOH cannot be dissolved completely. Thus, solid–liquid two-phase reaction may occur in the system. On the other hand, extraordinarily, a large amount of PEG may lead to an increase in undesirable side reactions and difficulty of product washing. Each of them is harmful for making high-quality products. The content of KOH and PEG used in this study is an optimum value for this reaction.

3.3. FT-infrared spectra studies

Fig. 3 shows the FT-infrared spectra of PVC (A) and the DPVCs obtained by catalyzations of PEG 200 (B), PEG 400 (C), PEG 800 (D) and iodine doped PEG 400 sample (E), respectively. As can be seen from Fig. 3C and D, the C–Cl stretching bands at about 615 cm^{-1} disappeared and the characteristic CH_2 stretching bands in the range of 2900 and 2800 cm^{-1} were very weak, in comparison with Fig. 3A [28]. These confirmed that the reaction conversions were sufficiently high in both cases. Furthermore, these spectra showed strong and sharp bands of =C–H out-of-plane deformation ($\delta_{=\mathrm{CH}}$) at 1005 cm^{-1} and strong broad conjugated C=C stretching vibration ($\nu_{\mathrm{C=C}}$) bands centered at about 1530 cm^{-1} [29]. In addition, absorption bonds around 3010 cm^{-1} due to $\nu_{=\mathrm{CH}}$ are also observed. These indicated that the DPVC products have long *trans* conjugated double bonds [30]. The Raman spectra also demonstrate this result. The reaction may proceed by an ionic mechanism [31].On the other hand, the $\delta_{=\mathrm{CH}}$ and $\nu_{\mathrm{C=C}}$ band of extensively dehydrochlorinated PVC obtained from NH_2Na/liquid NH_3 or in situ formed *t*-BuOK were found at 990 and 1600 cm^{-1}, respectively [19,22]. These observations implied that the DPVCs prepared by PEG catalyzation has longer conjugated sequences, because longer polyene segments tend to have more enhanced absorption of $\nu_{\mathrm{C=C}}$ at lower frequencies and $\delta_{=\mathrm{CH}}$ at higher frequencies

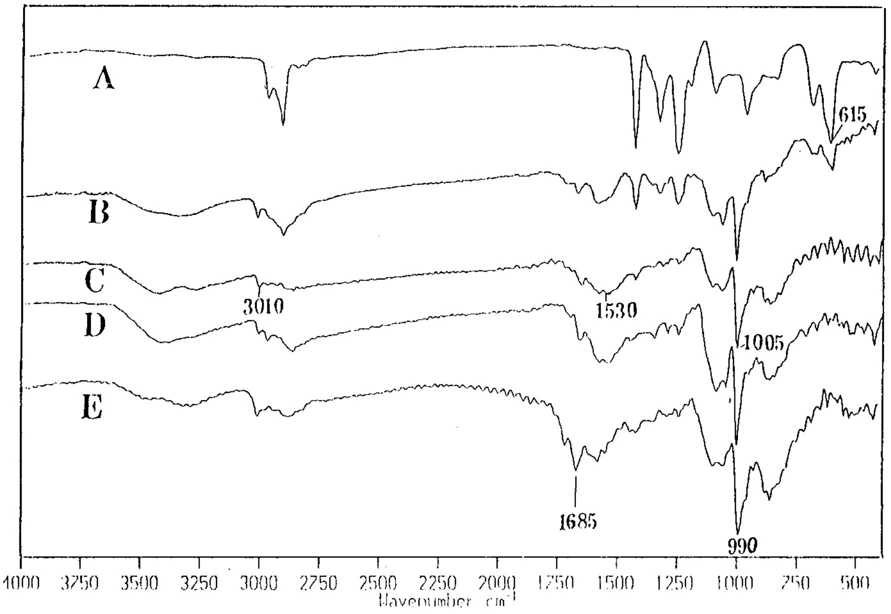

Fig. 3. FT-infrared spectra of: (A) PVC; (B) DPVCs prepared by catalyzation of PEG 200 (reacted for 4 h); (C) PEG 400 (reacted for 1 h); (D) PEG 800 (reacted for 1 h); and (E) iodine doped DPVC obtained from sample C.

[28,29]. The spectrum of the DPVC prepared by the catalyzation of PEG 200 also showed polyene bands (Fig. 3B). However, the C–Cl band was still found at 600–630 cm^{-1}, indicating a lower reaction conversion. The C=O and C≡C bands usually showed in the spectra of thermally or from solution process are not found in Fig. 3B–D, indicated a low side reactions of oxidation and over-dehydrochlorination [32,33]. In the infrared spectra of DPVC products, a broad and weak hydroxyl group bond was observed at around 3400 cm^{-1}, this may be due to: (1) some residual PEG that remained in spite of attempts to remove it; (2) substitution of the –OH group on the polyene chain. It can be seen from the elemental analysis and UV-spectra study that the conversion of the reaction is high and the undesirable side reaction were kept to an acceptable minimum. Hence, the –OH bond of the product in infrared spectra may be mainly due to the former reason.

Iodine doped DPVC made from PEG 400 system showed a spectrum of Fig. 3E. The $\nu_{C=C}$ bands shifted to higher frequencies (centered at about 1680 cm^{-1}), and the $\delta_{=CH}$ band became broader and shifted to a lower frequency (990 cm^{-1}). These demonstrated that the polyene sequences of DPVC have been shortening by doping reaction.

3.4. FT-Raman spectra studies

The 1064 nm excited FT-Raman spectrum of the DPVC obtained by the catalyzation of PEG 800 and reacted for 1 h is shown in Fig. 4A. This spectrum is similar to that of *trans* PA prepared through Shirakawa procedure [34]. It has a good signal-to-noise (S/N) feature although the sample is dark in color. The 1477 cm^{-1} band (ν_2) is assigned to a mode mainly consisting of the C=C stretching vibration. The 1291 and 1093 cm^{-1} bands are attributed to mixtures of C–C stretching and CH in-plane bending vibrations. The band at 1006 cm^{-1} belongs to that of C–C single bond stretching vibration. It has reported that the positions and shapes of the bands of C=C and C–C stretching vibrations,

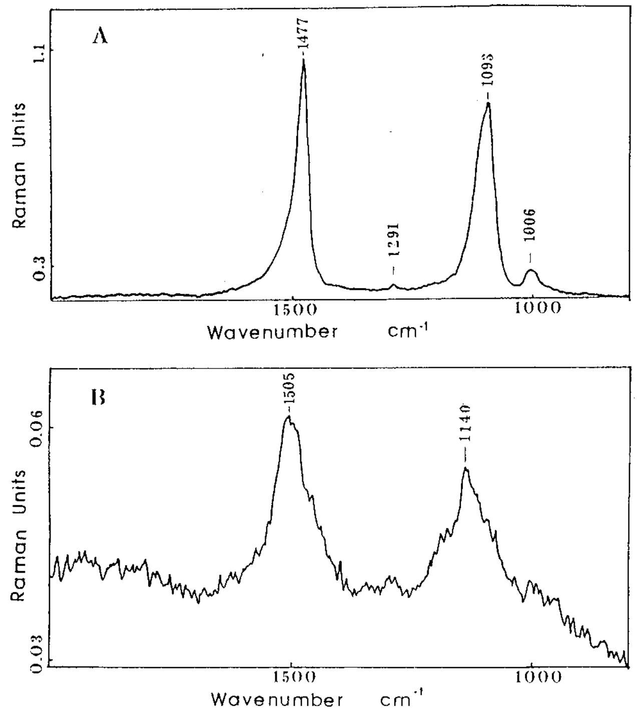

Fig. 4. FT-Raman spectra of DPVC (A) and iodine doped DPVC (B) prepared by catalyzation of PEG 800 and reacted for 1 h.

Table 2
Results of FT-Raman spectroscopic measurements on DPVCs (ν_2, $n_{C=C}$) and iodine doped DPVCs (ν'_2, $n'_{C=C}$) prepared at room temperature

Catalyst	t (h)	f_H	ν_2 (cm^{-1})	ν'_2 (cm^{-1})	$n_{C=C}$	$n'_{C=C}$
PEG 800	1	98	1477.5	1505.2	28.3	15.8
PEG 800	4	90	1481.6	1482.4	25.5	25
PEG 400	1	84	1479.8	1513.3	26.7	13.6
PEG 400	4	90	1480.1	1484.3	26.5	24
PEG 200	4	46	1486.6	1593.4	22.8	1.7

especially the former, are sensitive to the number of conjugated bonds $n_{C=C}$ [35–37]. According to the calculation method described by Maddams et al. [36], the $n_{C=C}$ of the sample described here is about 28. This value is almost twice that of the DPVC formed by two-phase reaction with KOH reported by Kise [16,38]. Iodine doped DPVC sample showed a spectrum of Fig. 4B. This spectrum has a worse S/N feature because of stronger fluorescence affection. Furthermore, the two main bands had become broader and much weaker, and their peaks shifted to 1505 and 1140 cm^{-1} indicating a $n_{C=C}$ of 16. This behavior is much similar to that of conducting polymers such as PA and polypyrrole. The ν_2 band positions and corresponding $n_{C=C}$ for various DPVCs and their doped samples are listed in Table 2. It is clear from this table that the samples obtained at higher reaction conversion (f_H) have longer polyene sequences. The $n_{C=C}$ of the DPVC obtained from PEG 800 was decreased from 28 to 25 as the reaction time increased from 1 to 4 h. This is in a good agreement with the results of elemental analysis and UV/visible spectra. In Table 2, it is interesting to note that the change of $n_{C=C}$ to $n_{C=C'}$ after doping of I_2 is strongly dependent on the reaction time regardless of the type of PEG. The above investigation indicated that the doping process might damage the conjugated structure of the DPVC. Hence, it is suggested that this difference may be due to the content of the I_2 incorporated into the DPVC product during the doping process. However, to obtain the real reason for this question we need further evidence.

It should be noted here that the conductivity measurement of doped DPVCs was unsuccessful because of the difficulty of obtaining high-quality pellets from the polymer powders.

4. Conclusions

Poly(ethylene glycol)s with molar masses of 200 to 800, are extraordinarily active and selective catalysts for dehydrochlorination of PVC with KOH. PEGs act as both the solvents for the base and the catalysts for the reaction. The highest conversion of the dehydrochlorination of PVC in this homogeneous system was measured to be 98% (f_H), and the products have long polyene structure ($n_{C=C} = 23$–28) and shows a doping property similar to that of PA. The catalyst activity of the PEG is PEG 800 > PEG 400 > PEG 200. In an optimal reaction time, the conversion of the reaction reaches its maximum. However, as the reaction time increases, the main reaction is completed, and side reactions still occur in the reaction system, which results in the damaging of the conjugated structure and decreasing of the dehydrochlorination conversion of the product. The synthesis method developed in this study is significant because it is suited for mass production of high-quality DPVC at a convenient and moderate condition and it has potential applications in dehydrohalogenation of other halide polymers.

Acknowledgements

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