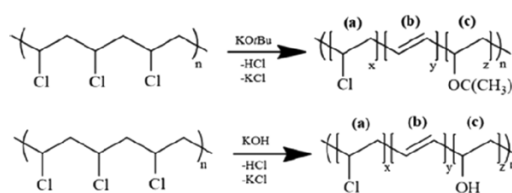# Controlled Dehydrochlorination of Poly(vinyl chloride) for Fabrication of Membranes with Polyacetylene-Like Structure: XPS Analysis and Ion Exchange Membrane Discussion

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Abstract: Poly(vinyl chloride) (PVC) can be dehydrochlorinated by strong bases, *e.g. tert*-butoxide and hydroxide, to attain polyacetylene-like highly conjugated polymer chains. Dehydrochlorinated PVC (DHPVC) can be further functionalized by additional reactions to obtain ion exchange membranes, battery membranes, semiconductors, *etc*. However DHPVC resin is not available for membrane casting because of its low solubility. Therefore dehydrochlorination was performed directly on PVC membranes in this research. The extent of dehydrochlorination and the length of conjugation were controlled by adjusting conditions such as base/PVC ratio and solvent type. X-ray photoelectron spectrometry and elemental analysis were used to detect Cl, C, O, and H contents of the products. A calculation method that uses parameters of atomic approximations, was proposed to mathematically express trends of "degrees of dechlorination, dehydrochlorination, unsaturation, and substitution" with respect to the amount of base used. Up to 64.5% unsaturation and 96.6% dechlorination of PVC membranes were achieved. In addition, theoretical ion exchange capacity (IEC_{theo}) was defined with a suggestion that charged functional groups can be attached to the polymer backbone by double bonds, allowing ion exchange membranes to be manufactured. By tailoring the degree of unsaturation in dehydrochlorinated species, theoretically up to 18 meq/g of *IEC* would be reached if all double bonds would be functionalized. Scanning electron microscopy analysis showed that *tert*-butoxide products had a porous structure. FTIR and UV-Visible spectroscopy results verified the formation of long polyene sequences. Dehydrochlorination may be a legitimate method for recycling PVC waste into functional membrane materials.

Keywords: poly(vinyl chloride), dehydrochlorination, DHPVC, conjugation, XPS.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most used plastics because of its favorable chemical and mechanical properties. It is broadly used, *e.g.* for manufacturing pipes, bottles, electrical cables, packing materials, wall coverings and furnishings due to its low cost and good processability. Annual consumption of PVC was *ca.* 62 million tons in 2016, and its consumption is increasing year by year.[1,2] Substantial consumption of PVC is causing waste treatment problems at it is usually landfilled or incinerated. Landfilling is not environmentally friendly because of its resistance against natural decomposition and chlorine release.[3-5] When incinerated, halogen compounds and toxic organic compounds, *e.g.* dioxin, are produced which are very harmful to the human body and other living beings.[6-10] Therefore, PVC waste recycling is considered as an important issue.

Chemical modification of PVC is an alternative method of recycling.[11-13] PVC can be modified by substitution of Cl with another functional group[14-18] or by elimination of HCl with strong bases,[19,20] termed "dehydrochlorination". We prefer dehydrochlorination to describe elimination reaction over dechlorination because the latter includes substitution products as well. Yoshioka *et al*. and several other groups carried out dehydrochlorination of PVC by using strong bases such as NaOH and KOH.[21-28] Some researchers used a stronger base, potassium *tert*-butoxide (KO*t*Bu), for dehydrochlorination of PVC.[29,30] Dehydrochlorinated PVC (DHPVC) has a structure similar to that of polyacetylene (PA), which may exhibit electrical conductivity, too.[31-34]

Functionalization of dehydrochlorinated PVC can also be achieved by reaction of double bonds. Direct addition of a couple of Lewis acid and base is a feasible method for functionalization of DHPVC. Another expedient method is attaching functional groups through free-radical reactions through double bonds of DHPVC, which can be activated by a free radical initiator, and double bond(s) of functional molecules such as styrene or fullerene.[20,35-37]

In this work, we devised a facile method for dehydrochlorination of bulk PVC structures, *i.e.* membranes, provided that they are in proper thickness. Highly dehydrochlorinated PVC resin is not soluble in common solvents due to near-nonpolar

nature of conjugated carbon chains, which was also confirmed by our solubility tests. Therefore, it is almost impossible to cast a membrane from highly DHPVC resin. On the other hand, DHPVC membrane is not a convenient process due to the disadvantageous kinetic factors of the solid state. Therefore, there is not much work in the literature about dehydrochlorination of undissolved bulk PVC structures such as membranes, fibers or chips. We ran dehydrochlorination reaction directly on PVC membranes from the beginning in order to acquire already-cast DHPVC membranes. Resultant products preserved the membrane form, which made a new membrane casting step out of DHPVC product needless.

Although we confirmed presence of highly conjugated sequences in DHPVC membrane *via* Fourier transform infrared (FTIR) and UV-Vis spectroscopy techniques, we could not detect any measurable conductivity thereof even after iodine doping. Apart from this, this method would serve as a means of recycling PVC waste and manufacturing functional materials. To illustrate, PVC waste can be dissolved and cast membrane, and then dehydrochlorination and further functionalization steps can be used to build novel membrane devices. Besides membranes, thin films, fibers and chips can be dehydrochlorinated efficiently with a desired degree of dehydrochlorination.

2. Experimental

2.1. Materials

Poly(vinyl chloride) (PVC) resin (MW=48,000 g/mol) was donated by Hanhwa Company. Potassium *tert*-butoxide (KO*t*Bu, 98.0%) and potassium hydroxide (KOH, 85.0%) were purchased from Sigma-Aldrich and Samchun, respectively. Solvents of *n*-butanol (99.0%), *tert*-butanol (99.0%), tetrahydrofuran (THF, 99.0%) and polyethylene glycol 400 (PEG 400, 99.5%) were purchased from Samchun and stored with molecular sieves. Methanol (99.5%) was purchased from Samchun and used for KCl extraction and washing beside deionized water. For solubility tests of DHPVC membranes, dimethylacetamide (DMAc, 99.5%), dimethyl sulfoxide (DMSO, 99.8%) and *N*-methyl-2-pyrrolidone (NMP, 99.5%) were purchased from Samchun and used as is. Iodine (99.8%) and chloroform (99.5%) were purchased form Samchun for use in iodine doping.

2.2. Preparation and reaction of membranes

2.2.1. Casting PVC membranes

A solution was prepared by dissolving PVC resin in THF at a ratio of 1:10 (PVC:THF). Prepared solution was cast at a thickness of 45 μm using a P100 auto film applicator (Lab Q, Korea). Then it was dried in a 60 ºC oven for 24 h, and cut into 3 cm × 3 cm size pieces for further use.

2.2.2. Dehydrochlorination reaction with KO*t*Bu

PVC membrane was dehydrochlorinated with KO*t*Bu under conditions shown in Table 1. PVC membrane and a magnet bar were placed in a 50 mL vial. 30 mL of *n*-butanol and 2 mL of THF were added onto this. 1.0 M THF solution of KO*t*Bu was prepared under inert atmosphere. It was charged into the flask by means of a syringe at required amount (0.5 mL to 8 mL) after diluting to 8 mL when required so as to obtain 3:1 alcohol:THF ratio. Mixture was stirred at ambient temperature (~25 ºC) slowly for 24 h. Another batch was placed in an oil bath of 50 ºC and stirred for 24 h. In order to get rid of KCl byproduct confined in DHPVC matrix, it was extracted in a Soxhlet extractor with methanol solvent under inert atmosphere for 24 h. Membrane was dried in a vacuum oven at 45 ºC for 2 h. All preparations were carried out in a glove box.

2.2.3. Dehydrochlorination reaction with KOH

It was performed according to a method adapted from a work of Guo *et al.*[27] PVC membrane and a magnetic bar were placed in a 50 mL vial. 22 mL of PEG and 10 mL of THF were added onto this. The flask was sealed with a rubber stopper and continuously purged by nitrogen gas to maintain an inert atmosphere. 1 mL to 8 mL of a 1.0 M PEG solution of KOH was completed to 8 mL by adding extra PEG so as to obtain 3:1 PEG:THF mixture, and then purged by nitrogen gas for 15 min. This was later injected into the vial by means of a syringe. Mixture was stirred slowly at ambient temperature (~25 ºC) 4 h (Table 2). Membrane was extracted in a Soxhlet extractor with methanol solvent under inert atmosphere for 24 h. Then it was dried in a vacuum oven at 45 ºC for 2 h.

2.3. Characterizations

Structural changes of PVC and DHPVC products were moni-

Table 1. Conditions for PVC-KO*t*Bu reactions

Sample name	Reagent ratio (PVC:KO*t*Bu)	Solvent (3:1)	Temperature (ºC)	Duration (h)
DHPVCM1	1:0.25	*n*-butanol+THF	25	24
DHPVCM2	1:0.5	*n*-butanol+THF	25	24
DHPVCM3	1:0.75	*n*-butanol+THF	25	24
DHPVCM4	1:1	*n*-butanol+THF	25	24
DHPVCM5	1:4	*n*-butanol+THF	25	24
DHPVCM6	1:0.25	*n*-butanol+THF	50	24
DHPVCM7	1:0.5	*n*-butanol+THF	50	24
DHPVCM8	1:0.75	*n*-butanol+THF	50	24
DHPVCM9	1:1	*n*-butanol+THF	50	24
DHPVCM10	1:4	*n*-butanol+THF	50	24

Table 2. Conditions for PVC-KOH reactions

Sample name	Reagent ratio (PVC:KOH)	Solvent (3:1)	Temperature (°C)	Duration (h)
DHPVCM11	1:0.5	PEG+THF	25	4
DHPVCM12	1:1	PEG+THF	25	4
DHPVCM13	1:4	PEG+THF	25	4

tored by FTIR spectroscopy and ^{13}C solid nuclear magnetic resonance (NMR) spectroscopy. FTIR spectra were measured with attenuated total reflectance (ATR) (IRPrestige-21) at a scan number of 20 and a resolution of 4 cm^{-1} in the range of 4000 cm^{-1} to 600 cm^{-1}. NMR (Agilent 400 MHz 54 mm NMR DD2, Agilent Technologies Inc.) was used to determine ^{13}C atoms of a selected DHPVC membrane. X-Ray photoelectron spectroscopy (XPS) and elemental analyzer (EA) were used to determine the elemental content of the DHPVC products. XPS and EA data were collected on a MultiLab 2000 (Thermo Fisher Scientific Inc.) and FlashEA 1112 (Thermo Finnigan), respectively. The length of the conjugated double bond was estimated on the basis of UV-Visible spectra collected on a S-3100 (SCINCO Co.) spectrophotometer in the range of 240 nm to 820 nm. To monitor PVC and DHPVC morphology changes, SEM images of PVC and DHPVC products were recorded on a LYRA3 XMU (TESCAN Co.) instrument at an acceleration voltage of 10 kV. All samples were coated with platinum before analysis. Thermal Gravimetrical Analysis curves were recorded on a TGA N-1000 instrument (SCINCO Co.) under a nitrogen atmosphere. Temperature was altered from 25 °C to 800 °C at a 10 °C/min rate. The tensile strength of PVC membrane and DHPVC membranes were measured using a universal testing machine according to ASTM D-882 Standard. The size of specimens was 1.8 cm × 19.5 cm. Before measurement, all sample were conditioned at 25 °C, 50% RH during 40 h. Sheet resistance measurements were performed using a four-point-probe (FPP-2400, Dasol Eng Co., Ltd.) and a two-point-probe.

3. Results and discussion

3.1. Dehydrochlorination with KO*t*Bu

3.1.1. Physical properties
3.1.1.1. Solvent and temperature effect
Use of *tert*-butanol instead of *n*-butanol in the solvent mixture concluded in a more sluggish reaction during same duration (24 h). As a result, less intense discoloration was observed in the end of the reaction. Therefore, only *n*-butanol was used as the solvent here to imitate alcohol counterpart of *tert*-butoxide

base. Isopropanol or ethyl alcohol use may work as well though those were not tried herein. Using higher temperature would favor almost all degradation reactions, in particular elimination reactions. Especially in KO*t*Bu reactions, we observed a notable difference between the yield of 50 °C and 25 °C reactions. Discoloration trend and XPS results indicate that higher temperature is required for high dehydrochlorination yield. Therefore, most of the characterizations and discussion were carried out about products of reactions performed at 50 °C hereafter. Furthermore, since the lack of catalyst such as PEG 400 in this reaction, a longer time (24 h) was required to observe sufficient discoloration here, compared to the duration of KOH/PEG 400 system (4 h). Bulky size of *tert*-butoxide base or of its salt (KO*t*Bu) may be another significant reason for the need of longer reaction time besides low solubility of the base in *n*-butanol and weaker interaction of the same solvent with PVC lattice.

3.1.1.2. Discoloration
Figure 1 shows discoloration trend resulting from elimination reaction of membranes. Color of DHPVC membrane gradually changes from orange to brown and to black as more base is introduced. The reason for this trend would be formation of polyacetylene-like polymer out of PVC and its containing conjugated polyene sequences, when dehydrochlorination reaction occurs. As the length of the polyene increases, it is reported that color of polyene sequence would near black.[21] Therefore, it can be inferred from the trend of discoloration in Figure 1 that conjugated polyene sequences are generated by dehydrochlorination reaction in this work, and also conjugation length extends upon increase of base/PVC ratio.

3.1.1.3. Solubility
Membranes cut into 1 cm × 1 cm size were placed in 5 mL vials containing THF, DMAc, DMSO, and NMP solvents. DHPVCM6 membrane completely dissolved in THF, DMAc and NMP, but only slightly dissolved in DMSO. DHPVCM7 (1:0.5) membrane did not dissolve in THF completely, but to a great degree (Figure 2). However, it did not dissolve well in other solvents, but only slightly or none. DHPVCM8 (1:0.75) membrane does not dissolve well in
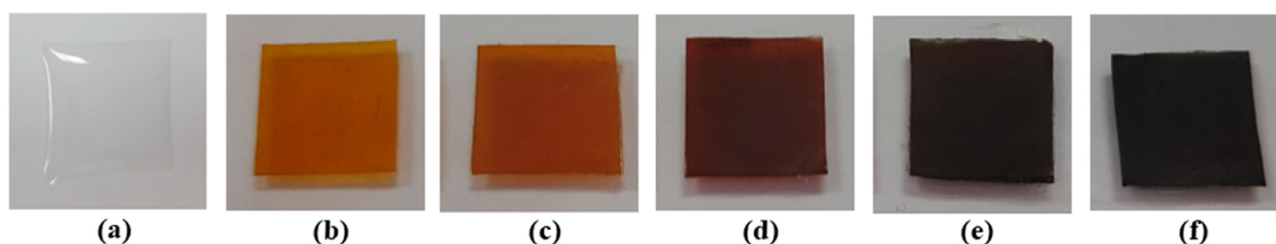
Figure 1. Discoloration trend of DHPVC membranes depending on the amount of base: (a) PVC, (b) DHPVCM6 (1:0.25), (c) DHPVCM7 (1:0.5), (d) DHPVCM8 (1:0.75), (e) DHPVCM9 (1:1), and (f) DHPVCM10 (1:4) obtained by KO*t*Bu reaction at 50 °C.
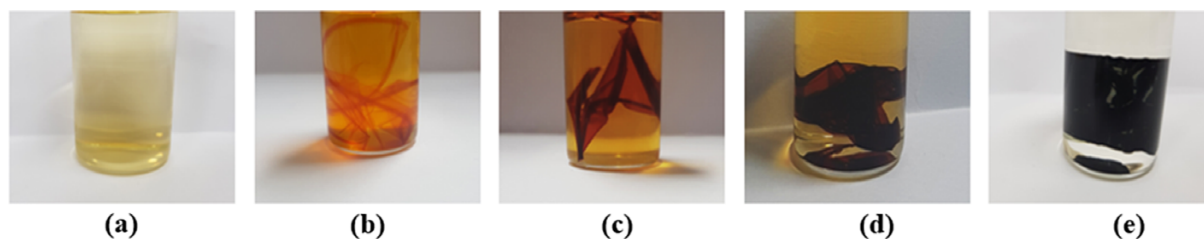
Figure 2. Photographs of (a) DHPVCM6 (1:0.25), (b) DHPVCM7 (1:0.5), (c) DHPVCM8 (1:0.75), (d) DHPVCM9 (1:1), and (e) DHPVCM10 (1:4) dissolved in THF solvent (membranes obtained by KO*t*Bu reaction at 50 °C).

any solvent. As the degree of dehydrochlorination increases, DHPVC membranes become less soluble in common solvents. It is obvious that, DHPVC polymer product which possesses more than ~45% of dehydrochlorination degree are not completely soluble in THF or other solvents, therefore it is required to start with PVC membrane to fabricate DHPVC membranes with such high dehydrochlorination degreesAs degree of dehydrochlorination increases, number of double bonds and length of conjugated polyene sequences increase, which means that it turns more insoluble. Therefore, we can deduce that in order to make membranes of DHPVC with degrees of dehydrochlorination above a certain level, this method of dehydrochlorination over membranes is quite helpful to achieve that.

3.1.1.4. Electrical conductivity

DHPVC membranes were tested on four-point and two-point probes for sheet resistance and bulk resistance after doping with iodine for two hours in a chloroform solution of iodine. Nevertheless, all resistance values were so large that no detectable values were observed. As can be seen from SEM images in the related section, the cross-section structure looks quite porous and rough for almost all DHPVC membranes prepared with KO*t*Bu base. This sort of structure may suffer low conductivity due to poor contact of layers. Besides, XPS results and weight changes show that substitution reactions happen to a considerable degree. Weight loss of PVC membranes due to dehydrochlorination was usually observed less than expected despite high degree of dehydrochlorination. This also indicates that bulky and heavy *tert*-butoxide groups substitute Cls to some extent. As a consequence, attachment of several bulky *tert*-butoxide groups to polyvinyl chain may be playing a significant role in obstructing favorable contact between polyene chains.

3.1.2. Structural analysis
3.1.2.1. Structure of dehydrochlorinated PVC

When PVC and a strong base are mixed for chemical modification, principally two types of reaction take place. First one is an elimination reaction where HCls are removed from the backbone of PVC to form double bonds *via* E2 mechanism. Second one is a substitution reaction where *tert*-butoxide ($OC(CH_3)_3$) groups replace Cls of PVC *via* S_N2 mechanism. Nevertheless, the latter is less likely to occur than the elimination reaction because of its bulky size and resultant steric hindrance. Scheme 1 shows the possible structure of the resulting DHPVC product of PVC and KO*t*Bu reaction. In this structure, there are unreacted Cls, double bonds and dangling $OC(CH_3)_3$ substituents.
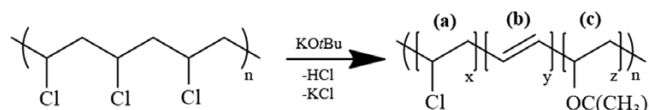

Scheme 1. Reaction scheme for dehydrochlorination reaction with KO*t*Bu: (a) Unreacted chloride, (b) dehydrochlorination product (C=C double bond), and (c) substitution product (ether).

3.1.2.2. Fourier transform infrared spectroscopy

Figure 3 shows FTIR spectra of PVC membrane and DHPVC membranes. The individual peaks are listed in Table 3.

As shown in Figure 3, PVC membrane shows strong signals at 1428, 1328, 1252, and 685 cm^{-1}. These peaks correspond to CH_2, CHCl, and C-Cl vibrations. In DHPVC membranes, however, the intensity of these characteristic peaks is getting weaker as more KO*t*Bu is used. In addition, new peaks appearing at 3016 (#2), 1677 (#9), 1632 (#10), and 1000 cm^{-1} (#20) indicate to the =CH (#2,#20) and C=C (#9,#10) peaks. These bands are sign of occurrence of dehydrochlorination and formation of double bonds subsequently. Since change of peak intensity is greater in DHPVCM10 (1:4) than in DHPVCM6 (1:0.25), it can be assumed that degree of dehydrochlorination is affected by the amount of strong base. In addition to these, C-O stretching mode and CH_3 deformation mode are observed at 1228 cm^{-1} and 1060 cm^{-1}, and 1378 cm^{-1}, respectively. These peaks can be attributed to *tert*-butyl groups which substitute Cls and form ethers. This is evidence to the fact that substitution reaction also takes place as a side reaction.

Hydroxide peaks observed around 3400 cm^{-1} is very likely an indicator of alcohol groups or enols of ketone groups which
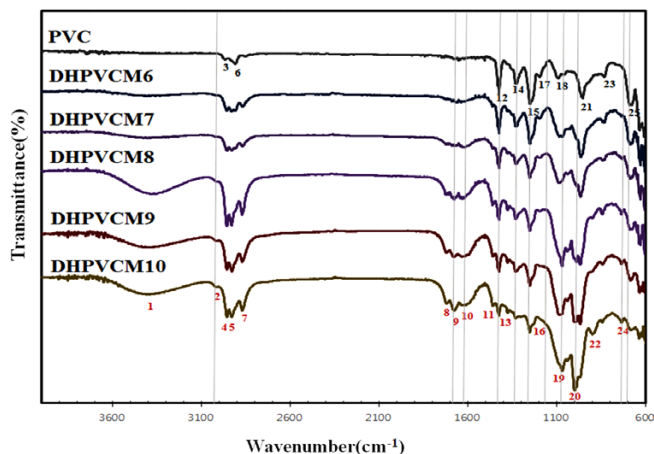
Figure 3. FTIR spectra of PVC and DHPVC membranes obtained by KO*t*Bu reaction at 50 °C.

Table 3. FTIR absorption peaks for PVC and DHPVC membranes

Peak number	Wave number (cm⁻¹)	PVC membrane	DHPVC membrane
1	3400	-	O-H stretching
2	3016	-	=C-H stretching
3,6	2973, 2912	CH₂ stretchings	-
4,5,7	2959, 2931, 2870	-	CH₂ stretchings (*shifts*)
8	1719	-	C=O stretching
9,10	1677, 1632	-	C=C stretchings
11,13	1461, 1378	-	Weak CH₂ and CH₃ deformations
12,14	1428, 1328	CH₂ deformation (*Wagg*)	CH₂ deformation (*Wagg*, *Weakened*)
15	1252	CCl out of plane angular deformation	CCl out of plane angular deformation (*Weakened*)
16	1228	-	C-O stretching
17	1200	CCl out of plane angular deformations	-
18	1096	C-C stretching	-
19	1060	-	C-O stretching
20	1000	-	=CH out of plane deformation
21,23	956, 834	CH deformations (*Rock*)	CH deformations (*Rock*)
22,24	899, 738	-	CH deformations (*New*)
25	685	CCl stretching	CCl stretching (*Weakened*)

formed *via* oxidation of double bonds. The progress of oxidation might be similar to that of *β*-oxidation observed in fatty acids. Under oxidative conditions, especially terminal double bonds of conjugated systems may catch oxygen with relative ease. This may evolve to a ketone, or else an epoxide may remain to turn to a diol when water is added. The peak at 1719 cm⁻¹ is indicative of such a ketone group.

3.1.2.3. ¹³C Solid NMR spectroscopy

Figure 4 shows ¹³C NMR spectrum of DHPVCM10 (1:4) taken at solid state of the membrane. The broad peak at 133.9 ppm indicates the presence of double bonds, which is the main point of this NMR analysis. In addition, a peak appears at 58.1 ppm which can be assigned to unreacted CHCl groups.[38] Weak peaks at 68.5 ppm and 78.0 ppm may denote carbons bound to oxygen of *tert*-butoxide group (#4 and #4'). Methylene groups (CH₂) shown with #2' and #2 in Figure 4 show peaks at 20.3 ppm (or

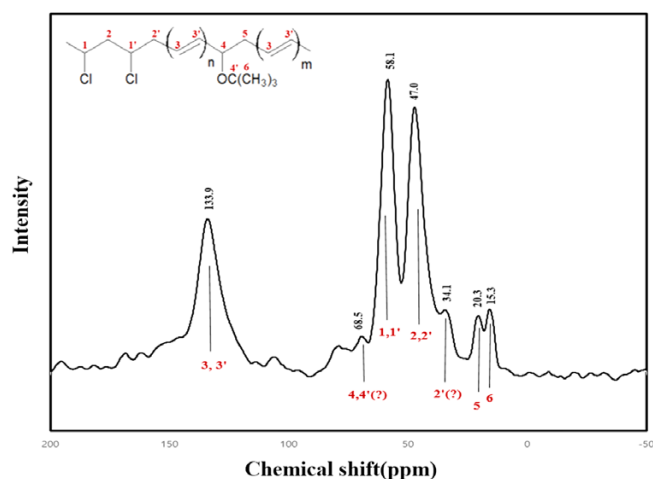**Figure 4.** ¹³C Solid NMR Spectrum of DHPVCM10 obtained by KO*t*Bu reaction.

34.1 ppm) and 47.0 ppm, respectively. The peak at 34.1 ppm (or the one at 20.3 ppm) can be assigned to the ethylene group denoted with #5. Methyl carbons of *tert*-butoxide group appear at 15.3 ppm.

3.1.3. X-ray photoelectron spectroscopy
3.1.3.1. Derivation of formulas

As shown in Scheme 1, when PVC and a strong base react, elimination and substitution reactions occur together with a competition. Elimination is the mainly aimed reaction in our work nonetheless substitution reaction occurs as well unavoidably. Double bonds formed *via* elimination reaction are subject to oxidation by aerial oxygen to some extent. Therefore, relative abundances of C, Cl, and O atoms were investigated by XPS analysis in order to calculate the relative degree of unsaturation (conjugated or single double bonds) caused by elimination reaction. Since XPS method is not suitable for measuring H content, this was additionally ascertained by elemental analysis (EA). Elemental ratios provided by XPS analysis and elemental analysis were used together to express the relevant abundances of C (N_C), Cl (N_{Cl}), O (N_O), H (N_H) atoms (Table 4). The H/C (N_H/N_C) ratio acquired from elemental analysis is multiplied by N_C value of the XPS data (Table 5) to obtain N_H value. The relative abundances of C and O atoms inherited from, and the relative numbers of Cl and H atoms that previously existed in pristine PVC resin were denoted with N_C^0, N_O^0, N_{Cl}^0, and N_H^0, respectively.

Degree of dechlorination (DoDC), degree of substitution (DoSub), degree of dehydrochlorination (DoDHC), and degree of unsaturation (DoUns) were calculated based on the found relative atomic abundance values. DoDC was calculated according to the ratio of Cl abundances before and after the reaction. DoDC involves both elimination and substitution reactions, since Cl can be removed either by elimination or by substitution reactions. DoSub is the expression for unavoidable concurrent replacement of Cls by *t*BuO⁻ base. DoSub value is subtracted

Table 4. Elemental ratios acquired by XPS and EA methods for PVC and DHPVC membranes produced by the reaction with KO*t*Bu at 25 °C and 50 °C for 24h. Ratio of H atoms was calculated by combining two data

	Sample name	C (%)	Cl (%)	O (%)	H/C (EA data)	H (XPS-EA)
	PVC	65.4	31.0	3.6	1.53	99.8
	DHPVCM1 (1:0.25)	68.0	26.0	6.0	1.48	100.5
	DHPVCM2 (1:0.5)	71.3	20.3	8.4	1.42	101.3
T=25 °C	DHPVCM3 (1:0.75)	74.8	16.0	9.2	1.37	102.8
	DHPVCM4 (1:1)	77.3	11.5	11.2	1.33	102.8
	DHPVCM5 (1:4)	81.7	5.5	12.7	1.27	103.7
	DHPVCM6 (1:0.25)	68.9	24.1	7.1	1.46	100.3
	DHPVCM7 (1:0.5)	74.3	17.0	8.7	1.41	104.5
T=50 °C	DHPVCM8 (1:0.75)	78.5	11.4	10.1	1.36	106.8
	DHPVCM9 (1:1)	80.3	6.6	13.1	1.32	106.0
	DHPVM10 (1:4)	83.8	1.2	15.0	1.26	105.6

Table 5. Degrees of dechlorination (DC), substitution (Sub), dehydrochlorination (DHC), and unsaturation (Uns) for DHPV membranes produced by the reaction with KO*t*Bu at 25 °C and 50 °C for 24 h. All degrees are based on initial Cl amount (N_{Cl}^0)

Sample name	DoDC (%)	DoSub (%)	DoDHC (%)	DoUns (%)
DHPVCM1 (1:0.25)	16.9	1.7	15.2	9.2
DHPVCM2 (1:0.5)	36.2	3.3	32.9	21.4
DHPVCM3 (1:0.75)	51.3	4.3	47.0	34.7
DHPVCM4 (1:1)	65.4	5.2	60.3	43.3
DHPVCM5 (1:4)	84.1	6.1	78.0	59.0
DHPVCM6 (1:0.25)	23.4	2.1	21.2	12.3
DHPVCM7 (1:0.5)	47.1	5.0	42.1	31.6
DHPVCM8 (1:0.75)	65.5	6.8	58.7	46.2
DHPVCM9 (1:1)	80.1	7.8	72.3	52.1
DHPVM10 (1:4)	96.6	8.2	88.4	64.5

from DoDC value to obtain the DoDHC value. DoUns values were calculated by taking the oxidation of the double bond into consideration, which was calculated by subtracting DoOxi value from DoDHC value.

From the atomic abundancies, relative number of C=C double bonds (expressed as number of unsaturation hereby, N_{uns}), relative number of oxidation incidents which took place on C=C double bonds (N_{oxi}), relative number of dehydrochlorination incidents (N_{DHC}), relative number of substitution incidents of Cls by *t*BuO⁻ anions (N_{Sub} or N_{tBu}) can be calculated by our derived formulas.

First of all, two coefficients denoted by (α) and (β) were used for ease to represent ratios of Cl and O atoms to C atoms in PVC resin material (Eq. (1)). Initial number of H atoms (N_H^0) is expressed by dependence on initial number of C atoms (N_C^0) (Eq. (1)).

Relative number of *tert*-butoxide groups attached to polymer chain *via* substitution in the reaction between PVC and KO*t*Bu/THF/*n*-BuOH mixture is calculated by Eq. (2). *tert*-Butoxide groups add 1 O, 4 C and 9 H atoms for each molecule. Therefore, its number is related to each of O, C, H atoms and those numbers can be used to find N_{tBu} (Eq. (2)). Final number of H atoms (N_H) can be calculated depending on N_H^0 (from Eq. (1)), N_{DHC} (from Eq. (7)), N_{tBu} (from Eq. (2)), and the number of oxidation incidents which resulted in diol formation if any (Eq. (3)). δ coefficient is described below.

In order to determine N_{oxi} happened for a product composed of 100 C, Cl, O atoms in total, a comparison of the amounts of

oxygen atoms in PVC and DHPVC is used. For oxidation of double bonds, two ways of oxidation can be assumed to have occurred: first one is monooxidation, which results in a carbonyl group such as in β-oxidation of fatty acids;[39] second one is dioxidation, which results in a diol. Therefore, an oxide coefficient denoted by δ was defined, which multiplies with N_{oxi} to express involvement of oxygens generated by oxidation, and can take values between 1 and 2. We assumed ketones form by a majority over diols hence a value of 1.0 was adopted to represent the number of oxygens joined to the structure *via* oxidation for the simplicity of calculations and approximations (Eq. (4)). N_C^0 inherited from pristine PVC resin can be expressed as dependent of N_H, N_{Cl}, N_O, and α, β, δ coefficients by reversing Eq. (3) (Eq. (5)). All other parameters were expressed as N_C^0 dependents. Relative abundance of Cl atoms previously existed in pristine PVC resin (N_{Cl}^0), can be calculated as a dependent of N_C^0 (Eq. (6)). This is used as a reference to determine all degrees. N_{DHC} can be found by Eq. (7) as a dependent of N_C^0. Then N_C^0 can be used to calculate N_{uns} since N_{oxi} can be readily determined by Eq. (4), which is also expressed as a dependent of N_C^0 found by Eq. (5). Subtraction of N_{oxi} from N_{DHC} gives N_{uns} (Eq. (8)).

All values are calculated by using XPS and EA data, and shown in Table 5. Changing trends can be followed on the graphs in Figure 5.

$$\alpha = N_{Cl}^0 / N_C^0; \quad \beta = N_O^0 / N_C^0; \quad N_H^0 = (2-\alpha) \times N_C^0 \tag{1}$$
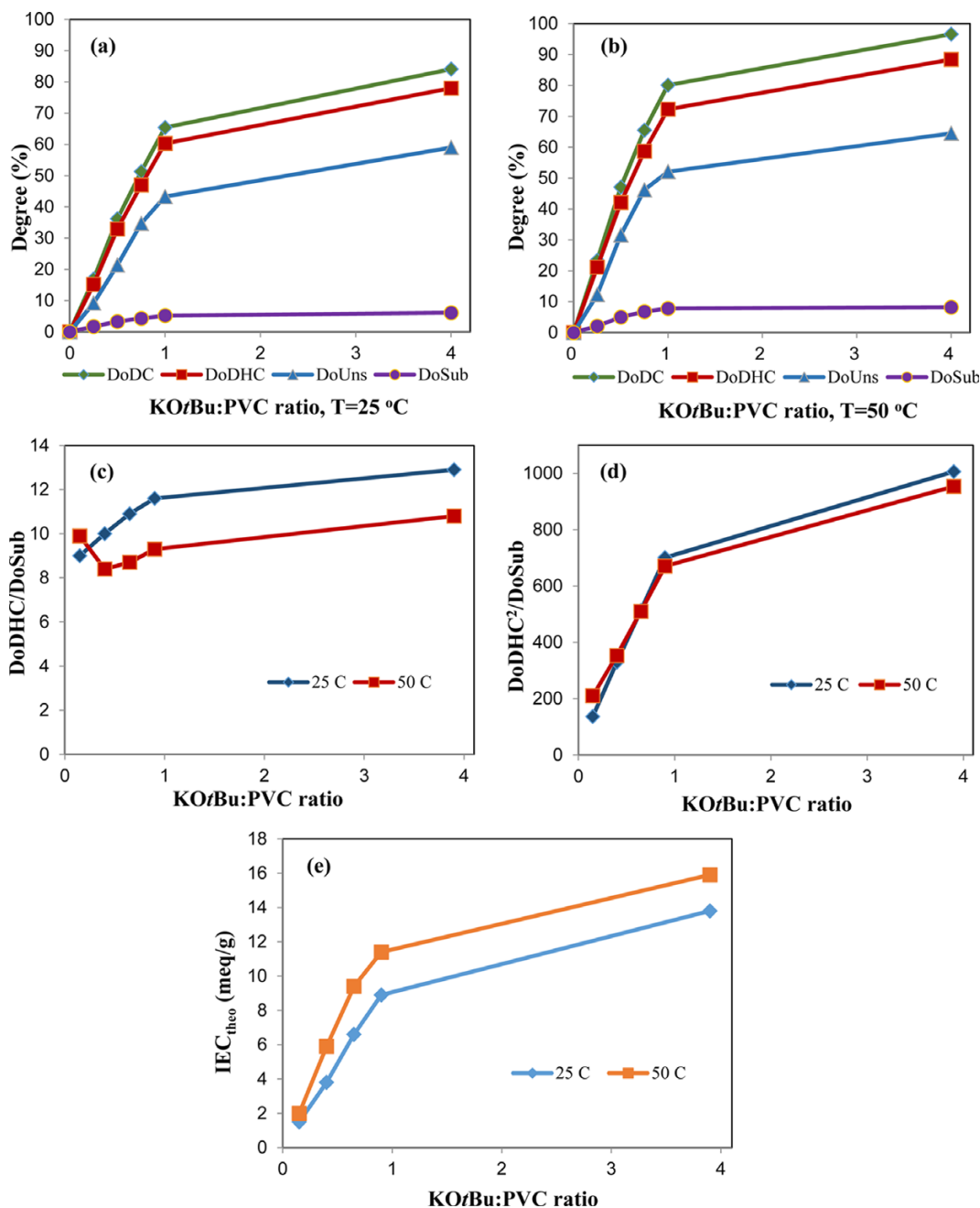
Figure 5. Trend of degrees of dechlorination (DC), dehydrochlorination (DHC), unsaturation (Uns) and substitution (Sub) for DHPVC membranes obtained by the reaction of PVC membrane with KO*t*Bu at (a) 25 °C and (b) 50 °C for 24 h. (c) Ratio of DoDHC/DoSub and (d) ratio of DoDHC^2/DoSub. (e) Trend of theoretical ion exchange capacities. All parameters are plotted against KO*t*Bu/PVC ratio.

$N_{tBu}=(N_C-N_C^0)/4$ from C atoms, and also
$N_{tBu}=N_O-N_O^0-\delta\times N_{oxi}$ from O atoms,
when δ is taken 1,

$$N_{tBu}=N_O-N_O^0-N_{oxi} \qquad (2)$$

$N_H=N_H^0-N_{DHC}+9N_{tBu}+2(\delta-1)\times N_{oxi}$
$=[(4\beta-4\delta\beta-4\delta\alpha-1)/(2\delta)]\times N_C^0+N_{Cl}+[(2\delta-2)/\delta]\times N_O+[(4\delta+1)/(2\delta)]\times N_C$,
when δ is taken 1,

$$N_H=(5/2)\times N_C+N_{Cl}-[(4\delta\alpha+1)/2]\times N_C^0 \qquad (3)$$

$N_{oxi}=[N_O-N_O^0-N_{tBu}]/\delta=[4N_O-N_C+(1-4\beta)N_C^0]/(4\delta)$,
when δ is taken 1,

$$N_{oxi}=[4N_O-N_C+(1-4\beta)N_C^0]/4 \qquad (4)$$

$N_C^0=[2\delta\times(N_H-N_{Cl})+4(1-\delta)\times N_O-(4\delta+1)\times N_C]/(4\beta-4\delta\beta-4\delta\alpha-1)$,
when δ is taken 1,

$$N_C^0=[5\times N_C+2\times(N_{Cl}-N_H)]/(4\alpha+1) \qquad (5)$$

$N_{Cl}^0=N_{Cl}+N_{tBu}+(N_{uns}+N_{oxi})=N_{Cl}+(N_O-N_O^0-\delta\times N_{oxi})+(N_{uns}+N_{oxi})$
$=N_{Cl}+N_O-N_O^0+N_{uns}+(1-\delta)\times N_{oxi}$,
when δ is taken 1

$$N_{Cl}^0=N_{Cl}+N_O-N_O^0+N_{uns} \qquad (6)$$

$$N_{DHC}=N_{Cl}^0-N_{Cl}-N_{tBu}=[(4\alpha+1)\times N_C^0-4N_{Cl}-N_C]/4 \qquad (7)$$

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$N_{uns} = N_{DHC} - N_{oxi}$

$= \{[(4\alpha+1)\times\delta+(4\beta-1)]\times N_C^0 - 4\delta\times N_{Cl} - 4\times N_O + (1-\delta)\times N_C\}/(4\delta),$

when δ is taken 1,

$N_{uns} = (\alpha+\beta)\times N_C^0 - N_{Cl} - N_O$ (8)

Degree of dechlorination (DoDC) $= 1-[N_{Cl}/N_{Cl}^0] = 1-[N_{Cl}/(\alpha\times N_C^0)]$ (9)

Degree of substitution (DoSub) $= N_{tBu}/N_{Cl}^0 = [(N_C-N_C^0)/4]/(\alpha\times N_C^0)$ (10)

Degree of dehydrochlorination (DoDHC) = DoDC-DoSub

$= 1-(1/\alpha)\times\{(1-4\beta)\times N_{Cl}+N_O-\beta\times N_C)/(N_C-4N_O)\}$ (11)

Degree of oxidation (DoOxi) $= N_{oxi}/N_{Cl}^0 = N_{oxi}/(\alpha\times N_C^0)$ (12)

Degree of unsaturation (DoUns) $= N_{uns}/N_{Cl}^0 =$ DoDHC$-$DoOxi (13)

W_{100} (g) $= 12.01\times N_C + 35.45\times N_{Cl} + 16.00\times N_O + 1.01\times N_H$ (14)

IEC_{theo} (meq/g) $= 1000\times N_{uns}/W_{100}$

$= 1000\times\{[((4\alpha+1)\times N_C^0 - 4N_{Cl}-N_C)/4] - N_{oxi}\}/W_{100}$ (15)

Through addition reactions on double bonds of DHPVC species, proper agents would be added to the polymer backbone in order to generate ionic sites for the sake of ionic exchanging. Either ionic addition of sulfonic acid groups and amines or addition of vinyl groups *via* free-radical polymerization can be used as means of giving ion exchange capability to DHPVC membranes. Therefore, it can be asserted that theoretical ion exchange capacity (IEC_{theo}) of such ion exchange polymers depends on the number of double bonds in the structure of membranes. This value can be calculated by using a virtual weight (W_{100}) of C, Cl, O atoms of 100 moles in total (Eq. (14)). Dividing number of double bonds (N_{uns}) to this weight (W_{100}) gives IEC_{theo} (Eq. (15)).

3.1.3.2. Degrees of reactions and theoretical ion exchange capacity (IEC_{theo})

As the used amount of base (KO*t*Bu) increases, dehydrochlorination and thus unsaturation degrees increase. Some substitution up to 12.9% takes place inevitably (Figures 5(a),(b)), but it is clearly outscored by elimination reactions (Figures 5(c),(d)). Figure 5(d) shows the cumulative efficiency of dehydrochlorination (DoDHC squared) over substitution sharply increases as base concentration is increased. This value does not differ much between two temperatures as unsaturation degrees are close. Figure 5(c) indicates that higher temperature promotes substitution reactions considerably as well as elimination reactions.

All reaction degrees are greater in case of 50 °C with respect to 25 °C as rate constants of reactions rise when temperature is elevated according to Arrhenius equation. Substitution and elimination reactions are second order herein. However, PVC membrane may be acting as a stationary solid phase. Therefore, the reaction proceeds according to a sort of pseudo-first order manner. Even though we did not collect kinetic data this time, reaction of PVC with KO*t*Bu/THF/*n*-BuOH system proceeds so slow that a satisfactory discoloration completes after at least 12-15 h. Especially *n*-BuOH is not compatible with PVC structure and it also obstructs penetration of KO*t*Bu into PVC. Again, it may not be a highly preferable solvent for KO*t*Bu indeed. Not-

withstanding, its mixture with THF worked well so far. We actually compared *n*-BuOH with *tert*-BuOH and cyclohexanol, which are other bulky alcohols, as a result *n*-BuOH was the most compatible with KO*t*Bu. Besides base and solvent factors, PVC itself would show a different behavior at different temperatures. PVC polymer becomes softer and expands at higher temperature so that KO*t*Bu can penetrate more into the lattice and this would increase the yield.

There is almost a linear relationship between the base amount (concentration) and the outcomes up to between 70-80% of dechlorination degree at 1:1 KO*t*Bu:PVC ratio. When this ratio nears 1, linear trend disappears due to a possible overload or saturation of the system. Maximum dechlorination ratio has been 96.6% for the reaction at 50 °C and 84.1% for 25 °C. In spite of the disadvantage of long time required for the reaction, dechlorination ratio can be deemed quite satisfactory. Highest dehydrochlorination and unsaturation degrees have been 88.4% and 64.5%, respectively. The difference between these arises from the altered double bonds consumed by oxidations. Ketone and alcohol peaks observed on FTIR spectra support this inference. However, we assumed in our calculations that most of the oxidation would result in ketone groups *via* one oxygen atom capture (monooxygen oxidation). After all, we can conclude that a good deal of unsaturation degree can be achieved by KO*t*Bu dehydrochlorination method.

We are envisioning to further functionalize these highly unsaturated and conjugated DHPVC membranes for several applications spanning from semiconductors to ion exchange membranes and battery membranes. Particularly, atom transfer radical polymerization (ATRP) method can be used to attach functional groups to the double bonds. For this reason, we esteem the number of double bonds in DHPVC membrane is the key factor for understanding the capacity of membrane material to be used in any application. To put in another way, we can define an "active site index" for materials carrying potentiality to be used as precursors for making functional materials. This is a ratio of number of potential sites in the material to its weight. To illustrate, active site index can be a precursor for ion exchange capacity in case that all active sites can be modified to desired functional groups. Hence, we referred to this as theoretical ion exchange capacity (IEC_{theo}) in our calculations and graphical representations. IEC_{theo} was found 15.9 meq/g for 50 °C, and 13.9 meq/g for 25 °C. This value is correlated with number of double bonds, N_{uns} and degree of unsaturation, DoUns (Eqs. (14), (15)). These are extremely high and actually impractical IEC values, yet highly promising for high IEC ion exchange membrane development.

3.1.4. UV-Visible spectroscopy

It can be perceived from spectra of DHPVC6 to DHPVC10 that wavelength range of bands broadens and this range tends to extend towards longer wavelengths (red shift). In other words, $\lambda_{max-edge}$ value and mean wavelength of the band tend to shift towards red region. This is because the band gap between HOMO&LUMO narrows, as longer conjugation sequences form (Figure 6). This is in accordance with the fact that by increasing the degrees of dehydrochlorination and unsaturation by increasing the amount of the base (*tert*-butoxide, *etc*), longer conjugations
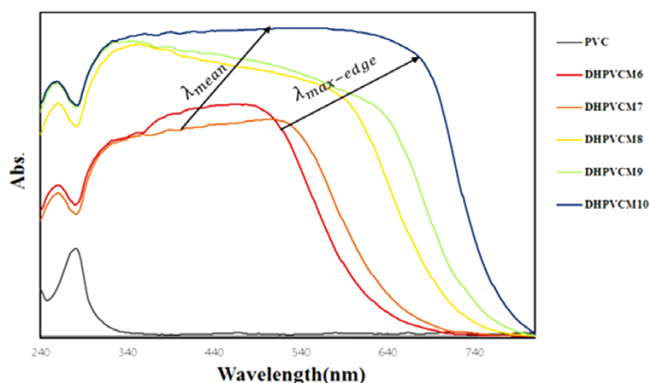
Figure 6. UV-Visible spectra of PVC and DHPVCM6 (1:0.25), DHPVCM7 (1:0.5), DHPVCM8 (1:0.75), DHPVCM9 (1:1), DHPVCM10 (1:4) membranes obtained by the reaction with KOtBu at 50 °C for 24 h (PVC:base ratios in parantheses).

Table 6. $\lambda_{max\text{-}edge}$ measured by UV-Vis spectroscopy and corresponding conjugation number (n) values calculated for DHPVC membranes obtained by the reaction with KOtBu at 50 °C for 24 h

Sample name	$\lambda_{max\text{-}edge}$ (nm)	n
DHPVCM6 (1:0.25)	505	12
DHPVCM7 (1:0.5)	523	13
DHPVCM8 (1:0.75)	600	17
DHPVCM9 (1:1)	627	19
DHPVCM10 (1:4)	675	22

can be obtained. It can be inferred from the figure that the length of conjugation sequences is not fixed around a certain value rather it is ranging within a broad interval. Therefore, we can allege that there are several double bonds standing alone and also conjugations start from 2 double bonds and may built by up to several 10 s or more conjugated double bonds.

We developed an empiric formula to demonstrate the relationship of λ_{max} with conjugation number (n). Herein, since frequency of λ_{max} depends on several factors and can be located in

anywhere within a broad band, we focused on $\lambda_{max\text{-}edge}$, which is the maximum absorption near the right end of the absorbance band. This approximation may be helpful for establishing an understandable relationship about how the amount of dehdy-rochlorination agent affects the conjugation length. Sondheimer *et al*. worked on this kind of relations observed in UV-Vis spectroscopy.[40] We used their approximations to set the following equation which assumes a linear relationship between λ^2_{max} and n: $\lambda^2_{max} = \alpha \times n$. $\lambda_{max} \approx 481$ nm was the maximum absorption of n≈11 samples in their work. So, the alpha coefficient can be taken as 21,032 nm². For DHPVCM6, $\lambda_{max\text{-}edge}$(1:0.25)≈505 nm, and for others has been as follows: $\lambda_{max\text{-}edge}$(1:0.5)≈523 nm, $\lambda_{max\text{-}edge}$ (1:0.75)≈600 nm, $\lambda_{max\text{-}edge}$(1:1)≈627 nm, $\lambda_{max\text{-}edge}$(1:4)≈675 nm (PVC:KO$t$Bu ratio in the bracket). Approximate conjugation lengths are found as follows: $n_{0.25}$≈12, $n_{0.5}$≈13, $n_{0.75}$≈17, $n_{1.0}$≈19, $n_{4.0}$≈22 (Table 6).

Even though absorbance at these wavelengths may not be the highest in some of the cases, this trend shows the consistent influence of reaction conditions on the length of conjugation. As can be seen from Figure 1, the color of the membranes is also in a trend of decoloring. Longer conjugations and growing absorbance range causes darkening of the orange color to brown and then to black.

3.1.5. SEM images

Figure 7 shows the surface and cross section images of PVC and DHPVC products. As can be seen in Figure 7(a), no peculiarities were observed on the surface of initial PVC membrane. However, as shown in Figures 7(b) and (c), as dehydrochlorination ratio increased, PVC surface deformed and stoma like pores formed. Similar to the surface, cross section of PVC membrane had a clean view initially, but more pores, voids and undulated layers were observed as dehydrochlorination rate increased. THF solvent is being absorbed and PVC swells to some extent. Such swelling, slight dissolution of PVC and accumulation of KCl crystals within the membrane would be the causes of such pores, voids and wavy layers. A subsequent washing-off of KCl
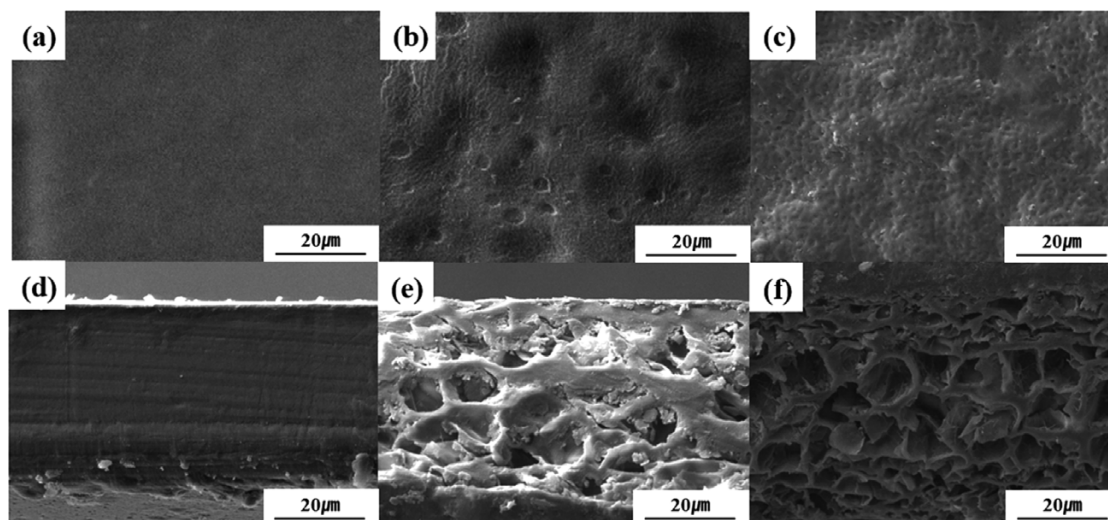
Figure 7. Surface SEM images of PVC and DHPVC membranes obtained by the reaction with KOtBu at 50 °C for 24 h: (a) PVC, (b) DHPVCM7 (1:0.5), (c) DHPVCM10 (1:4). Cross section images of PVC and DHPVC membranes: (d) PVC, (e) DHPVCM7 (1:0.5), (f) DHPVCM10 (1:4) (PVC:KOtBu ratio in the bracket).
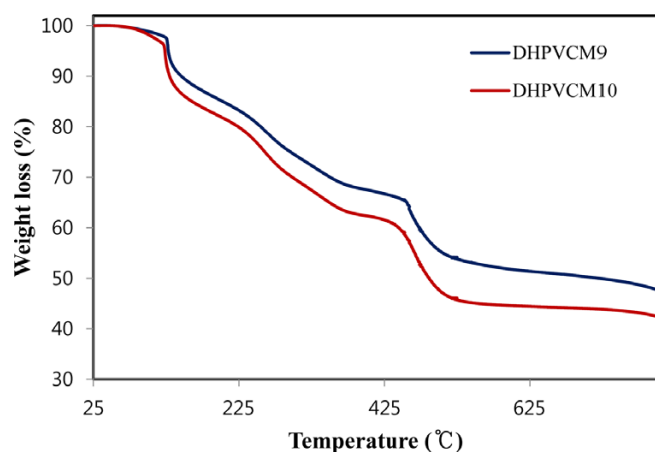
Figure 8. TGA curves of DHPVCM9 (1:1) and DHPVCM10 (1:4) obtained by the reaction with KOtBu at 50 °C for 24 h.

Figure 9. Photographs of (a) PVC, (b) DHPVCM11 (1:0.5), (c) DHPVCM12 (1:1), and (d) DHPVCM13 (1:4) obtained by the reaction with KOH/PEG 400 at 25 °C.

Figure 10. Photographs of (a) DHPVCM11 (1:0.5), (b) DHPVCM12 (1:1), and (c) DHPVCM13 (1:4) dissolved in THF (obtained by the reaction with KOH/PEG 400 at 25 °C for 4 h).

would leave such voids.

3.1.6. Thermal analysis

Figure 8 shows TGA curves obtained by treating two selected DHPVC membranes with increasing temperature and recording changes in their weight. DHPVC membranes possess a complicated composite structure. It is rather different than PVC polymer which mainly consists of (-CH_2-CHCl-) units. An irregularly substituted polyacetylene-like backbone, confined KCl molecules left after washing, absorbed solvents (n-butanol) are the main components of the solid-phase structure. There might be cross-linking between the chains as well.

Degradation of alcohol impurities as $tert$-BuOH, evaporation of any left n-BuOH and dehydration would be the cause of first mass loss starting around 125 °C. Pendent HCls left from elimination reaction begin thermal dehydrochlorination from lowere temperatures and maximizes around 300 °C. After thermal elimination of HCl, aromatic compounds leave the structure around 450 °C, and also polymer backbones tend to cross-link more and cyclic moieties start to form as well.
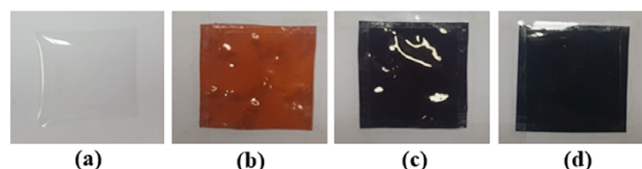
DHPVCM9 and DHPVCM10 show a similar pattern, but there is a difference in mass loss. From about 235 °C, the difference began to grow, with a final difference of about 6% around 800 °C. This difference appears to be due to the difference in degrees of dehydrochlorination. DHPVCM10 membrane exhibited greater mass loss where more content removal had occurred with elimination reaction. Actually, Cl content is slightly lower in DHPVCM10 and less dehydrochlorination would be expected, however it did not come out so. However, it can be claimed that more unsaturated and conjugated liner chain system with such a composite structure would be less stable and subject to greater extent of decomposition under thermal treatment.
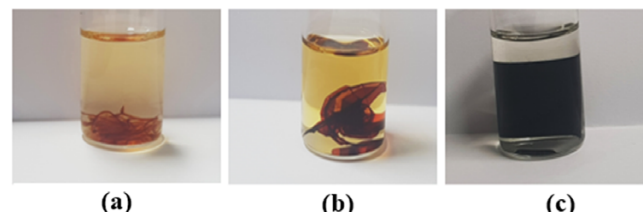
3.2. Dehydrochlorination with KOH

3.2.1. Physical properties
3.2.1.1. Discoloration

Figure 9 shows the color change of PVC membranes reacted with KOH. As shown in Figures 1 and 2, as the amount of strong base used in the reaction increases, color of membrane gradu-

ally becomes darker. Due to assistance of PEG 400 catalyst, discoloration occurs faster here than in KOtBu reaction which lasted 24 h for denser discoloration though. Color and conjugation length relation will be discussed later. However, hydroxide and $tert$-butoxide bases behave essentially differently and their strengths of basicity are different so that such discoloration difference has been observed as a result.

3.2.1.2. Solubility

Membranes cut into 1 cm×1 cm size were placed in 5 mL vials containing THF, DMAc, DMSO, and NMP. None of the membranes dissolved in these solvents. As observed in solubility tests of DHPVC-KOtBu membranes, highly dechlorinated/dehydrochlorinated DHPVC is not satisfactorily soluble in THF or other solvents (Figure 10). Therefore, this method provides opportunity to fabricate membranes of highly dechlorinated PVC (DHPVC).

3.2.2. Structural analysis
### 3.2.2.1. Structure of dehydrochlorinated PVC

A possible reaction scheme for PEG-catalyzed reaction of PVC and PVC was depicted below (Scheme 2). Similar to the reaction with KOtBu, both elimination and substitution reactions may happen simultaneously. Major product is expected to be that of elimination and minor product is alcohol groups, which is the main difference between KOH and KOtBu reaction products. Hydroxide does not suffer a steric hindrance as $tert$-butoxide does when acting as a nucleophile. Hence we may observe higher oxygen atomic ratios in KOH reaction prod-
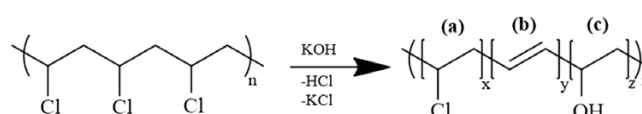
Scheme 2. Reaction scheme for dehydrochlorination reaction with KOH: (a) unreacted chloride, (b) dehydrochlorination product (C=C double bond), and (c) substitution product (alcohol).

Table 7. FTIR absorption peaks for PVC and DHPVC membranes obtained by the reaction with KOH/PEG 400 at 25 °C

Peak number	Wave number (cm⁻¹)	PVC membrane	DHPVC membrane
1	3660	-	OH stretching
2	2988	-	CH₂ stretching
3	2973	CH₂ stretching	-
4	2912	CH₂ stretching	CH₂ stretching
5	1720	-	C=O stretching
6	1660	-	C=C stretching
7	1428	CH₂ deformation (*Wagg*)	CH₂ deformation (*Wagg*)
8	1392	-	CH₂ deformation (*Wagg*)
9	1328	CH₂ deformation (*Wagg*)	CH₂ deformation (*Wagg, Weakened*)
10	1252	CCl out of plane angular deformation	CCl/CO out of plane angular deformation
11	1096	C-C stretching	-
12	1062	-	C-O stretching
13	956	CH deformations (*Rock*)	CH deformations (*Rock, weakened*)
14	894	-	CH deformations (*New*)
15	834	CH deformations (*Rock*)	-
16	685	CCl stretching	CCl stretching (*Weakened*)
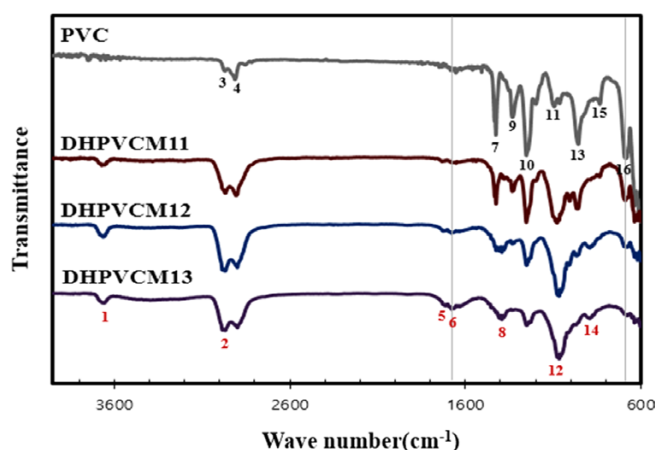
Figure 11. FTIR spectra of PVC and DHPVC membranes obtained by the reaction with KOH/PEG 400 at RT (~25 °C).

ucts than in KO*t*Bu products given that other conditions are identical.

3.2.2.2. Fourier transform infrared spectroscopy

FTIR spectra of PVC membrane, DHPVC membranes are shown in Figure 11 and the individual peaks are listed in Table 7. As shown in Figure 11, strong bands around 1660 cm⁻¹ (#6) appeared for samples DHPVCM 12 (1:1), DHPVCM13 (1:4). This peak indicates the presence of double bonds generated by the dehydrochlorination reaction. Peak intensity is greater in DHPVCM13 (1:4) than in DHPVCM12. It was also confirmed that the charac-

teristic peak of PVC gradually decreased from DHPVCM11 to DHPVCM13 (1428 cm⁻¹ (#7), 1328 cm⁻¹ (#9), 1252 cm⁻¹ (#10)). OH stretching peak appears around 3660 cm⁻¹ (#1), which is indicative of occurrence of S_N2 reaction between PVC and OH⁻. A strong peak around 1062 cm⁻¹ (#12) can be attributed either to C-O bond, which is between PVC chain and new OH group, or to C-C bond.

3.2.3. X-Ray photoelectron spectroscopy
3.2.3.1. Derivation of formulas

Elemental ratios of PVC and DHPVC membranes aquired by XPS and elemental analysis (EA) are shown in Table 8. In case of PVC and KOH/THF/PEG reaction, there are C atoms contributed by substitution, and hence abundance of C atoms is not altered. On the other hand, each hydroxide anion substituting a Cl brings 1 O and 1 H along. All these factors are considered, some formulas slightly differ from previous ones, though basics are same. Ratio of H and C atoms (H/C or N_H/N_C) is denoted by "v" for simplicity of formulas (Eqs. (16), (17)). Eq. 19 was extended and Eq. (20) was solved by relating 4 equations to each other (Eqs. (19)-(22)). Abundance of substitution incidents (N_{sub}) can be derived from the difference of abundances of oxygens coming from different sources (Eq. (22)). Abundance of dehydrochlorination (N_{DHC}) can be derived from the change of Cl atom abundances caused by elimination and substitution (Eq. (23)). Abundance of double bonds (N_{uns}) is found by Eq. (24). All reaction degrees (DoDC, DoDHC, DoSub, DoUns) can be calculated in a simpler fashion than in KO*t*Bu calculations due to simpler

Table 8. Elemental ratios acquired by XPS and elemental analysis (EA) methods: PVC membrane & DHPVC membranes produced by a reaction with KOH/PEG 400 at 25 °C during 4h. Ratio of H atoms were calculated by combining two data

Sample name	C (%)	Cl (%)	O (%)	H/C (EA data)	H (XPS-EA)
PVC	65.4	31.0	3.6	1.53	99.8
DHPVCM11 (1:0.5)	70.0	21.6	8.4	1.43	99.8
DHPVCM12 (1:1)	76.3	10.1	13.6	1.34	101.9
DHPVCM13 (1:4)	81.5	2.4	16.1	1.26	102.6

Table 9. Degrees of dechlorination (DC), substitution (Sub), dehydrochlorination (DHC) and unsaturation (Uns) for DHPV membranes produced by the reaction with KOH/PEG 400 at 25 °C during 4 h. All degrees are based on initial Cl amount (N_{Cl}^0)

Sample name	DoDC (%)	DoSub (%)	DoDHC (%)	DoUns (%)
DHPVCM11 (1:0.5)	34.8	7.0	27.8	21.0
DHPVCM12 (1:1)	72.3	16.1	56.2	46.2
DHPVCM13 (1:4)	93.7	18.9	74.8	63.5

structure of -OH than that of -OtBu group and the values are shown in Table 9. Theoretical ion exchange capacity can be found *via* number of double bonds, N_{uns}, and weight of total 100 moles of C, Cl, O atom system, W_{100}, parameters again (Eqs. (30), (31)).

$$\nu = N_H/N_C; \nu_0 = N_H^0/N_C^0 \text{ hence "} \nu_0 = 2-\alpha \text{" from Eq. (1)} \quad (16)$$

$$N_H = \nu \times N_C; N_H^0 = \nu_0 \times N_C^0 = (2-\alpha) \times N_C^0 = \nu_0 \times N_C \text{ since } N_C^0 = N_C \quad (17)$$

$$N_{Cl}^0 = \alpha \times N_C^0 = \alpha \times N_C; N_O^0 = \beta \times N_C^0 = \beta \times N_C \quad (18)$$

$$N_H = N_H^0 - N_{DHC} + N_{sub} + 2(\delta-1) \times N_{oxi} = \nu \times N_C \quad (19)$$

$N_{oxi} = (N_O - N_O^0 - N_{sub})/\delta$ when N_{sub} is retrieved from Eq. (18),
$$N_{oxi} = 0.5 \times [(\nu_0 - \nu - \alpha - 2\beta) \times N_C + N_{Cl} + 2N_O]$$
$$= 0.5 \times [(2-2\alpha-\nu-2\beta) \times N_C + N_{Cl} + 2N_O] \quad (20)$$

$$N_{Cl}^0 = N_{Cl} + N_{sub} + N_{DHC} = \alpha \times N_C^0 = \alpha \times N_C \quad (21)$$

$N_{sub} = N_O - N_O^0 - \delta \times N_{oxi} = N_O - \beta \times N_C - \delta \times N_{oxi}$,
when δ is taken 1,
$$N_{sub} = N_O - \beta \times N_C - N_{oxi} = (\alpha+0.5\nu-1) \times N_C - N_{Cl} - N_O \quad (22)$$

$$N_{DHC} = N_{Cl}^0 - N_{Cl} - N_{sub} = \alpha \times N_C - N_{Cl} - N_{sub}$$
$$N_{DHC} = (1-0.5\nu) \times N_C + N_O \quad (23)$$

$$N_{uns} = N_{DHC} - N_{oxi} = (\alpha+\beta) \times N_C - 0.5 \times N_{Cl} \quad (24)$$

Degree of dechlorination (DoDC)$= 1-[N_{Cl}/N_{Cl}^0]$
$$= 1-[N_{Cl}/(\alpha \times N_C)] \quad (25)$$

Degree of substitution (DoSub)$= N_{sub}/N_{Cl}^0 = N_{sub}/(\alpha \times N_C) \quad (26)$

Degree of dehydrochlorination (DoDHC)$=$ DoDC - DoSub
$$= 1-(1/\alpha) \times \{(1-4\beta) \times N_{Cl} + N_O - \beta \times N_C)/(N_C - 4N_O)\} \quad (27)$$
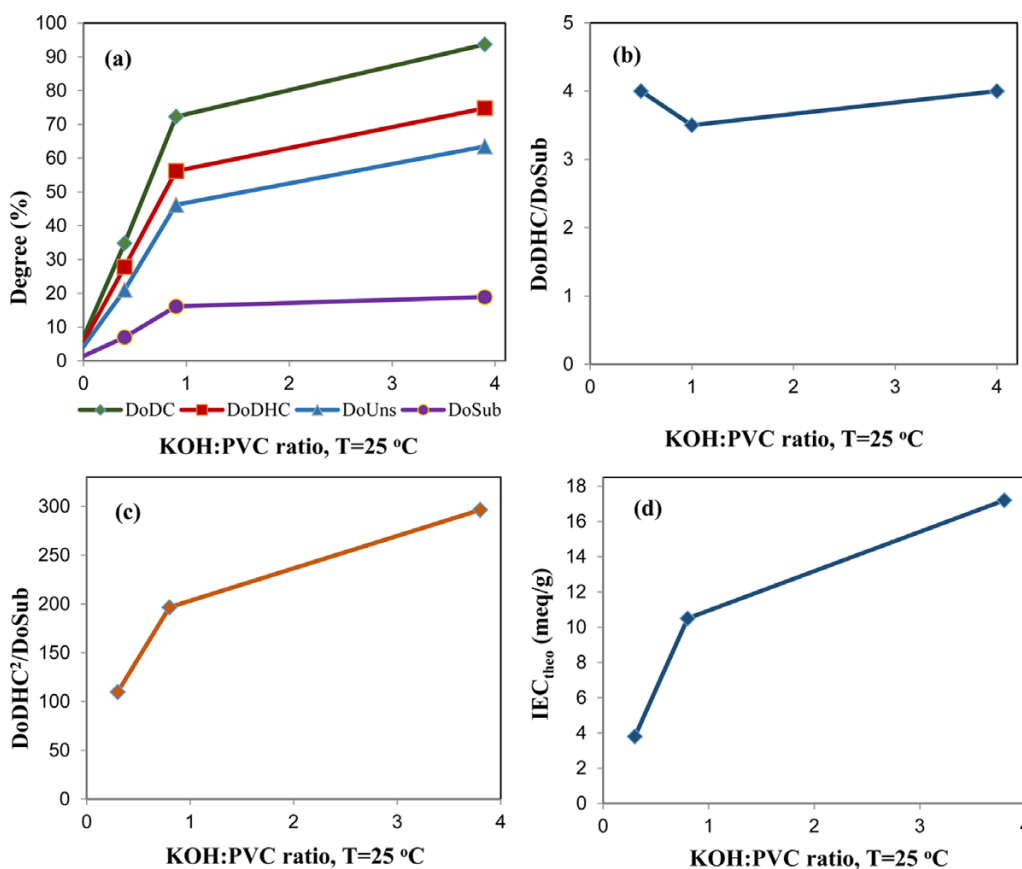
Degree of oxidation (DoOxi)$= N_{oxi}/N_{Cl}^0 = N_{oxi}/(\alpha \times N_C^0) \quad (28)$

Degree of unsaturation (DoUns)$= N_{uns}/N_{Cl}^0 =$ DoDHC$-$DoOxi $\quad (29)$

$$W_{100} (g) = 12.01 \times N_C + 35.45 \times N_{Cl} + 16.00 \times N_O + 1.01 \times N_H \quad (30)$$

IEC$_{theo}$ (meq/g)$= 1000 \times N_{uns}/W_{100}$
$$= 1000 \times [(\alpha+\beta) \times N_C - 0.5 \times N_{Cl}]/W_{100} \quad (31)$$


Figure 12. Trend of degrees of dechlorination (DC), dehydrochlorination (DHC), unsaturation (Uns) and substitution (Sub) for DHPVC membranes obtained by the reaction of PVC membrane with KOH at 25 °C for 4 h. (b) Ratio of DoDHC/DoSub and (c) ratio of DoDHC^2/DoSub. (d) Trend of theoretical ion exchange capacities. All parameters are plotted against KOH/PVC ratio.

3.2.3.2. Degrees of reactions and theoretical ion exchange capacity (IEC$_{theo}$)

KOH and KOtBu reactions differ in many ways. KOH or NaOH have not performed sufficient reactivity against PVC membrane even if a 10 M aqueous solution or a methanol or ethanol solution was used. Guo *et al.* used a PEG 400 solution of KOH to introduce it into a THF solution of PVC, and very high dehydrochlorination and dechlorination yields were achieved.[27] PEG has acted as a good solvent for KOH, and above all as a good catalyst for KOH and PVC reaction. These reactions completed within a few hours only. So, we modified this procedure to make it applicable for membrane systems. Using more PEG 400, which bears alcohol groups, to mix with THF at 3:1 ratio stopped PVC membrane from dissolving in THF to a great extent. The system worked very well and completed within a few hours.

Highest degree of dechlorination has been 93.7%, which is quite comparable to KOtBu system. Degree of unsaturation has been 63.5% at most. Degree of substitution has been almost two-fold of KOtBu system, mostly likely because of the smaller size of hydroxide base and also catalyst effect of PEG 400. Figures 12(b) and (c) demonstrate the result of this comparison
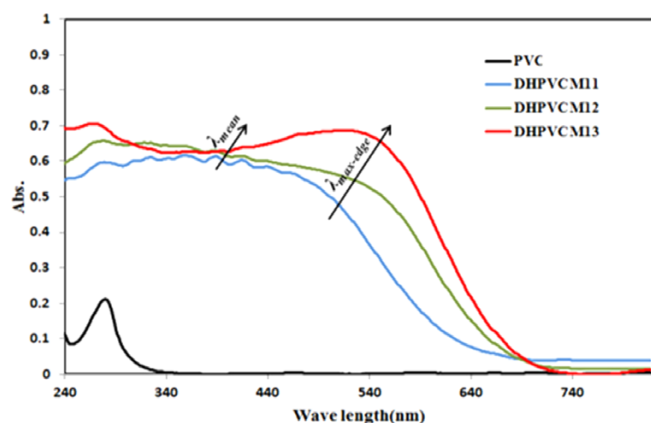
Table 10. $\lambda_{max-edge}$ and corresponding conjugation number (n) values measured (UV-Vis) and calculated for DHPVC membranes obtained by the reaction with KOH at 25 °C for 4 h

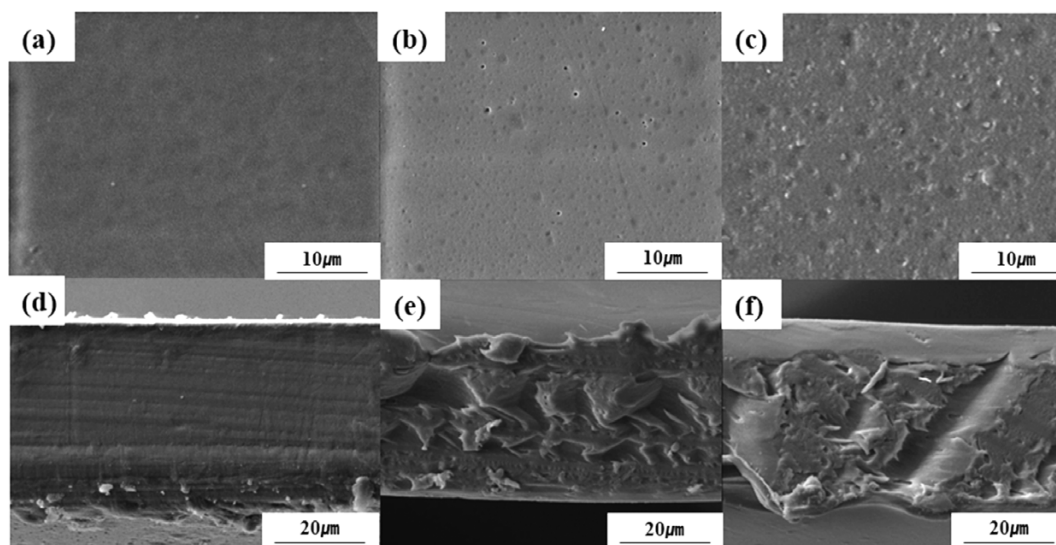| Sample name	$\lambda_{max-edge}$ (nm)	n
DHPVCM11 (1:0.5)	523	11
DHPVCM12 (1:1)	627	15
DHPVCM13 (1:4)	675	16

well when compared to graphs of Figure 5. On the other hand, ion exchange capacity of DHPVC membranes obtained by KOH/PEG 400/THF system would be as high as 17.2 meq/g theoretically. Substitution of Cls by hydroxide causes decrease in weight at all rates, however OtBu group is a much heavier one. Lighter weight of KOH-DHPVC membranes would promote IEC$_{theo}$.

3.2.4. UV-Visible spectroscopy

Figure 13 shows that spectra of DHPVC11-13 show a similar trend to those of DHPVC6-10 membranes. Range of the band enlarges towards red region, absorbance increases and discrete absorbance peaks turn to more continuous bands. Use of more KOH causes intensified unsaturation and longer conjugations apparently.

By the means of formula derived by Sondheimer *et al.*[40] ($\lambda_{max}^2 = \alpha \times n$; $\alpha = 21032$ nm^2), following conjugation lengths have been found for DHPVC-KOH membranes: for DHPVCM11, $\lambda_{max-edge}$ (1:0.5)≈492 nm, and for others has been as follows, $\lambda_{max-edge}$ (1:1)≈555 nm, $\lambda_{max-edge}$(1:4)≈572 nm (PVC:KOH ratio in the bracket). Approximate conjugation lengths are suggested as follows: $n_{0.5}$≈11, $n_{1.0}$≈15, $n_{4.0}$≈16 (Table 10). According to these results, there is a correlation between discoloration and conjugation length trends.

Similar amounts of KOtBu and KOH causes generation of conjugation sequences of slightly different lengths. Color intensities of similarly prepared DHPVC-KOtBu and DHPVC-KOH differ in a way that supports this deduction. Sterically hindered *tert*-butoxide base would prefer thermodynamically more preferred

Figure 13. UV-Visible spectra of PVC and DHPVC membranes obtained by the reaction with KOH/PEG 400 at 25 °C for 4 h.

Figure 14. Surface SEM images of PVC and DHPVC membranes obtained by the reaction with KOH/PEG 400 at RT (~25 °C) for 4 h: (a) PVC, (b) DHPVCM11 (1:0.5), (c) DHPVCM13 (1:4). Cross section images of PVC and DHPVC membranes: (d) PVC, (e) DHPVCM11 (1:0.5), (f) DHPVCM13 (1:4).
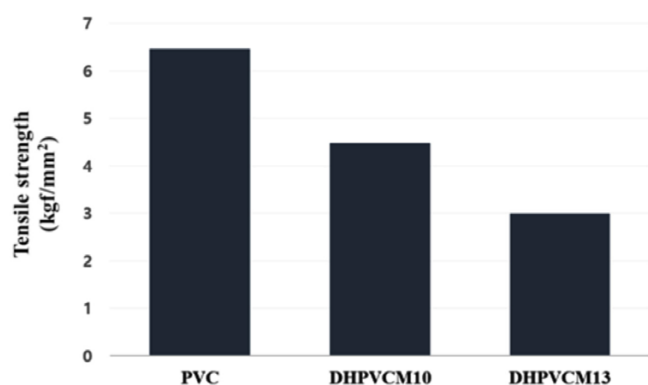
Figure 15. Tensile strength of PVC, DHPVCM10 (KOtBu), and DHPVCM13 (KOH).

longer conjugations, however tiny hydroxide base would be kinetically more advantageous to hydrogens at various positions on the polymer chain.

3.2.5. SEM images

Figure 14 shows the surface and cross section images of PVC and DHPVC products prepared by the reaction of PVC membrane with KOH/PEG 400/THF mixture. Surface of the membranes and also cross-sections in particular were less modified morphologically when compared to those of KOtBu products. DHPVC-KOH membranes have smoother and more continuous structure. There are less pores on the surface and large pores or deformations are not seen throughout the cross-section. This would explain why Guo *et al.* could observe relatively good electrical conductivity for iodine doped DHPVC membranes, whereas sheet resistance has been overwhelmingly high for DHPVC-KOtBu membranes so that these membranes can be called insulators like their parent PVC membrane.

3.3. Mechanical properties of PVC and DHPVC membranes

Figure 15 depicts a bar graph comparing tensile strength values of PVC membrane and DHPVC membranes. Tensile strength of PVC (7.5 kgf/mm^2) decreases to 4.5 kgf/mm^2 and 3.0 kgf/mm^2 after dehydrochlorination with KOtBu and KOH, respectively. Tensile strength of PVC accords well with average tensile strength value of PVC membranes. Since the abundance of polar C-Cl bonds diminishes in the structure of the polymer due to dehydrochlorinaton, intermolecular interactions are expected to weaken. Therefore, we regard this intrinsic structural change causes a weakening in the tensile strength of membranes by 40% (KOtBu) and 60% (KOH). Degrees of dehydrochlorination are similar in case of DHPVCM10 and DHPVCM13. It is not very clear here to us what the main reason may be to cause such a difference in the mechanical strengths of two membranes. However, we know well that OH- anions can diffuse into the depth of the membrane better than tBuO- anions can do. Therefore, a chemical and structural alterations are more likely to happen in a wider scale of the polymer lattice in case of KOH reaction. Dehydrochlorination and

other side reactions would happen more in KOH reaction and the intermolecular interactions of the resulting polymer would have become weaker.

Elongation of all three kinds of membranes have occurred around 0.1%, and the membranes broke sooner than we expected, which suggests that the elasticity of either membrane is quite low. Therefore, calculation of Young's Modulus resulted abnormally high values. PVC and DHPVC membranes are flexible, yet rather tough materials.

4. Conclusions

Dehydrochlorination of PVC membranes has been carried out successfully by using two different dehydrochlorination agents: KOtBu and KOH. Highly dechlorinated DHPVC membranes were synthesized which also contain long conjugation sequences. If not started with PVC membrane, DHPVC membranes which underwent more than ~45% dechlorination could not be prepared since low solubility of dehydrochlorinated PVC would be a handicap to cast membranes from DHPVC resin, a powder product. This method proposed by this work brings along a fair solution to the difficulty of manufacturing such DHPVC membranes. Dechlorination and unsaturation degrees can be controlled with manipulating used base, solvent, catalyst, temperature, concentration etc. Various colors, solubilities, morphologies, membrane texture and mechanical properties can be achieved by modifying those parameters.

DHPVC membranes obtained by dehydroclorination reaction with KOtBu/THF/*n*-BuOH system yielded 64.5% unsaturation and 96.6% total dechlorination within 24 h. These are quite satisfactory degrees of reactions in several ways. Dechlorinating PVC to such a great extent is appreciable for recycling efforts. Also, highly unsaturated products can be benefitted for manufacturing new application materials. On the contrary, besides use of KOtBu base whose handling is inconvenient, disadvantageous cost aspect and requirement of long time for the reaction are drawbacks of this system. Moreover, DHPVC structure is supposed to resemble that of polyacetylene hence some conductivity would be expected. However, KOtBu membranes did not show any detectable conductivity so far since membrane structure deforms inside the lattice so that electrical conductivity may not be observed probably due to such deformed structure and also distracting effect of *tert*-butoxide groups bound to polymer chain.

Having little reactivity over PVC when used as aqueous or alcohol solution, KOH acts as a good dehydrochlorinating agent in the presence of PEG 400 catalyst as demonstrated by others before on PVC dissolved in THF. KOH was used for the first time directly on a PVC membrane as a dehydrochlorination agent and the yield has been satisfactory. Up to 63.5% of unsaturation and 93.7% of total dechlorination was achieved with KOH agent within just 4 h. With respect to KOtBu system, KOH reaction system requires shorter time, uses reagents with smaller cost, which are also easier to prepare and handle. In addition to these, it provides membranes with smoother texture and structure. These factors make it a more convenient dehydrochlorination agent over KOtBu.

Finally, it is worth mentioning promising aspects of this work for recycling PVC and manufacturing valuable technological devices out of PVC. PVC waste can be classified, cleaned and reconstructed as membranes of desired thickness to be used in the synthesis of highly dehydrochlorinated PVC (DHPVC) membranes. These membranes can be further functionalized by additional reactions to obtain ion exchange membranes, battery membranes, semi-conductors etc. Ion exchange membranes to be obtained from DHPVC membranes would exhibit super ion exchange capacity. PVC resin can also be used for manufacturing such valuable devices.

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