

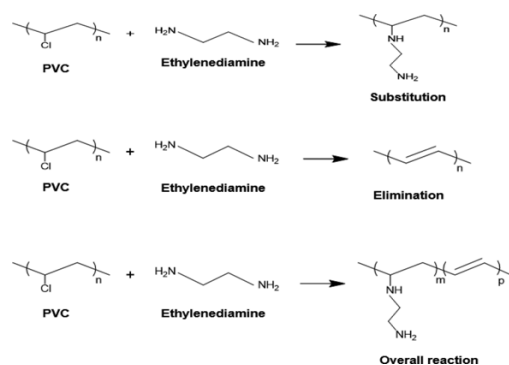
Elimination and Substitution Compete During Amination of Poly(vinyl chloride) with Ethylenediamine: XPS Analysis and Approach of Active Site Index

Eun Ji Park[†]
 Byoung Chul Park[†]
 Young Joong Kim
 Ali Canlier*
 Taek Sung Hwang*

Department of Chemical Engineering and Applied Chemistry, College of Engineering,
 Chungnam National University, Daehak-ro 99, Yuseong-gu, Daejeon 34134, Korea

Received January 19, 2018 / Revised April 2, 2018 / Accepted April 10, 2018

Abstract: Various chemical modification methods have been tried on PVC polymer materials for recycling and functionalization purpose. These methods employ substitution, elimination (dehydrochlorination) and grafting polymerization processes. PVC is treated with ethylenediamine (EDA) for amine grafting since it is a reactive amine for substitution and efficient removal of chlorides. Nevertheless, optimum conditions for substitution (amination) and significance of its competition with elimination have not been reported in detail so far. In this study, PVC resin has been treated with 99% EDA and 80% EDA (aqueous), and also 9.1% THF solution of PVC has been treated with 99% EDA at varying temperatures (RT to 85 °C or RT to 65 °C). Additionally, PVC membranes have been treated with 99% EDA and 80% EDA (aqueous) at three different temperatures (RT, 50 °C, 75 °C). Effects of temperature and solvent on the degrees of amination and dehydrochlorination have been elaborated. Up to 99% dechlorination and 34% amination is possible with the use of EDA. Direct amination of membranes facilitates production of ready-cast aminated PVC membranes. FTIR Spectroscopy was used to study chemical structures. Morphology was observed *via* scanning electron microscopy (SEM) and atomic contents were analyzed *via* X-ray photoelectron spectroscopy (XPS) in order to survey the degree of amination etc. UV-Visible Spectroscopy was used to characterize the length of conjugation.



Keywords: PVC, membrane, ethylenediamine, amination, dehydrochlorination, XPS.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most common plastics material used in manufacturing industry. Among its miscellaneous application areas are construction, packaging, pipes, toys, medical devices-tools and even membrane applications.¹⁻³ It is a ubiquitous plastic material widely preferred due to its chemical and physical properties and cost advantages. Besides coarse uses, PVC has been studied academically for cutting edge technologies as well. The spectrum of such PVC applications stretches to a broad area of catalysts, ultrafiltration membranes, heterogeneous ion exchange membranes etc, biomedical tools and devices.⁴⁻⁸

Acknowledgments: This work was supported by the Commercializations Promotion Agency for R&D Outcomes Grant funded by the Korean Government (MSIP) (2017, 2017K000215, Joint Research Corporations Support Program). This work was also supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea (NRF-2015H1C1A1035652). This research was supported by the Ministry of Trade, Industry and Energy (MOTIE) and the Korea Institute for the Advancement of Technology (KIAT) (N0002383, 2018).

*Corresponding Authors: Taek Sung Hwang (tshwang@cnu.ac.kr), Ali Canlier (alicanlier@gmail.com)

[†]Authors contributed equally to this work.

In the last few decades, many different reactions of PVC including processes of elimination, dehydrochlorination, grafting polymerization *via* cationic and free radical pathways and substitution have been reported. Concept of chemical modification of PVC is basically about dechlorination process which includes both substitution and elimination mechanisms.⁹⁻¹¹ Among these mechanisms, substitution has been widely investigated for modification of PVC structure. Yoshioka *et al.*¹² studied reactions with five nucleophiles: I⁻, SCN⁻, OH⁻, N₃⁻ and phthalimide anion. They could achieve more than 90% dechlorination, but degree of substitution was less than 30%. Yoshinaga and co-workers¹³ investigated the effect of solvent with alkaline (NaOH) on dechlorination of PVC. Dehydrochlorination was dominant over substitution in their work as well.

Recently, PVC has been treated with ethylene diamine (EDA) for highly efficient degree of substitution. Balakrisnan *et al.*¹⁴ have reported that PVC treated with aqueous solution of EDA can be linked to poly(ethylene glycol) (PEG) in the presence of a linker agent. As they proposed, PVC material which is grafted by amine groups can be furthermore attached some functional groups to gain the PVC surface hydrophilicity or biocompatibility. Works of Shi *et al.*⁷ and Simmchen *et al.*⁸ show the significance of such grafted PVC or another plastic materials for blood bag applications. Amine-grafted PVC is expected to be a softer material to use in blood bag manufacturing, which also possess more hydrophilic

surface than PVC bags. In a membrane technology related work of Allan *et al.*, PVC was aminated with 90% aqueous solution of EDA for further sulfonation.¹⁵ In Eldin's report,¹⁶ chlorines of PVC were substituted with terminal primary amine groups *via* an amination reaction with EDA in a solution of tetrahydrofuran (THF). Although substitution reaction of PVC with EDA has been widely used for further reactions, as far as we know, the optimum conditions for substitution has not been reported in detail. Various conditions of concentration parameters such as 80%-90% aqueous solution or concentrated EDA, and various temperatures have been used in amination reaction of PVC with EDA so far. Degree of substitution (or amination) have not been focused and mentioned in past works,¹⁴⁻¹⁸ thus we decided to elucidate effects of such varying conditions on reaction mechanisms and degree of amination *etc.* Aminated PVC (APVC) can be an important gadget for manufacturing ion exchange tools, biomedical devices, agents of metal recovery, CO₂ capture, catalysis and so on. Amination can be carried out on PVC resin, dissolved PVC or PVC membrane. APVC resins and already-dissolved APVC can be used to cast membranes if their solubility is adequate. Elaboration and comparison of all these cases including physical states and reaction conditions is one of the significant aspects of this work. Also thin membranes of PVC were aminated for the first time in our work.

To summarize, various forms of PVC was treated with 80% aqueous solution of EDA or 99% EDA at varying temperatures (RT~85 °C) in this study. Amination of PVC dissolved in THF solvent was also investigated at various temperatures (RT~65 °C) since dissolving PVC granules is supposed to favor kinetics and reactivity between EDA and PVC. Products of such reactions are mentioned hereafter either with a general name, PVC-EDA or with codes starting with APVC and numbers for each product. We confirmed that contrary to findings of Krishnan *et al.*,⁴ PVC would not react with EDA with high yields (~100%) as mentioned by them within 4 h or such short durations at room temperature however we tried. Using higher temperatures is required to increase the reactivity of PVC with EDA for similar length reactions.

Our experiments confirmed that PVC can be successfully aminated with EDA as reported by several researchers.¹⁴⁻¹⁸ However, mixture of EDA and H₂O prepared as 80w% EDA did not react well with PVC at low temperatures. Early results of FTIR for such products showed -NH₂ peaks at first, but repetition of drying process in longer durations resulted in disappearance of same -NH₂ peaks. Therefore, either waterless EDA (99%) should be used for PVC resin or a THF solution of PVC should be reacted with EDA for more efficient amination of PVC around room temperature

Finally, we discussed how "nitrogen content, degree of dehydrochlorination, degree of substitution and degree of overall

dechlorination" were influenced with respect to the physical state of PVC being dissolved by a solvent (THF), being in resin or membrane form, presence of H₂O and temperature. "Time/duration of the reaction" was not treated as a parameter in our work. We set time at an optimum duration (4 h) for PVC resin & dissolved PVC, and a rather longer time (24 h) for PVC membrane based on experience and related references to obtain the best degrees of amination. Longer times would lengthen the work too much. Comparing the effect of the time factor will be a separate kinetics work which is worth studying in our lab. In order to synthesize PVC-EDA products with the highest nitrogen content, and the best physical and chemical properties, it is crucial to establish best conditions favoring amination over elimination. In case that elimination prevails, highly dehydrochlorinated PVC (DHPVC) species can be prepared with EDA, which acts as a dehydrochlorination agent. DHPVC may possess long polyene sequences depending on the degree of elimination.¹⁸⁻²⁰ DHPVC can be further grafted through double bonds, *e.g. via* sulfonation.²¹⁻²³ As elimination and substitution mechanisms result in different types of products, it is vital to control the competition between two mechanisms in order to obtain the desired polymer required for any application.

FTIR spectroscopy was used to confirm the chemical structure of PVC-EDA species. Morphology was monitored with SEM, and elemental composition (C, N, O, Cl) was analyzed with XPS in order to reveal "nitrogen content, degree of dehydrochlorination, degree of substitution and degree of overall dechlorination" UV-Visible spectroscopy was used to estimate approximate length of conjugation in products and its correlation with degree of elimination.

2. Experimental

2.1. Materials and chemicals

PVC resin of average molecular weight ~48,000 was kindly donated by Hanwha Co., Korea. Anhydrous ethylene diamine (EDA, assay ≥99%) was purchased from Samchun Chemical and used as received. Tetrahydrofuran (THF, assay ≥99.5%) was purchased from Sigma-Aldrich. Deionized water (DI water) was used for all aqueous processes.

2.2. Amination of PVC resins and its THF solutions

PVC resin was aminated with 99% EDA and 80% aqueous solution of EDA under conditions shown in Table 1. 1 g PVC resin was added to 10 g of 99% EDA or 12 g of 80% aqueous solution of EDA in 50 mL bottles. To determine the effect of solvent, 1 g PVC resin was dissolved in 10 g THF (~11.2 mL) and

Table 1. Weight ratios and temperature conditions for reactions of PVC resin (APVC1-19) and membrane (APVCM) vs. EDA

Sample Code	PVC (g)	EDA (99%) (g)	EDA (80%) (g)	THF (g)	Temp (°C)
APVC1~7	1	10	-	-	25-85 (intervals of 10)
APVC8~14	1	-	12	-	25-85 (intervals of 10)
APVC15~19	1	10	-	10	25-65 (intervals of 10)
APVCM1~3	~0.1	30	-	-	25, 50, 75
APVCM4~6	~0.1	-	30	-	25, 50, 75

followed by dropwise addition of 10 g 99% EDA. Each bottle was purged with nitrogen gas and vigorously stirred in oil bath maintained at various temperatures between RT and 85 °C for 4 h. For THF solution, the highest temperature was 65 °C, since the boiling point of THF is 66 °C. Products in THF solution were precipitated with addition of DI water in the end. After completion of these steps, aminated resins or precipitates of the products were filtered on paper filters, and washed with copious amount of DI water in order to remove unreacted EDA and other byproducts (HCl, EDA·HCl, etc). Finally, all products were dried in a vacuum oven for 2 days.

2.3. Amination of PVC Membranes

A 75 µm thick membrane was cast from a 20% THF solution on glass plate with a doctor blade. It was dried and cut into 3cmx-3cm pieces for further use. These pieces were put in vials and 99% EDA or 80% aqueous solution of EDA were added onto them according to the conditions in Table 1. After closing the vials tightly, they were either left at room temperature or kept in ovens of 50 °C and 75 °C during 24 h each. Aminated membranes were laid in H₂O for 1 day and then dried in a vacuum oven for another day. FTIR and XPS analysis were carried out on these for comparing degree of amination in membranes to that in resins.

2.4. Characterizations

A Shimadzu FTIR spectrometer (Shimadzu Corporation, Japan) was used to record Fourier-transform infrared (FTIR) spectra of PVC-EDA products and structures were characterized. The spectra were obtained *via* attenuated total reflectance (ATR) unit with a scan number of 20 and a resolution of 4 cm⁻¹. Wavelength varied from 4000 cm⁻¹ to 600 cm⁻¹. Scanning electron microscopy (SEM) (JEOL Instrument, JSM-6700, Thermo NORAN) was used to monitor the morphology of PVC and aminated PVC samples. The accelerating voltage was set to 5 kV, and the sample was coated with platinum in advance by using an ion sputterer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Multilab 2000 XPS system with a monochromatic Al K α source (Thermo Scientific, America). Operation conditions were set at 15 kV, 150 W and beam size of 500 µm. UV-Visible spectra were recorded on a Photodiode Array UV-Vis Spectrophotometer S-3100 (SCINCO, Korea). Absorbance was measured in the range of 240~960 nm. Sample disks of ~350 µm thickness were prepared with a pressing tool prior to analysis.

3. Results and discussion

3.1. Physical properties of aminated PVC

Digital photographs of PVC-EDA samples of different conditions are shown in Figure 1. Last photo shows pristine PVC as a reference. As temperature is elevated, PVC-EDA in 99% EDA solution tends to gain darker color. This can be attributed to an increase in *degree of dehydrochlorination* and *lengthening conjugation* as temperature rises.

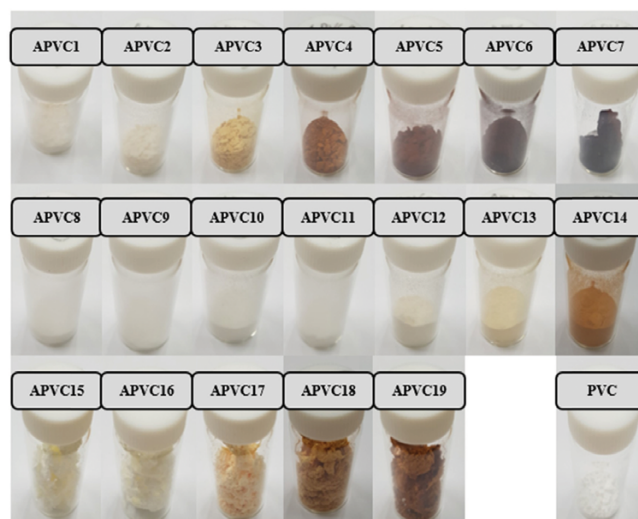


Figure 1. Discoloring trend of PVC after treatment with (*upper series*) 99% EDA at different temperatures (RT→85 °C); (*middle series*) 80% EDA (aqueous) at different temperatures (RT→85 °C); and (*lower series*) EDA in THF solvent (50w%).

Solubility tests showed that PVC-EDA species obtained with 99% EDA at temperatures higher than 45 °C dissolve little or none in THF (APVC4-7). As to aqueous EDA reactions (80%), most products were soluble in THF (APVC8-13) except for the one of 85 °C (APVC14). At higher temperatures, *degree of dehydrochlorination* occurs higher since more vinyl chlorides transform into polyene sequences *via* elimination. Highly dehydrochlorinated PVC tends to show polyacetylene-like structure which contains long conjugated polyene sequences. Polyacetylene (PA) is an insoluble, air-sensitive and infusible black powder as described in Refs. 24-26. Insolubility of PA can be attributed mainly to formation of almost apolar conjugation sequences.

Another factor that would contribute to insolubility is *amine cross-linkings* within or between polymer chains. Cross-linking effect becomes more visible at higher temperatures at which a dynamic reactivity is enforced between amine sites (primary amines, successively formed secondary and tertiary amines) and still unreacted chlorine sites on PVC backbone. Such cross-linking phenomenon was described in Refs. 4, 27. In case of reaction with 80% EDA aqueous solution, PVC-EDA samples exhibit lighter discoloration varying from white to yellowish, and yellowish to brown. It is a typical trend reported in Ref. 15 as well. Hydrogen bonding and protonation of EDA in aqueous solution disfavor both cross-linking and dehydrochlorination effects. As a noticeable phenomenon, contrast to samples PVC1 - PVC14, samples in THF solution remain as homogeneous solutions even after the end of reaction time. Following the addition of H₂O into THF mixture, products precipitate suddenly. These precipitates are stiff solids, and they happened to be less soluble in THF than we expected. These five samples (APVC15-19) resulted in bulky solids after steps of precipitation, filtering and washing probably due to dense cross-linking and abrupt phase change, but discoloration shows a similar trend as in PVC-EDA products of 99% EDA.

Using prolonged reaction times for PVC membrane reactions

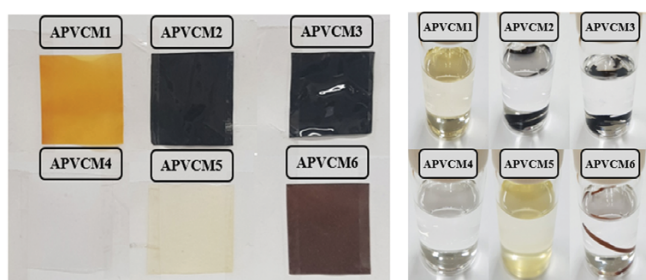


Figure 2. Discoloring trend of PVC membranes after treatment with EDA at different temperatures (RT, 50 °C, 75 °C) (left) and solubility trend of the same (right) are shown. Upper series is for 99% EDA, and lower series is for 80% EDA.

causes denser discoloration at all temperature cases and even also geometrical deformation at high temperature (75 °C). Thin membranes are affected substantially in terms of texture and structure when temperature is near softening temperature of PVC (~80 °C). Thickness is altered and surface becomes wavy at such high temperature. Since 85 °C showed aggressive alterations, we adopted 75 °C as maximum temperature for membrane reactions.

Only RT product of 99% EDA-membrane system dissolves in THF, other two are insoluble. On the other hand, RT and 50 °C products of 80% EDA-membrane system are both soluble in THF (Figure 2). This observation is evidence to the greater extents of amine cross-linking and dehydrochlorination in 99% EDA system compared to 80% EDA-membrane system.

3.2. FTIR Spectroscopy

FTIR spectra of PVC resin, PVC-EDA products, PVC membrane and aminated PVC membranes are shown in Figures S1-S4. PVC spectrum is included in each figure for comparison. Figure 3 shows spectra of products obtained at highest temperature for each physical state and thus, shows most of amination effect. Found FTIR bands of PVC are listed in Table 2 which mainly

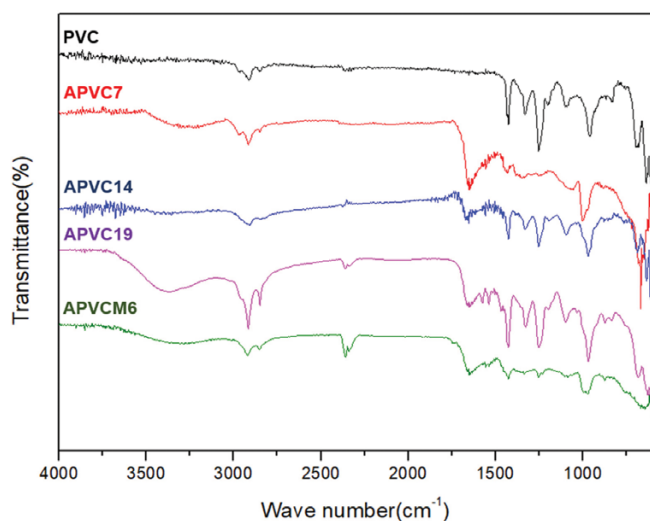


Figure 3. FTIR spectra of PVC, APVCM7 (99% EDA), APVCM14 (80% EDA), APVCM19 (THF soln), and APVCM6 (Membrane). FTIR spectra of other products can be checked in Supporting information (Figures S1-S4).

Table 2. Principal band assignment for the FTIR spectrum of PVC

Wavenumber (cm ⁻¹)	Assignment
2973	Stretching C-H of CHCl
2912	Stretching C-H of CH ₂
1428	Deformation (Wagg), CH ₂
1330 and 1252	Deformation, C-H of CHCl
1097	Stretching, C-C
960	Rocking, CH ₂
689, 636, and 618	Stretching, C-Cl

agree with Ref. 28. As shown in Figure S1 (spectra for 99% EDA products), strong and broad stretching bands appear around 3300 cm⁻¹ for samples APVCM5, APVCM6, and APVCM7, which were treated at 65 °C or higher temperatures. This indicates the presence of amine groups, -NH₂ and/or -NH. Also a new peak around 1060 cm⁻¹ is indicative of C-N bonding of amines. As temperature increases, contrast to the broad band around 3300 cm⁻¹, intensity of peaks at 1427 (CH₂ wagging), 1331 and 1255 cm⁻¹ (deformation of C-H in CHCl moiety) gradually weaken. Also, three C-Cl peaks in fingerprint region disappear and transform into a new peak of -NH wagging mode. Thus, it is clear that PVC is dechlorinated by both elimination and substitution reactions.

The peak appearing around 1620 cm⁻¹ can be attributed to stretching mode of C=C bonds. Out of plane deformation band around 1003 cm⁻¹ as well as a weak and overlapped peak of =C-H stretching band around 3000 cm⁻¹ also justify formation of double bonds *via* elimination. We can infer from these data that amination (substitution) and elimination reactions occur simultaneously. In addition to this, primary amine functional groups may be undergoing cross-linking within or between polymer chains. Therefore, strong scissoring band of -NH₂ around 1565 cm⁻¹ is not clearly observed after APVCM4 (55 °C) since broad C=C band seems to overlap it. Furthermore, frequent cross-linking incidents may be related to this observation.

Figure S2 shows the FTIR spectra for PVC-EDA products of 80% EDA. A similar trend of weakening and strengthening bands are observed as in 99% EDA products here as well. However, scissoring -NH₂ peaks can be apparently observed here around 1565 cm⁻¹ at lower temperatures (RT-55 °C). Likewise, a broad and slightly divided broad band is observed around 3420 cm⁻¹, which is likely to be evidence to a mixture of -NH₂ and -NH functional groups. 80% EDA products showed conspicuous =C-H stretching band around 3005 cm⁻¹. Broad and complicated peak between 1550 cm⁻¹-1750 cm⁻¹ also denotes the formation of various unsaturated species including conjugation sequences with diverse lengths. Presence of water constantly feeds the solution with hydroxide ions (OH⁻). Hydroxides may both bolster elimination reactions and substitution reactions yielding alcohol groups in a competition with EDA.

FTIR spectra for PVC-EDA products obtained *via* THF solutions are shown in Figure S3 N-H stretching band around 3350 cm⁻¹ starts to appear weakly since 35 °C and grows above that. Likewise, a peak around 1575 cm⁻¹ may be attributed to scissoring band of primary amines (-NH₂). Amination reaction may be strong and prominent in THF solutions at higher temperatures. Dissolved PVC polymers may be aminated more homogeneously

via substitution reactions but this does not rule out occurrence of elimination reactions. Appearance of C=C stretching band around 1620 cm^{-1} supports this deduction. In a dilute PVC and concentrated EDA solution in THF solvent, amine cross-linking is not much likely to happen. On account of this, PVC-EDA products mostly exist as dissolved species in THF. However, addition of water causes coagulation into stiff masses or hard solids (not like soft powder structure). This may be because of a late cross-linking which happens during the coagulation process.

PVC-EDA membranes display somewhat shifted peaks than resin products. Stretching band of N-H appears first at $50\text{ }^{\circ}\text{C}$ in 99% EDA reactions. It though does not stand out in the spectrum of 80% EDA product obtained at same $50\text{ }^{\circ}\text{C}$. Elimination peaks of C=C bond around 1620 appears earlier again in case of 99% EDA reaction. After weakening or disappearance of 1428 cm^{-1} , 1330 cm^{-1} , 1252 cm^{-1} peaks of C-H deformations, a new peak appears around same 1428 cm^{-1} , signaling well amination and remaining methylene (CH_2) moieties of PVC and joining methylenes of EDA. Late appearance of a strong band around for 80% EDA product explains the fainter color of their membranes compared to those of 99% EDA (Figure 2).

3.3. SEM Analysis

PVC resin is composed of granules in $2\text{--}4\text{ }\mu\text{m}$ size. As can be seen in Figures S5 and S6, the morphology of granules did not change largely after reactions carried out at low temperatures. Amination and elimination reactions may have happened mostly on the surface of the granules, and happened less through the core. Especially in case of 99% EDA, PVC granules seem to have fused into larger clusters at $T > 65\text{ }^{\circ}\text{C}$. Since the glass transition temperature of PVC is $85\text{ }^{\circ}\text{C}$, APVC7 ($85\text{ }^{\circ}\text{C}$) granules fused most at $T=85\text{ }^{\circ}\text{C}$. This effect may have caused more homogeneous

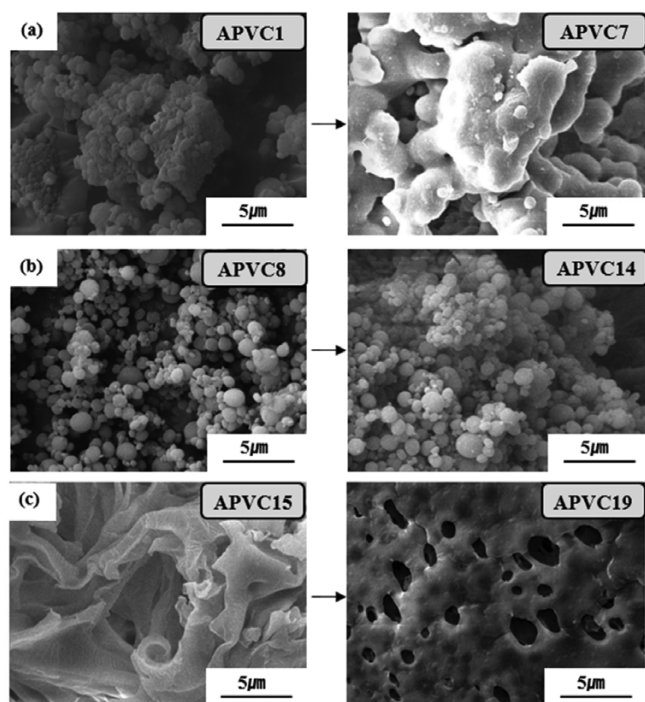


Figure 4. SEM images of APVC products: (a) 99% EDA (RT, $85\text{ }^{\circ}\text{C}$), (b) 80% EDA (RT, $85\text{ }^{\circ}\text{C}$), and (c) EDA in THF (RT, $65\text{ }^{\circ}\text{C}$).

amination and further cross-linking through EDAs at such high temperatures. Therefore, more frequent cross-linking may have urged this morphological variation. But the reaction of PVC resin with 80% aqueous EDA solution did not show significant change of morphology, but somewhat merging of granules were observed at higher temperatures.

In case of THF use to dissolve PVC resins, more homogeneous reactions can be expected to happen between PVC and EDA compared to solid state PVC-EDA solution systems (APVC1-14). From kinetical aspect, there is a greater chance of collision between vinyl chlorides and EDAs in solution state. Therefore, we may expect higher probability of substitution of Cls by EDAs. This can be confirmed with FTIR and XPS analyses data. FTIR spectra show actually relatively stronger N-H stretching bands for THF solution products. XPS data will be discussed in the next section. Cross-linking through especially open end of EDA depends on reaction conditions such as concentration of solution, reagent ratio and temperature. Since all PVC and products are dissolved in THF, addition of water causes a rapid coalescence and solidification of the products into stiff clusters. Continuous morphologies of APVC15-19 products support this interpretation in our opinion (FIGURE S7). During this coalescence and water treatment for long time, cross-linking may have progressed to a higher extent.

3.4. X-ray photoelectron spectroscopy (XPS)

3.4.1. PVC resin

Poly(vinylchloride) experiences mainly two kinds of reactions as shown in Figure 5: (1) *Amination* by substituting Cls with

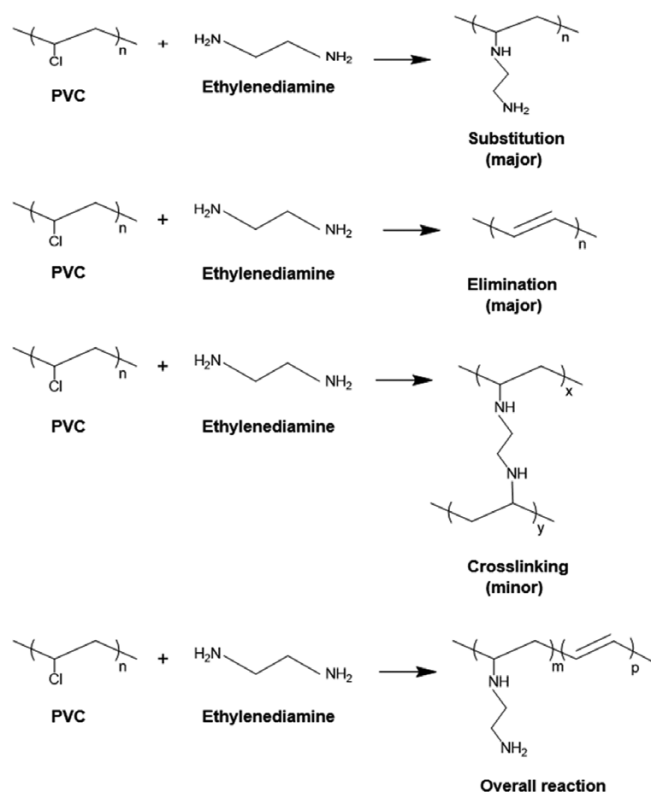


Figure 5. Reaction scheme showing mechanisms of amination and dehydrochlorination of PVC by ethylenediamine (EDA).

EDAs via S_N2 mechanism to yield EDA grafted PVC sequences, (2) *dehydrochlorination* by eliminating HCl via E2 mechanism to yield C=C double bond sequences. Therefore, the products are referred to as PVC-EDA (or APVC for detailed assignment) for general purpose in this report. Since both mechanisms cause loss of Cl, both can be counted as *dechlorination* (Eq. S1). From elemental ratios of C, Cl and N in a product, extent of these changes can be estimated approximately. By taking O ratio into consideration as well, extent of oxidation occurred on conjugated sequences (double bonds) can be estimated too. Due to restrictions of elemental analysis instruments about halogen rich compounds, we preferred employing XPS analysis instead in order to reveal changing trends of *dechlorination*, *amination*, *dehydrochlorination* and *abundance of double bonds* depending on reaction conditions such as temperature and physical state of PVC. Mathematical evaluation of XPS data, calculation principles, equations and approximations are given in Supporting Information part in Calculations section.

Comparison of substitution (amination) and elimination (dehydrochlorination) efficiencies via XPS analysis results implies that elimination is favored over substitution in almost all cases (Figure 6(a)) since almost all "Degree of Amination/Degree of Dehydrochlorination" ratios are less than unity. The difference between the two grows against amination as temperature is increased however yield of amination grows as well in case of 99% EDA system. Same trend is observed for 80% EDA system when $T \geq 45$ °C. This is probably because H atoms on α -carbon (CH_2) are kinetically more accessible than secondary C atoms where substitution occurs. In addition, as more EDAs join to polymer chain, although there will be hydrogen bonding which may favor neighborhood of EDAs, steric hindrance between bound EDA and attacking EDA cannot be underestimated. On the other hand, lengthening conjugation of double bonds contribute more to the thermodynamic preference of elimination mechanism.

The trend occurs in favor of amination slightly when temperature is increased in THF system. In case of THF system where PVC is completely dissolved, kinetics and rate order of the reaction would be different than two other systems in which PVC is mostly in solid phase. Whereas PVC-EDA products have existed as dissolved species in THF until their precipitation with addition of water, new cross-linking reaction may have happened during coagulation and precipitation. Formation of stiff and large-size solids support this inference. These solid products of THF system are almost insoluble in THF and DMF, although they were dissolved in THF before the reaction. Similar stiffness and insolubility trend were observed for products of 99% EDA system obtained at relatively high temperatures. As PVC softens at higher temperatures, PVC-EDA and PVC molecules would find more chances to collide and create cross-linking. Even though we omitted cross-linking effect from our calculations using XPS data, these observations provide an insight about cross-linking phenomena to some extent.

We believe that presence of water suppresses all sorts of reactions and phenomena including nucleophilicity and basicity of EDA in case of 80% EDA system. This is so because EDA is partially protonated by dissociation of water. On the other hand,

hydroxides formed by protonation of EDA would compensate for some dehydrochlorination. FTIR results and discoloring trend of products in 80% EDA system accord well with these interpretations. As solubility of highly cross-linked or highly dehydrochlorinated products can be expected to be very low, we may argue that vinyl chlorides react little and are mostly intact in products of 80% EDA system up to 75 °C where "Degree of Dechlorination" is as low as around 20% yet (Figure 6(c)). This value soars lower than or near bottom values of other two systems at lower temperatures than this (<65 °C).

According to the "(Degree of Amination)²/Degree of Dehydrochlorination" graph (Figure 6(b)), 55 °C is the optimal temperature for a better efficiency of amination over elimination in case of THF system. Such an optimal temperature is RT (~25 °C) for 99% EDA system, and 45 °C for 80% EDA (aqueous) system. This means that longer reaction periods can be adopted at these temperatures for succeeding higher amination yields. Temperatures between 45 °C and 55 °C would work well for both 99% EDA and 80% EDA systems.

With respect to our experiment duration (4 h), degree of amination is the true indicator for the best amination condition. Among three reaction systems, amination generally takes place best when 99% EDA system is used in the reaction. As temperature is increased to 55 °C, degree of Amination rises suddenly up to around 15% and a new trend starts. This can be accepted as the threshold of temperature for reaching higher amination degrees for PVC resin.

Above 65 °C, rate of increase in elimination degree slows down for 99% EDA system. This might be due to early completion of dechlorination process as can be seen on the amination trend. Amination in 99% EDA system is more advantageous against elimination at lower temperatures. Overall outcome effect is more apparent at 55 °C as the trend of multiplied effect of amination indicates (Figure 6(a),(b)).

In case of THF, amination already starts with a considerable ratio (2.75%) at room temperature. This ratio rises fast up to 14% at 65 °C which is the final temperature for THF reactions. The trend implies that using a higher boiling point solvent such as DMF may boost amination higher than 20%. And also, whole dechlorination seems to take place with higher ratios when temperature is higher than 65 °C.

Low solubility results of most of the products of 99% EDA and THF systems, which were obtained from solubility tests with THF, DMF and NMP solvents and SEM images indicate that some cross-linking reactions would occur even at low temperatures inevitably. Low degrees of dehydrochlorination at lower temperatures opt out the strong effect of apolar conjugation sites on low solubility of the related species.

PVC granules remain in solid state and morphologically undisturbed in most cases of 99% EDA and 80% EDA reactions. We can assume that most amination and elimination reactions take place particularly on the surface of granules and at a weakening extent towards the core. Granules tend to melt and fuse when temperature is elevated to higher temperatures near 85 °C as SEM images show (Figures S5 and S6). Factors such as intense amination, amine cross-linking and formation of conjugated sequences lower the solubility of PVC products tremendously.

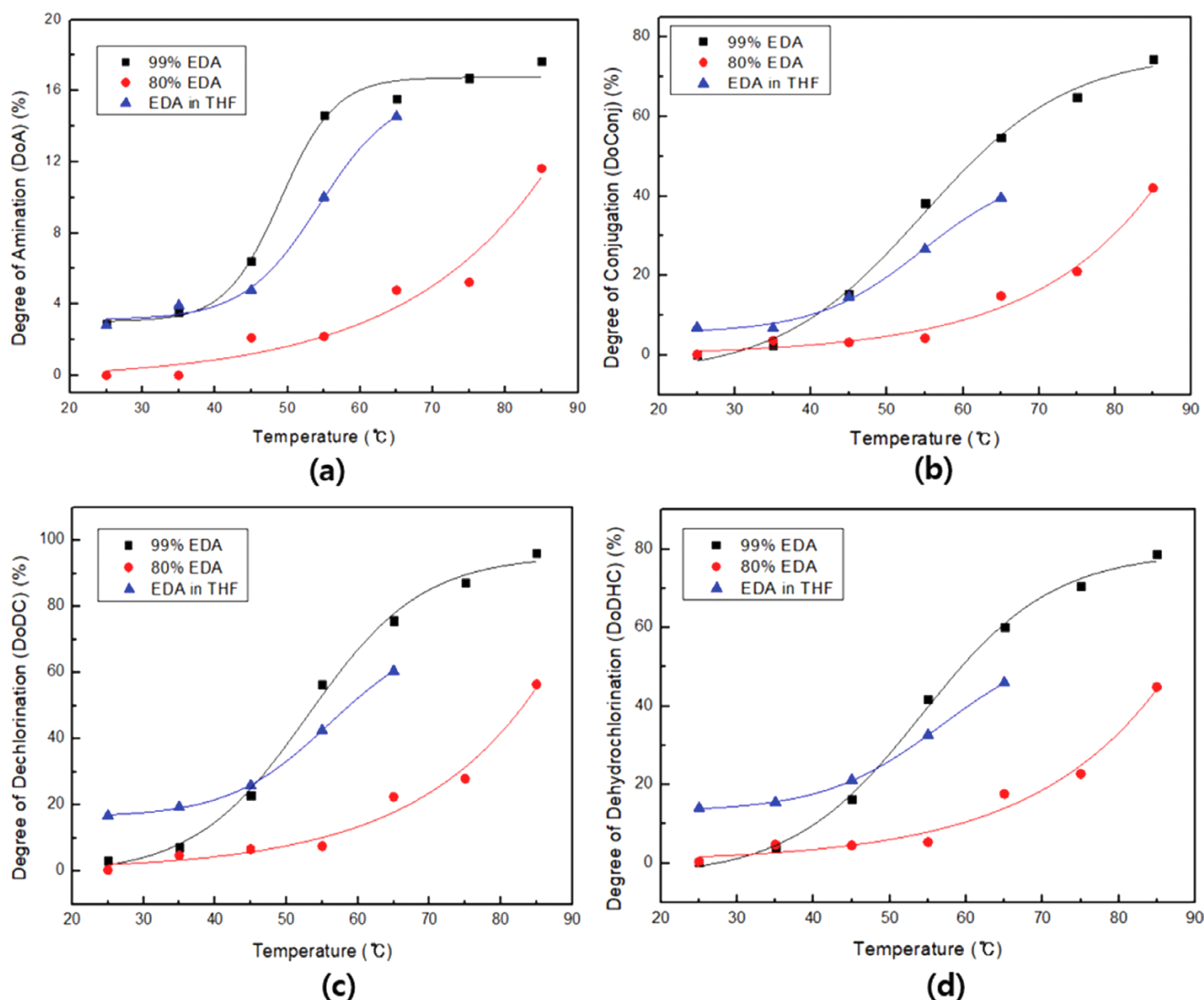


Figure 6. Trend graphics for PVC resin and THF-dissolved PVC treated with 99% EDA and 80% EDA (aqueous) on temperature. (a) Degree of Amination, (b) Degree of Unsaturation, (c) Degree of Dechlorination, and (d) Degree of Dehydrochlorination.

In case of THF reactions, however, products don't preserve granular morphology anymore. We expected to observe high solubility for THF reaction products. However, the colorful products, which were obtained at temperatures > 35 °C, were little or non-soluble in all three solvents (THF, DMF, NMP). The products exhibit swelling behavior when they are kept in these solvents. We were able to cast membrane from APVC15 and APVC16 of THF system though. Only these two products of THF system were soluble again in THF. As the trend of solubility is checked for two other types of reactions, we can roughly conclude that the products with a degree of dechlorination lower than 20% tend to be soluble. This means that products with ~4% amination can be solved in THF to cast membranes. This kind of membrane derived from EDA-grafted-PVC can be alkylated to quaternary amines in order to synthesize anion exchange membranes. In this case, theoretically it is possible to reach ion exchange capacities more than 2 meq/g. Under these conditions, maximum of IEC_{theo} for all species would be as high as 8.34 meq/g (Figure 7(c)), if membranes could be cast from all products.

For a pursuit for deriving cation exchange membranes out of PVC-EDA products, sulfonation of amine sites and double bonds would result in sulfonated amines and double bonds. This means reaching a higher-than-expected ion exchange capacity is feasible for cation exchange membranes obtained from PVC-EDA products by this manner since sulfonation of double bonds multiplies the effect.

3.4.2. PVC membranes

Due to formation of mostly insoluble products, we concluded that it is better to conduct amination on already cast-PVC membranes under a few of the conditions for the sake of comparing mainly degree of amination and other trends. Degree of amination has been as high as 37% at most in case of 99% EDA-membrane system. This would mean a substantial theoretical ion exchange capacity turnover can be reached with these aminated PVC samples. And cation exchange membranes can be manufactured likewise.

Estimated "Theoretical Ion Exchange Capacity" would be as high as 11.90 meq/g for aminated PVC membrane under con-

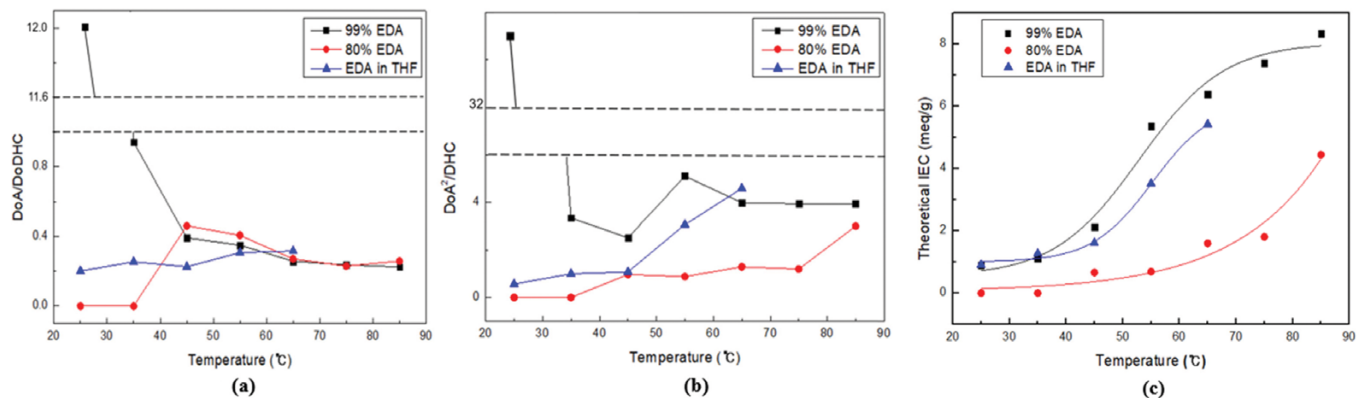


Figure 7. Dependence of (a) “Degree of Amination/Degree of Dehydrochlorination”, (b) “Square of Degree of Amination/Degree of Dehydrochlorination”, and (c) “Theoretical ion exchange capacity” on temperature for when PVC is treated with 99% EDA, 80% EDA, and EDA in THF.

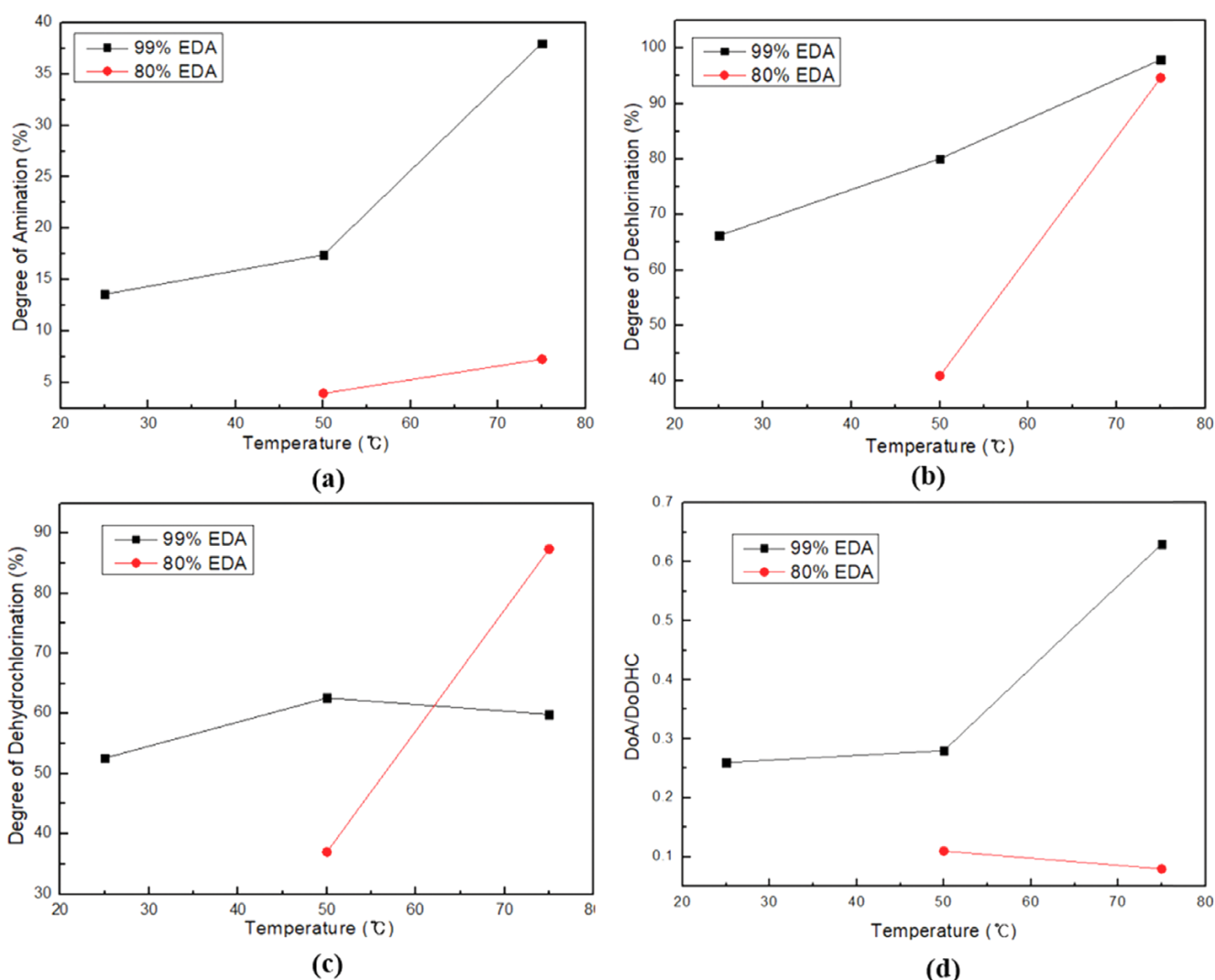


Figure 8. Theoretical analysis of PVC-EDA membranes treated with 99% and 80% EDA at RT, 50 °C, 75 °C. Dependence of (a) Degree of Amination, (b) Degree of Dechlorination, (c) Degree of Dehydrochlorination, and (d) Degree of Amination/Degree of Dehydrochlorination ratio on temperature.

ditions of “99% EDA and $T=75\text{ }^{\circ}\text{C}$ ”. Using prolonged reaction times at milder conditions such as RT would almost quadruple Degree of Amination up to 13.66% for 99% EDA system. “Theoretical Ion Exchange Capacity” would be 4.62 meq/g for this grafted membrane which is fairly higher than most of the resin

systems. Trend of DoA/DoDHC in membrane systems differs than that of resin systems. Prolonged reaction times let elimination reactions reach a balance with substitution within time. Accordingly, DoA/DoDHC ratio starts lower at room temperature and then rises as temperature is increased for membrane

systems. By avoiding thermal vulnerability of PVC membranes, using higher temperatures helps with obtaining higher Degree of Amination.

Degree of Dehydrochlorination has been observed to demonstrate a noticeably different trend than its resin system in case of 99% EDA-membrane system. As temperature is increased from 50 °C to 75 °C, amination keeps accelerating though dehydrochlorination seems to have reached saturation around 60%. As to 80% EDA-membrane system, temperature rise causes acceleration of dehydrochlorination probably due to contribution of hydroxides. The color of PVC-EDA membrane obtained with 80% EDA at 50 °C is just fainted whereas the corresponding membrane is black in case of 99% EDA system (Figure 2). This suggests that dechlorination and also dehydrochlorination are not favored in 80% EDA system as much as in 99% EDA system at RT and 50 °C. Due to sharp increase of dehydrochlorination in 80% EDA system, cumulative dechlorination degrees in 80% and 99% EDA systems are near.

3.5. UV-visible spectroscopy

Degree of dehydrochlorination can be determined with XPS data. However, length of conjugation can be more accurately estimated by UV-Vis spectroscopy method. Figures 9-11 show the UV-visible spectra of APVC products prepared by the reaction of PVC resin and EDA at different conditions. A 45 μm thin membrane of PVC was used for UV-Vis spectroscopy whereas PVC-EDA disks were more than twofold thicker. The overall absorption intensity has been lower in spectra of samples prepared under low temperature conditions. Nevertheless, it tends to increase markedly and a broad absorption band without discrete maxima emerges by stretching to higher absorption and longer wavelength region as degree of dehydrochlorination increases together with rising temperature. The typical maximum of the band (λ_{max}) shifts to higher wavelengths as described in Ref. 29 when higher temperatures are used.

Shift of absorption maxima and shoulders towards longer wavelengths indicate that longer conjugated polymer sequences (polyenes) form at higher temperatures. For example, whereas

breadth of absorption band does not exceed 500 nm in spectrum of APVC1, longest wavelength of the bands gradually increases with regard to rising temperature in other samples. λ_{max} of broad band appears around 580 nm in APVC7 spectrum and a region up to 800 nm is slightly covered by the band (Figure 9). As XPS data indicates that Cl content dramatically decreases from 31.83% to 1.23% (see Table S1 for XPS data of APVC1 and APVC7), these results also imply that extraordinary long conjugated polyene segments are created at higher temperature conditions. Since 99% EDA system yielded higher dehydrochlorination degrees in all cases (Figure 6), longer conjugations and greater absorbance performance can be expected for similar amount and thickness of samples produced by 80% EDA and THF systems. In addition, spectra of 99% EDA system products transform from a combination of discrete absorption peaks to a continuous band when $T \geq 65$ °C. This is the temperature where degree of unsaturation exceeds 40% obtained at $T=55$ °C and reaches 55% at $T=65$ °C.

A similar trend to that of 99% EDA system has been observed for other two systems (APVC8 ~ APVC 19), but overall absorption is lower than that of samples of 99% EDA system. Darkening trend of colors depending on increasing temperature, and also XPS data (degree of unsaturation etc.) support findings of UV-Vis spectroscopy of the two systems.

Conjugation length of polyene systems have been estimated by using Raman spectroscopy³⁰ or UV-Vis spectroscopy³¹ previously. Differing lengths of conjugation cause slight changes in absorbance and wavenumber around 1500 cm^{-1} in Raman spectroscopy since the strength of bonds and polarizability factors vary depending on the length. In case of UV-Vis spectroscopy, a four-maxima-band (A-D maxima) or overlapping mixtures of four-maxima bands can be observed depending on the length of conjugation.

Spectra of all APVC products and PVC demonstrate a common peak at low wavelength region ($\lambda < 300$ nm) which corresponds to electronic absorption of either remaining C-Cl bonds ($\lambda_{\text{max}} \approx 280$ nm) or short conjugations of $(\text{C}=\text{C})_n$, where $n=2,3,4$. Almost all species experience absorption with maxima starting

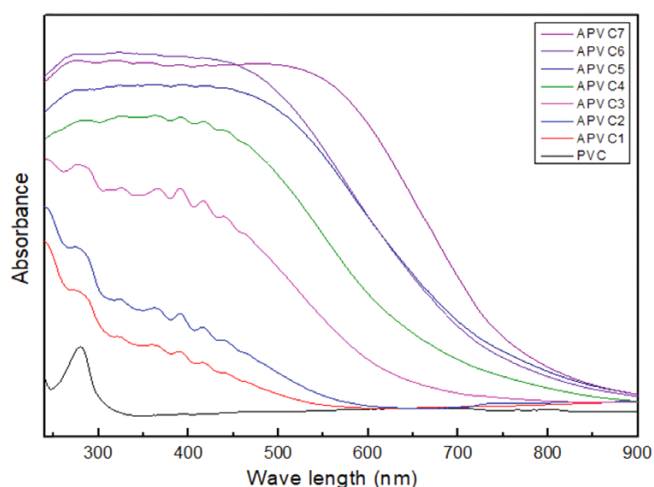


Figure 9. UV-Vis spectra of PVC-EDA made with 99% EDA solution at different temperatures.

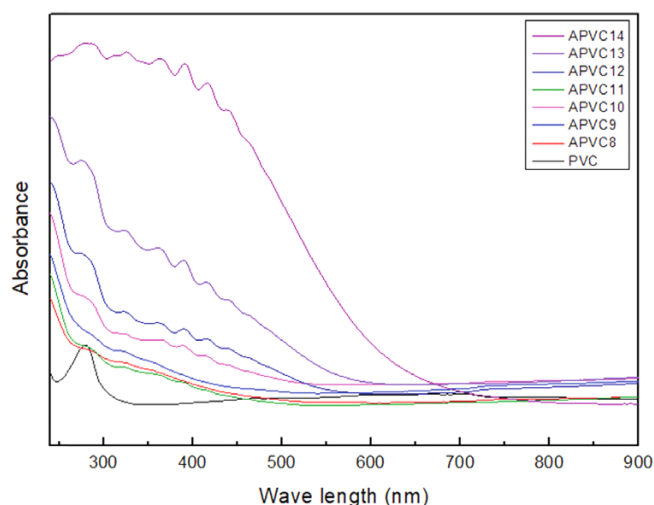


Figure 10. UV-Vis spectra of PVC-EDA made with 80% EDA solution at different temperatures.

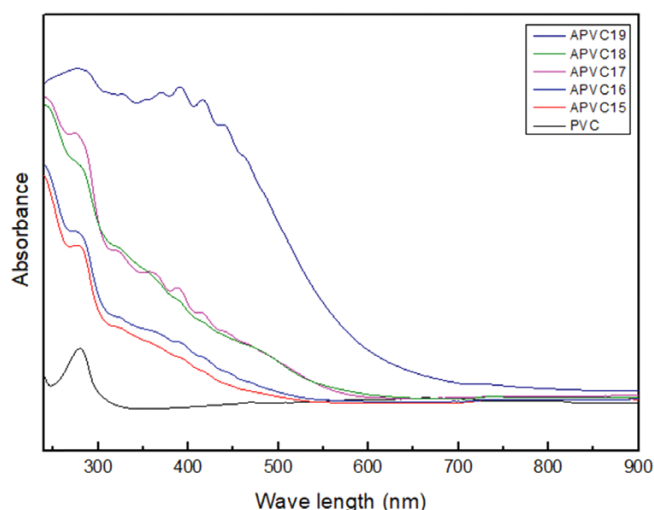


Figure 11. UV-Vis spectra of PVC-EDA made with 99% EDA in the presence of THF at different temperatures.

around $\lambda_{\max-A} \geq 300$ nm. According to Refs. 32, 33, length of conjugation (n) is suggested to be 2 ($\lambda_{\max-C} \approx 227$ nm), 3 ($\lambda_{\max-B} \approx 252$ nm, $\lambda_{\max-C} \approx 263$ nm, $\lambda_{\max-D} \approx 274$ nm), 4 ($\lambda_{\max-A} \approx 272$ nm, $\lambda_{\max-B} \approx 283$ nm, $\lambda_{\max-C} \approx 296$ nm, $\lambda_{\max-D} \approx 310$ nm), 5 ($\lambda_{\max-A} \approx 290$ -295 nm, $\lambda_{\max-B} \approx 310$ nm, etc.) or 6 ($\lambda_{\max-A} \approx 313$ -323 nm, etc.) around these wavelengths. Since several conjugation lengths would be mixed in our reaction systems, extra D bands are likely to be observed towards longer wavelengths. We define $\lambda_{\max-D}$ or $\lambda_{\max-edge}$ for the simplicity of analysis herein to indicate the edge of the band plateau where D band peak of longest conjugation appears and absorption starts to descend. Approximations of Sondheimer *et al.*³¹ can be used to establish an equation using the linear relationship between λ_{\max}^2 and n (conjugation length). Since $\lambda_{\max}^2 = a \times n$, and $\lambda_{\max} \approx 481$ nm is the maximum absorption of $n \approx 11$ samples in their work, thus the coefficient 'a' can be taken as 21032 nm^2 .

$\lambda_{\max-edge}$ reaches up to 580 nm in case of APVC7 which was prepared with 99% EDA at 85 °C. It corresponds to conjugation length, $n=16$. Of course longer conjugations are possible but the frequency would be lower for them. Over 65 °C conjugations overlap more and more and continuous bands are observed in case of 99% EDA system. The trend of multiple maxima is does not cease to appear until highest temperatures of the two other systems. $\lambda_{\max-edge}$ behavior of 80% EDA and THF systems are quite similar so as to be around 480 nm. This wavelength corresponds to a conjugation length of $n=11$. Nevertheless, real color of APVC19 (80% EDA system product at $T_{\max}=85$ °C) looks a little bit darker than that of APVC14 (THF system product at $T_{\max}=65$ °C).

Growing absorbance at wavelengths smaller than 300 nm actually may indicate the contribution of shorter polyene sequences ($n \leq 4$) having a number of conjugated double bonds as mentioned in Ref. 34. Hydrogen atoms at α -positions of the first carbon-carbon double bonds formed in PVC chain is called allylic secondary hydrogens. These hydrogens can be more suitably removed to form thermodynamically preferred conjugated sequences. Therefore, it is expected that long conjugated polyene sequences are formed gradually in polymer chain with this zipper effect.

Rising temperature may assist formation of longer conjugations. However, after some point, cross-linking and chain forming interactions may commence that limits the formation of much longer conjugation sequences at high temperatures. Instead, longer reaction durations and milder temperature conditions should be adopted to attain polyacetylene-like dehydrochlorinated PVC products *via* EDA reactions. UV-Vis spectroscopy and XPS findings imply that APVC 1~7 products possess relatively longer conjugated double bonds compared to APVC 8~14 and APVC 15~19.

According to Ref. 31, authors related the conjugation length and λ_{\max} to the degree of dechlorination. Results were as follows: $\lambda_{\max}=230$ nm for 2% dehydrochlorinated PVC, $\lambda_{\max}=460$ nm for 15% dehydrochlorinated PVC, etc. Since the reagents, mechanism and products mentioned there and in our work are not exact matches, direct comparison may be misleading but trends are comparable. Degree of unsaturation (oxidation excluded dehydrochlorination) turned out to be 74% in 99% EDA system, where $\lambda_{\max-edge} \approx 600$ nm and shoulder extends towards 800 nm, and almost 40% in two other systems, where $\lambda_{\max-edge} \approx 480$ nm and extends towards 600 nm.

4. Conclusions

Amination of PVC resin, PVC solution in THF and PVC membranes with ethylenediamine (EDA) resulted in partially aminated and mainly dehydrochlorinated products in varying amination and unsaturation degrees. XPS analysis was skillfully used to analyze surface characteristics and elemental composition of products. Increasing temperature favored both amination (substitution) and dehydrochlorination (elimination) reactions due to thermodynamic and kinetic factors. However, dehydrochlorination is more favored at higher temperatures as seen in dehydrochlorinated PVC synthesis efforts in which KOH, NaOH and other bases are used as dehydrochlorination agent. Longer reaction times at mild temperatures would reinforce amination over dehydrochlorination as results of membrane work suggest. 17.6% has been the highest degree of amination in PVC resin work, whereas it has been 33.7% for membranes. Up to 99% dechlorination has been accomplished with EDA use. These findings are highly promising for manufacturing ion exchange membranes with superior ion exchange capacity, *i.e.* anion exchange membranes (AEM), metal recovery agents, CO₂ adsorbents and toxic gas scrubbers, and also recycling and dehalogenation of PVC. This work successfully elaborated the process of PVC-EDA reaction in different states by evaluating the products with convenient calculation models. Also some conditions have been proposed to control amination and conjugation processes during these reactions in order for contributing research of functionalization and recycling of PVC.

Supporting information: Information is available regarding the FTIR Spectroscopy, SEM images and calculation for the PVC-EDA products. The materials are available *via* the Internet at <http://www.springer.com/13233>.

References

- (1) P. Jia, L. Hu, G. Feng, C. Bo, M. Zhang, and Y. Zhou, *Mater. Chem. Phys.*, **190**, 25 (2017).
- (2) C. Lăzăroaie, E. Rusen, B. Mărculescu, T. Zecheru, and G. Hubcă, *UPB Sci. Bull. Ser. B*, **72**, 127 (2010).
- (3) Y. Saeki and T. Emura, *Prog. Polym. Sci.*, **27**, 2055 (2002).
- (4) G. R. Krishnan, K. S. Niveditha, and K. Sreekumar, *Indian J. Chem.*, **52**, 428 (2013).
- (5) J. Zhu, Y. Su, X. Zhao, Y. Li, J. Zhao, X. Fan, and Z. Jiang, *Ind. Eng. Chem. Res.*, **53**, 14046 (2014).
- (6) S. M. Hosseini, M. Askari, P. Koranian, S. S. Madaeni, and A. R. Moghaddasi, *J. Ind. Eng. Chem.*, **20**, 2510 (2014).
- (7) Q. Shi, Q. Fan, W. Ye, J. Hou, S. C. Wong, X. Xu, and J. Yin, *ACS Appl. Mater. Interfaces*, **12**, 6 (2014).
- (8) J. Simmchen, R. Ventura, and J. Segura, *Trans. Med. Rev.*, **26**, 1 (2016).
- (9) S. Moulay, *Prog. Polym. Sci.*, **35**, 303 (2010).
- (10) G. Sneddon, J. C. McGlynn, M. S. Neumann, H. M. Aydin, H. H. Yiu, and A. Y. Ganin, *J. Mater. Chem. A*, **5**, 11864 (2017).
- (11) S. Balci, O. Birer, and S. Suzer, *Polymer*, **45**, 7123 (2014).
- (12) T. Kameda, M. Ono, G. Grause, T. Mizoguchi, and T. Yoshioka, *Polym. Degrad. Stab.*, **94**, 107 (2009).
- (13) T. Yoshinaga, M. Yamaye, T. Kito, T. Ichiki, M. Ogata, J. Chen, H. Fujino, T. Tanimura, and T. Yamanobe, *Polym. Degrad. Stab.*, **86**, 541 (2004).
- (14) B. Balakrishnan, D. S. Kumar, Y. Yoshida, and A. Jayakrishnan, *Biomaterials* **26**, 3495 (2005).
- (15) J. T. Allan, L. E. Prest, and E. B. Easton, *J. Membr. Sci.*, **489**, 175 (2005).
- (16) M. S. Mohy Eldin, T. M. Tamer, M. A. Abu Saied, E. A. Soliman, N. K. Madi, L. Ragab, and I. Fadel, *Adv. Polym. Technol.*, **0**, 21640 (2015).
- (17) J. Liu, Y. Q. Li, and W. J. Zheng, *Monatsh. Chem.*, **140**, 1425 (2009).
- (18) B. Balakrishnan, N. R. James, and A. Jayakrishnan, *Polym. Int.*, **54**, 1304 (2005).
- (19) M. de AMMS, M. Helena, R. M. N. De Assunção, H. M. Soares, A. P. Canganani, D. A. Cerqueira, and C. D. S. Meireles, *J. Appl. Polym. Sci.*, **115**, 1474 (2010).
- (20) L. Guo, G. Shi, and Y. Liang, *Polymer*, **42**, 5581 (2001).
- (21) R. Q. Fu, J. J. Woo, S. J. Seo, J. S. Lee, and S. H. Moon, *J. Membr. Sci.*, **309**, 156 (2008).
- (22) C. W. Hwang, C. M. Oh, and T. S. Hwang, *J. Adhes. Interface*, **15**, 1 (2014).
- (23) J. T. Allan, L. E. Prest, and E. B. Easton, *J. Membr. Sci.*, **489**, 175 (2015).
- (24) A. M. Saxman, R. Liepins, and M. Aldissi, *Prog. Polym. Sci.*, **11**, 57 (1985).
- (25) T. Masuda, *Encyclopedia of Polymeric Nanomaterials*, Springer-Verlag, Heidelberg, 2015.
- (26) J. A. Stowell, A. J. Amass, M. S. Beevers, and T. R. Farren, *Polymer*, **30**, 195 (1989).
- (27) A. Singh, M. S. M. Rawat, and C. S. Pande, *J. Appl. Polym. Sci.*, **118**, 876 (2010).
- (28) M. Beltran and A. Marcilla, *Eur. Polym. J.*, **33**, 1135 (1997).
- (29) L. Guo, G. Shi, and Y. Liang, *Synth. Met.*, **104**, 129 (1999).
- (30) A. Baruya, D. L. Gerrard, and W. F. Maddams, *Macromolecules*, **16**, 578 (1983).
- (31) M. Ghaemy and I. Gharaebi, *Eur. Polym. J.*, **36**, 1967 (2000).
- (32) F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).
- (33) D. Braun and D. Sonderhof, *Polym. Bull.*, **14**, 39 (1985).
- (34) K. Aouachria and N. Belhaneche-Bensemra, *Polym. Degrad. Stab.*, **91**, 504 (2006).