Chemical Modification of Rigid Poly(vinyl chloride) by the Substitution with Nucleophiles

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ABSTRACT: The reaction of rigid poly(vinyl chloride) (PVC) with iodide, hydroxide, azide, and thiocyanate as nucleophiles (Nu) in ethylene glycol (EG) resulted in the substitution of Cl by Nu additional to the elimination of HCl, leading to the dehydrochlorination of the rigid PVC. High substitution rates were observed for hydroxide, azide and thiocyanate, while the addition of iodide accelerated predominately the elimination of HCl. The substitution by thiocyanate resulted at 150°C in both thiocyanate and isothiocyanate structures, whereas at 190°C, only isothiocyanate was observed in the polymer. The dehydrochlorination yield increased with an increasing molar SCN/Cl ratio, resulting in a maximum substitution at high molar SCN/Cl ratios. When EG was replaced by diethylene glycol (DEG) as solvent, the dehydrochlorination was found to be accelerated. It was assumed that DEG has a higher compatibility with PVC, making it easier to penetrate the rigid PVC particle. For triethylene glycol (TEG), the rapid dehydrochlorination resulted probably in the coverage of the surface of the PVC particle by methyl methacrylate/butadiene/styrene (MBS), preventing the penetration by the solution. The substitution/dehydrochlorination ratio decreased in the order of EG > DEG > TEG because of the declining polarity of the solvent, stabilizing the activated S_N2 complex. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 36–44, 2010

Key words: rigid poly(vinyl chloride); chemical modification; nucleophilic substitution; thiocyanate; plastic recycling

INTRODUCTION

Poly(vinyl chloride) (PVC) is a common commodity plastic, and the production of the PVC is the third largest, after polyethylene (PE) and polypropylene.[1,2] In Japan, the PVC production was about 2.4×10^6 t in 2000. PVC is rarely used as a pure material. Its blends contain various additives, such as plasticizers and stabilizers. Flexible PVC contains between 15 and 40 wt % plasticizer, whereas PVC without plasticizer is distributed as rigid PVC. Methyl methacrylate/Butadiene/Styrene (MBS) is a frequently used impact modifier for rigid PVC. Rigid PVC has an excellent mechanical strength, and is commonly used for pipes, joints, and building materials. About 800,000 t/a PVC is used for the production of pipe, making this the most produced article from PVC. Also about 60% of the recycled PVC is reused for the production of pipes. However, the most of the waste PVC materials, used in the construction sector, is not recycled. To improve the recyclability of PVC materials, a new recycling method for rigid PVC will be proposed in this study.

Although many studies have investigated the dehydrochlorination of PVC, using dry and wet treatments,[3–12] an optimal solution for the problem of PVC recycling was not found yet. The main problem of the dry treatment is the production of polyenes and their cyclization. Therefore, the use of dehydrochlorinated PVC, obtained from dry processes, is limited to certain applications such as the use as blast furnace reductant. We developed a wet treatment process of PVC for the effective dehydrochlorination in aqueous NaOH at high temperature and pressure using an autoclave.[13–19] This process has already been put into practical use in Denmark. Recently, we have demonstrated the effective dehydrochlorination of PVC in NaOH/ethylene glycol (EG) solution at atmospheric pressure, making use of the high boiling point of EG (196°C). This dehydrochlorination reaction was found to occur via a combination of E2 and S_N2 mechanisms, as shown in Scheme 1.[20] We have focused on the S_N2 reaction for the dehydrochlorination of PVC in NaOH/EG solution. As shown in Scheme 2, the substitution of Cl in PVC by a nucleophile (Nu) in solution has a possibility to develop new polymers with new functional groups to upgrade PVC during its recycling.

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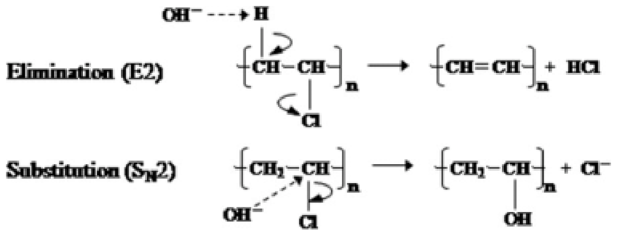


Scheme 1 Mechanism of the dehydrochlorination of PVC in NaOH/EG solution.

The new polymers are expected to be widely and effectively used depending on new properties, induced by the new functional groups.

Several investigations were made to introduce new functional groups into PVC.[21–24] In these investigations, the dissolved PVC was treated with sulfur containing nucleophiles, such as organic thiolates, mainly to obtain antimicrobial properties. Substitution yields of about 50% were achieved; however, elimination was avoided and chlorine remained in the polymer.

The purpose of this research, however, is the dehydrochlorination of PVC. Since dehydrochlorination of PVC leaves a rigid char coal like material, it is necessary to upgrade its properties to find useful applications for this material. This study has examined the upgrade recycling of rigid PVC, i.e., the substitution of Cl by Nu in solution. The examined Nu^- were I^-, SCN^-, OH^-, and N_3^-. The polymers, developed by the substitutions of Cl by I^- and SCN^- in solution are expected to have an increased conductivity and antibacterial activity, respectively. The polymer with N_3^- can be used for the further introduction of various kinds of functional polymers because of the high reactivity of the N_3-group.

EXPERIMENTAL

Materials

The rigid PVC and other chemicals of reagent grade were purchased from Kanto Chemical (Tokyo, Japan) and Wako Pure Chemical Industries (Osaka, Japan). Table I shows the composition of the rigid PVC pellets used. It consists primarily of PVC, MBS as an impact modifier, and Sn stabilizer.

$$\left[-CH_2-\underset{\mathrm{Cl}}{\underset{|}{CH}}-\right]_n + n\,Nu^- \longrightarrow \left[-CH_2-\underset{\mathrm{Nu}}{\underset{|}{CH}}-\right]_n + n\,Cl^-$$

Scheme 2 Reaction formula of the substitution of Cl in PVC by any nucleophile (Nu) in solution.

TABLE I
Chemical Composition of the Rigid PVC Pellets Used

	(wt %)
PVC	82.4
MBS	13.2
Sn stabilizer	2.47
Monoglyceride	0.99
Processing aid	0.82
LDPE	0.082
Pigment	0.012

MBS, Methyl methacrylate/Butadiene/Styrene; LDPE, Low density polyethylene.

The rigid PVC was pelletized to a size of 4 mm, cooled with liquid nitrogen, grinded, and then sieved. The particles with a size of 150–250 μm were used for further experiments. The Cl content in rigid PVC powder was 46.5 wt %. NaI, KSCN, NaOH, and NaN_3 were used as reagents for the substitution reaction.

Methods

The Nu/EG solution was prepared by dissolving the Nu in EG. A total of 50 mL of Nu/EG solution was given into a 100 mL flask; and then, the flask was heated to the reaction temperature of 150–190°C using a silicone oil bath under a N_2 flow of 100 mL min^{-1}. After the temperature reached 150–190°C, 1.0 g of the rigid PVC powder was added to the solution with the Nu/Cl (in rigid PVC) molar ratio of 0–8, and it was stirred for the required time. After the flask was cooled with water, the reactant was filtered, washed with deionized water and methanol, and dried under reduced pressure. Furthermore, diethylene glycol (DEG) and triethylene glycol (TEG) were used as solvents instead of EG.

Characterization

The Cl concentrations of the filtrate were determined using a Dionex DX-100 ion chromatograph and a Dionex model AS-16A column (eluent: 35 mM NaOH). The residue was treated at 850°C under a air flow of 100 mL min^{-1}, and the evolved gas was filtered by water and hydrogen peroxide/water traps. The Cl and I in the residue were determined by analyzing the solution in the traps with an ion chromatograph. The contents of C, H, N, and S in the residue were determined by combustion analysis. The residue was also analyzed by Fourier transform infrared spectroscopy (Bio-Rad Win IR-165). PVC and its substitution products, respectively, were grinded and mixed with KBr in a ratio of 1 : 4, and after that pelletized.

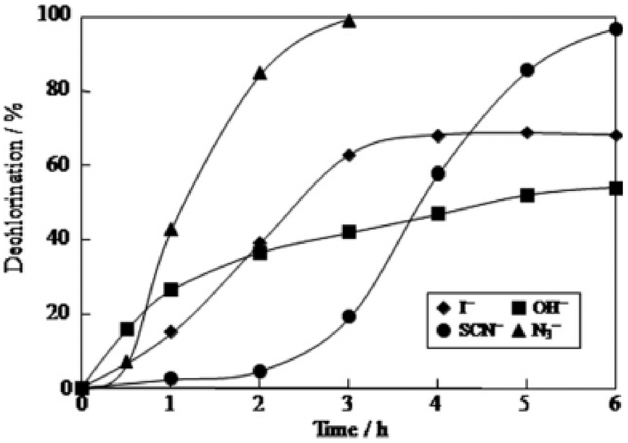


Figure 1 Effect of the nucleophile on the degree of dehydrochlorination of rigid PVC in Nu/EG solution with the Nu/Cl (in rigid PVC) molar ratio of 4 at 190°C.

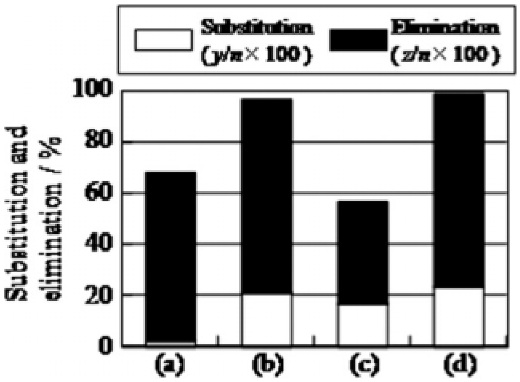


Figure 2 Effect of the nucleophile on the substitution of Cl in rigid PVC and the elimination of HCl resulting in the dehydrochlorination of rigid PVC in Nu/EG solution with a Nu/Cl (in rigid PVC) molar ratio of 4 at 190°C. Nu^-: (a) I^-, (b) SCN^-, (c) OH^-, (d) N_3^-. Time: (a) 6 h, (b) 6 h, (c) 3 h, (d) 3 h.

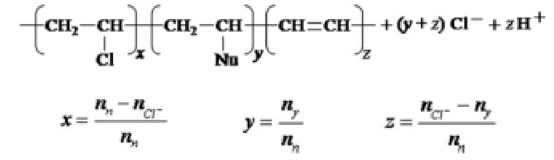
RESULTS AND DISCUSSION

Effect of nucleophile

Figure 1 shows the effect of the nucleophile on the dehydrochlorination yield of rigid PVC in Nu/EG solution with a Nu/Cl (in rigid PVC) molar ratio of 4 at 190°C. In this case, the dehydrochlorination yield was calculated as the percentage of the amount of Cl, released into the filtrate, compared with the content of Cl in the rigid PVC. For OH^-, the dehydrochlorination yield increased gradually with time, reaching 54% after 6 h, compared with 100% after 45 min for pure PVC[20] because of the protection of the surface of the rigid PVC by a cover of MBS. The MBS coating caused a reduction of the reactive surface area of the rigid PVC that was in contact with the hydroxide solution, resulting in a reduction of the dehydrochlorination yield.

The behavior of the other nucleophiles I^-, N_3^-, and SCN^- differed strongly from that of OH^-. Both N_3^- and SCN^- reached a dehydrochlorination yield of almost 100% within 3 and 6 h, respectively. The dehydrochlorination yield of I^- reached 68% after 6 h. The observation that the dehydrochlorination in the absence of any Nu^- is negligible, leads to the assumption that the dehydrochlorination was caused by the nucleophile. In opposite to OH^-, the behavior of the dehydrochlorination of N_3^-, SCN^-, and I^- resulted in an *S*-shaped curve. This can be explained by a change in the mechanism, caused by the difference in the acidity of the anions, used as nucleophiles. I^-, SCN^- ($pK_a = -1.8$), and N_3^- ($pK_a = 4.6$) are the anions of strong or medium acids,[25] whereas OH^- is a strong base. Most likely, OH^- has a strong affinity to the Cl neighboring hydrogen, resulting in a preference toward the elimination (Scheme 1), followed by the fast dehydrochlorination by a zipper mechanism.[26] This was also assumed for the dehydrochlorination of PVC in aqueous NaOH solution.[27] In opposite, strong acids prefer the reaction after the substitution mechanism, causing the release of small yields of Cl^- in the beginning of the reaction. In case, the new functional group is also a good leaving group, the new introduced weak bond results in an elimination followed by the rapid occurring zipper mechanism. It can be seen for e.g., I^-, which is similar to Cl^- also a good leaving group, that in the beginning the substitution is preferred. With the advancing reaction time and increasing iodine content of the polymer, I^- is eliminated, resulting in the rise of the dehydrochlorination yield until the dehydrochlorination of the accessible part of the PVC particle is completed. The maximum dehydrochlorination yield is determined by the ability of the nucleophile to penetrate the PVC particle.

Based on the elemental analysis of the residue, the effect of the nucleophile on the substitution of Cl and the elimination of HCl during the



$$-\!\left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_n\!- + yNu^- \longrightarrow -\!\left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_x\!\left[CH_2-\underset{Nu}{\underset{|}{CH}}\right]_y\!\left[CH=CH\right]_z\!- + (y+z)\,Cl^- + zH^+$$

$$x = \frac{n_n - n_{Cl^-}}{n_n} \qquad y = \frac{n_y}{n_n} \qquad z = \frac{n_{Cl^-} - n_y}{n_n}$$

Scheme 3 Calculation of the yields of substitution *y* and elimination *z*. The amount of substance is given by *n* with the indices as follows: *n* (total amount of chlorine), *x* (in the polymer remaining chlorine), *y* (nucleophile: I^-, OH^-, N_3^-, SCN^-), *z* (doublebonds), Cl^- (chloride detected by ion chromatography).

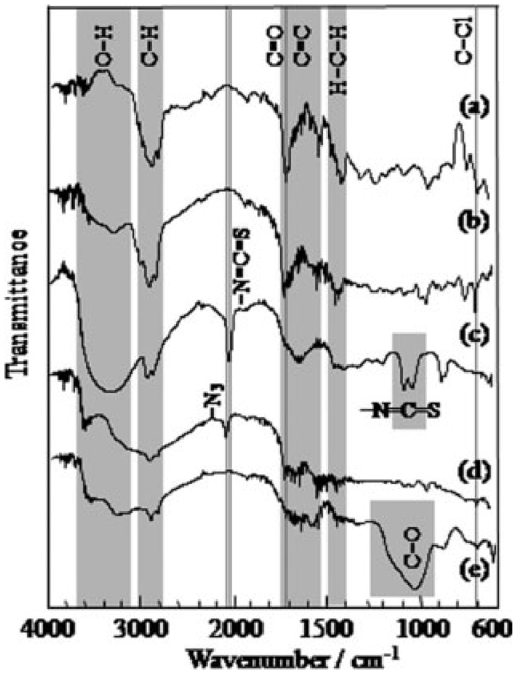


Figure 3 FTIR spectra of (a) rigid PVC, and the products obtained from the reaction of rigid PVC in Nu/EG solution with different nucleophiles (molar Nu/Cl ratio: 4) at 190°C. Nu^-: (b) I^-, (c) SCN^-, (d) OH^-, (e) N_3^-. Time: (b) 6 h, (c) 6 h, (d) 3 h, (e) 3 h.

dehydrochlorination of rigid PVC in Nu/EG solution with a Nu/Cl (in rigid PVC) molar ratio of 4 at 190°C was examined as shown in Figure 2. In this case, the yields of the substitution and elimination are calculated by the percentages of y and z to n, respectively, according to Scheme 3. The sum of the yields of the substitution and elimination represents the dehydrochlorination yield, and it is expressed by the quotient of $(y + z)$ and n. The amount of the remaining Cl is expressed by the quotient of x and n. In all cases, the substitution yield was lower than that of the elimination, showing that the elimination was favored over the substitution. For SCN^-, OH^-, and N_3^-, the substitution yields were relatively high, reaching about 20% [Fig. 2(b–d)]. The ratio between the substitution and the dehydrochlorination yield (the sum of substitution and elimination) was 0.04, 0.22, 0.30, and 0.24 for I^-, SCN^-, OH^-, and N_3^-, respectively, leading to the order $OH^- > N_3^- = SCN^- > I^-$. This corresponds with the nucleophilic reactivity constants in the order of I^- (7.42) > SCN^- (6.7) > N_3^- (5.78) > Cl^- (4.37).[28] I^-, SCN^-, and N_3^- were able to replace Cl^- from the polymer because of their stronger nucleophily. The low substitution yield of I^- is attributed to its subsequent elimination. These results are similar to the case of PVC resin,[29] indicating that additives such as MBS do not affect the substitution and elimination.

Figure 3 shows the FTIR spectra of rigid PVC, and its products obtained from the reaction of rigid PVC with different nucleophiles at 190°C. For the rigid PVC [Fig. 3(a)], the FTIR spectrum displays the absorption bands corresponding to the C—H stretching vibration with two peaks (2850 and 2917 cm^{-1}) and H—C—H deformation vibration (1437 $cm^{-1)}$, derived mainly from PVC. The peaks at 3023 cm^{-1} and 698 cm^{-1} indicate the H—CCl and the C—Cl stretching vibrations, respectively. The FTIR spectrum displays also the absorption bands corresponding to the C=O stretching vibration (1734 cm^{-1}) derived from methyl methacrylate in MBS. The peaks, corresponding to the C=O stretching vibrations, disappeared after the substitution with SCN^-, N_3^-, and OH^- [Fig. 3(c–e)], suggesting that MBS was dissolved by the solvent EG during the substitution process. The spectrum of the I^- substitution did not reveal significant differences from the original PVC sample [Fig. 3(b)]. The FTIR spectra of the other products, however, confirmed the substitution of Cl by the nucleophiles used during a S_N2 mechanism. The aliphatic C—H, H—C—H and C—Cl vibrations became smaller due to the elimination of HCl. For SCN, no Cl-related peaks were observed anymore. Therefore, peaks, corresponding to —N=C=S stretching vibrations, appeared at 2062 cm^{-1} (asymmetric), 1042 cm^{-1}, and 1084 cm^{-1} (symmetric), suggesting that only isocyanate groups were present in the polymer. A broad peak at 1654 cm^{-1} indicated the formation of polyene chains [Fig. 3(c)]. The absorption band of N_3^- centered at 2103 cm^{-1}, corresponding to the —N_3 stretching vibration [Fig. 3(d)]. The hydroxide substituted product showed a large broad absorption band centered at 1040 cm^{-1}, corresponding to the C—O stretching vibration [Fig. 3(d)]. The two peaks at 1596 cm^{-1} and 1650 cm^{-1}, corresponding to C—C stretching vibrations, might indicate shorter polyene sequences compared with the SCN substituted product. It is known that the increase in the length of the conjugated C=C double bond results in the change in color of the product from white to yellow, orange, red, brown, and black, depending on the conjugation rate. Therefore, the color of the products changed from white for the untreated PVC to black, dark brown, brown, and black for I^-, SCN^-, OH^-, and N_3^-, respectively. The difference in the color might be caused by different lengths of the conjugated systems, suggesting that the conjugated systems of the polymers, treated with SCN^- and OH^-, were shorter. However, it cannot be excluded that the type of the substitution group had an impact on the observed color.

Surprisingly, besides OH^-, also SCN^- and N_3^- showed the presence of hydroxide groups in their FTIR spectra. A broad O—H stretching vibration (3334 cm^{-1}) was found for SCN^-. Also the N_3^--product contained isolated hydroxide groups

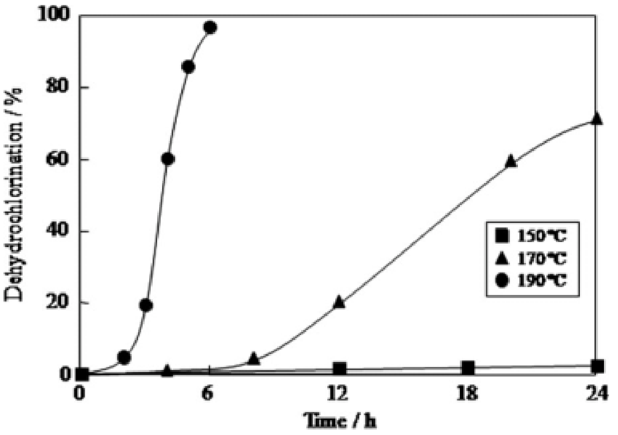


Figure 4 Effect of the temperature on the dehydrochlorination yield of rigid PVC in SCN/EG solution with a molar SCN/Cl ratio of 4.

according to the O—H stretching vibration at 3629 cm^{-1}. The origin of this finding might be the solvent. Ethylene glycol contains also hydroxide groups, which might undergo substitution reactions. The released hydroxide ions might be incorporated to some extent in the polymer.

Consequently, the dehydrochlorination of rigid PVC in the presence of a Nu/EG solution did not result only in the elimination of Cl$^-$ but also in its substitution by the nucleophile. SCN$^-$ and N$_3$$^-$ were effective nucleophiles, resulting in high substitutions yields. However, the use of the SCN-group may result in various unexpected reactions due to its high reactivity. In the next section, therefore, the effects caused by the substitution of Cl$^-$ by SCN$^-$ on rigid PVC were examined in detail. The effects of temperature, molar SCN/Cl (in rigid PVC) ratio, and the solvent used were investigated.

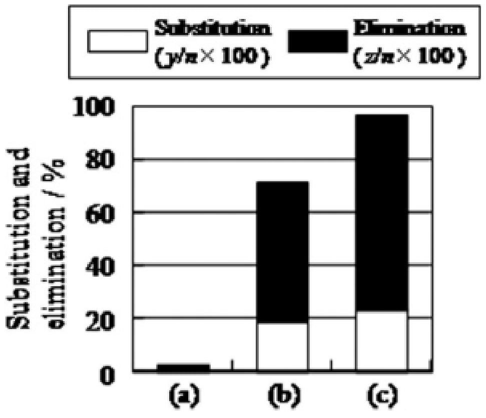


Figure 5 Effect of temperature on the substitution of Cl in rigid PVC with SCN in solution and elimination of HCl for the dehydrochlorination of rigid PVC in SCN/EG solution with the SCN/Cl (in rigid PVC) molar ratio of 4. Condition: (a) 150°C, 24 h (b) 170°C, 24 h (c) 190°C, 6 h.

Effect of SCN

Figure 4 shows the effect of the temperature on the dehydrochlorination yield of rigid PVC in SCN/EG solution with a molar SCN/Cl ratio of 4. The dehydrochlorination yield increased with the time, rapidly at 190°C, gradually at 170°C, and slightly at 150°C. The dehydrochlorination yield increased strongly with the temperature, reaching 96.7% after 6 h at 190°C. The reduction of the temperature resulted in a significantly deceleration of the reaction velocity, and 71.2 and 2.2% were obtained at 170°C and 150°C, respectively, after 24 h. Figure 5 shows the effect of the temperature on the substitution of Cl by SCN, compared with the elimination of HCl. The substitution yield increased with the temperature, reaching 0.9, 19, and 23.3% at 150, 170, and 190°C, respectively. It is noteworthy that the ratio between the substitution and the dehydrochlorination decreased with increasing temperature, resulting in 0.43, 0.27, and 0.24 at 150, 170, and 190°C, respectively. In contrast, the ratio between the elimination and the dehydrochlorination increased, reaching 0.57, 0.73, and 0.76 at 150, 170, and 190°C, respectively. This shows that high temperatures favor the elimination to the substitution. This is supported by the fact that high temperatures generally promote the elimination, although the elimination and substitution are competitive reactions.

Figure 6 shows the FTIR spectra of rigid PVC and the products, obtained after the reaction with SCN

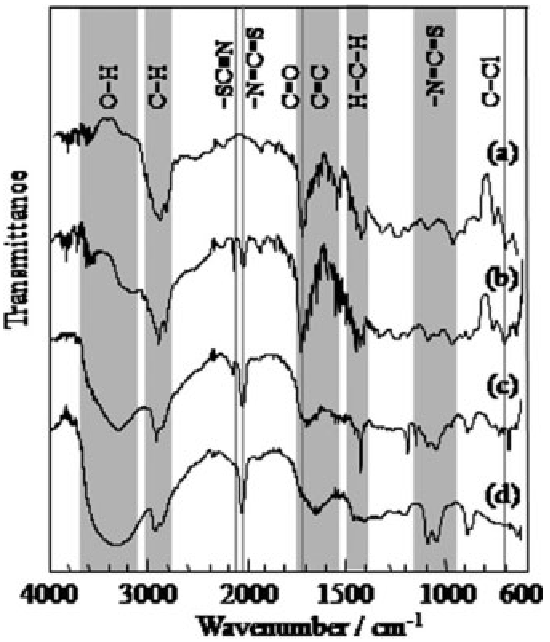


Figure 6 FTIR spectra of (a) rigid PVC and the products, obtained from the reaction with SCN at a molar SCN/Cl ratio of 4. Condition: (b) 150°C, 24 h (c) 170°C, 24 h (d) 190°C, 6 h.

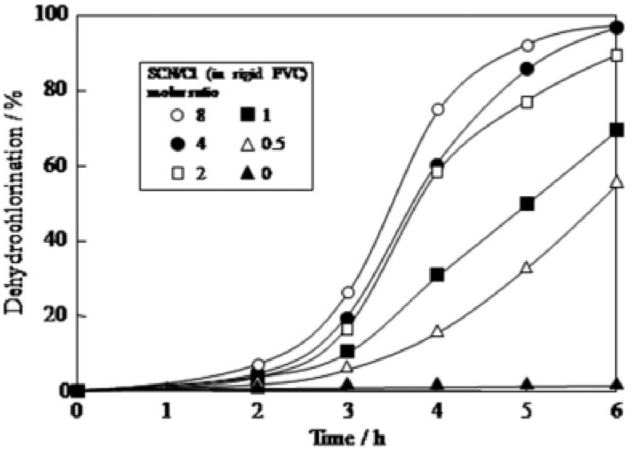


Figure 7 Effect of the molar SCN/Cl ratio on the degree of dehydrochlorination 190°C.

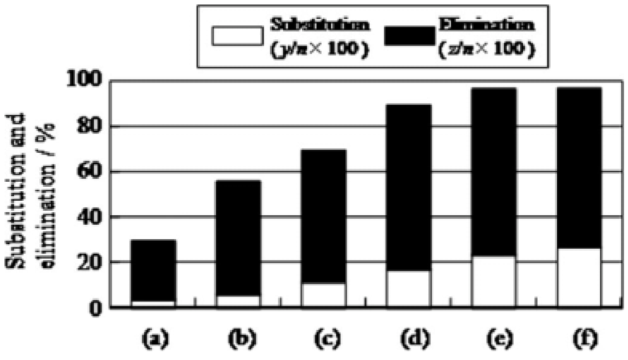


Figure 8 Effect of the molar SCN/Cl ratio on the yields of the substitution, elimination, and dehydrochlorination dependant on the molar SCN/Cl ratio at 190°C after 6 h of reaction time. SCN/Cl (in rigid PVC) molar ratio: (a) 0.25, (b) 0.5, (c) 1, (d) 2, (e) 4, (f) 8.

with a molar SCN/Cl ratio of 4 at 150, 170, and 190°C. The FTIR spectra of the products confirmed the substitution of Cl by SCN by a S_N2 mechanism. The FTIR spectrum of the product, obtained at 150°C [Fig. 6(b)], displayed the absorption bands derived from the —*S*—C≡N group (2151 cm^{-1}) and the —N—C—S group (2060 cm^{-1}). The absorption bands, derived from the —*S*—C≡N group, decreased in their intensity at 170°C and disappeared at 190°C, whereas the absorption bands derived from the —N—C—S group increased [Fig. 6(c,d)]. This indicates the isomerization of the —*S*—C≡N group, resulting in an increasing number of —N—C—S groups. It can be stated that the product at 150°C has a mixed structure of thiocyanate and isothiocyanate, whereas the product at 190°C consisted exclusively of isothiocyanate. The FTIR spectra for the products showed also the acceleration of the elimination of HCl by an E2 mechanism by the temperature. While at 150°C C—C stretching vibrations were not observed, their presence indicated isolated double bonds (1699 cm^{-1}) at 170°C and polyenes (1654 cm^{-1}) at 190°C. Therefore, the color changed from white for the rigid PVC to slightly yellow for the product at 150°C, and dark brown for the products at higher temperature.

Figure 7 shows the effect of the molar SCN/Cl ratio on the dehydrochlorination yield at 190°C. The addition of any concentration of SCN$^-$ supported the dehydrochlorination visibly. Even a small molar SCN/Cl ratio of 0.5 caused the release of more than 50% of the Cl$^-$ after 6 h of reaction. The dehydrochlorination yield increased with the molar SCN/Cl ratio after an initial time between 2 and 3 h, dependant on the concentration. It reached more than 90% of dehydrochlorination at a ratio of 8 after 5 h and at ratios of 2 and 4 after 6 h. Figure 8 shows the effect of the molar SCN/Cl ratio on the yields of various reactions during the dehydrochlorination at 190°C after 6 h of reaction. The elimination yield increased with increasing molar SCN/Cl ratio from 0 to 4, resulting in a maximum elimination yield of 73.4%, before it slightly decreased with molar ratios between 4 and 8. The substitution yield increased with an increasing molar SCN/Cl ratio, reaching 23.3 and 26.7% at molar ratios of 4 and 8, respectively. The ratio between substitution and elimination increased also with an increasing molar SCN/Cl ratio. These results indicate that already low SCN$^-$ concentrations catalyzed the elimination of Cl$^-$. The substitution was related to an equilibrium between double bonds and SCN$^-$ concentration. The rise in the SCN$^-$ concentration increased also the substitution yield. The elimination yield was not affected as long the dehydrochlorination yield did not reach its maximum. After that, the elimination yield was slowly reduced because of the change in the equilibrium conditions. However, difficulties in the filtratation of the reactants due to the high viscosity of highly concentrated SCN/EG solutions suggest that

TABLE II
Solubility Parameters for PVC and Different Solvents[30]

	(MPa)$^{1/2}$				
	δ_d	δ_p	δ_h	δ	$\Delta\delta$
PVC	18.82	10.03	3.07	21.54	–
TEG	16.0	12.5	18.6	27.4	–5.9
DEG	16.2	14.7	20.5	29.9	–8.4
EG	17.0	11.0	26.0	32.9	–11.4
H_2O	15.5	16.0	42.4	47.9	–26.4

δ_d: Dispersive term, δ_p: Polar term.

δ_h: A variety of association bonds, including hydrogen bonds and permanent dipole-induced dipole.

δ: Solubility parameter, $\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$.

$\Delta\delta = \delta_{PVC} - \delta_{solvent}$.

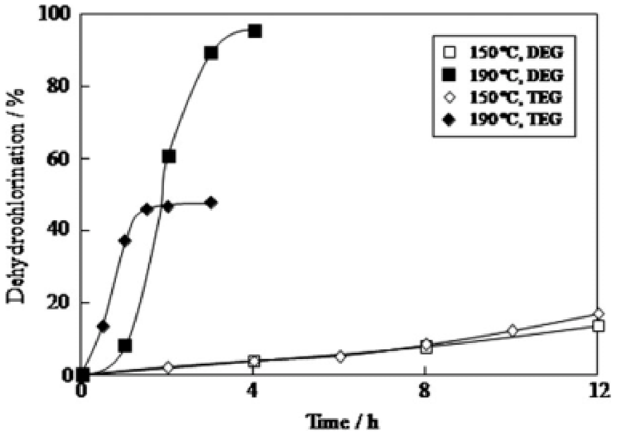


Figure 9 Effect of the temperature on the dehydrochlorination yield of rigid PVC in SCN/DEG or SCN/TEG solution with a molar SCN/Cl ratio of 4.

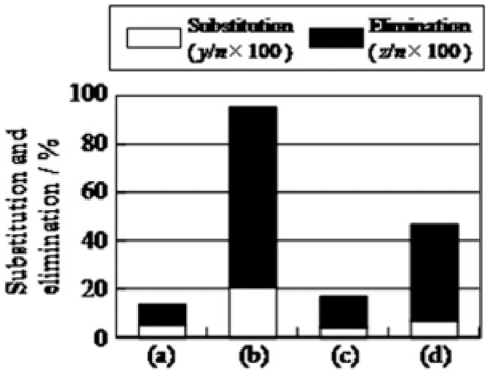


Figure 10 Effect of the temperature on the substitution of Cl by SCN and the elimination of HCl in SCN/DEG and SCN/TEG solutions with a molar SCN/Cl ratio of 4. SCN/DEG : (a) 150°C, 12 h (b) 190°C, 4 h. SCN/TEG: (c) 150°C, 12 h (d) 190°C, 3 h.

even if these solutions result in higher substitution yields, molar SCN/Cl ratios higher than 4, representing a KSCN concentration of 1 mol l^{-1}, should be omitted.

Effect of solvent

The ability of the solvent to penetrate the PVC particles has a big impact on the efficiency of the dehydrochlorination of PVC. Table II shows the solubility parameters for PVC and several solvents.[30] The compatibility between PVC and the solvents used is expressed by the difference of the solubility parameters, Δδ. A small difference in these values expresses a high compatibility, resulting in a good penetration of the PVC particle by the solvent, leading to the acceleration of the dehydrochlorination. The difference in the solubility parameters (Δδ) of the solvent and the PVC decreases in the order of TEG < DEG < EG < H_2O, leading to the assumption that TEG and DEG should be better media for the dehydrochlorination of PVC than EG. Therefore, the behavior of TEG and DEG as solvents during the reaction of rigid PVC was examined.

Figure 9 shows the effect of the temperature on the dehydrochlorination yield of rigid PVC in SCN/DEG or SCN/TEG solution with a molar SCN/Cl ratio of 4. Both solvents showed a rising dehydrochlorination yield with the time, rapidly at 190°C and gradually at 150°C. For DEG, the dehydrochlorination yield was 95.4% at 190°C after 4 h and 13.6% at 150°C after 12 h. The comparison with EG (Fig. 4: 96.7% at 190°C after 6 h and 2.2% at 150°C after 24 h) shows an acceleration of the reaction, confirming the better compatibility of the DEG with PVC.

The dehydrochlorination increased more rapid in TEG than in EG, however, after 1.5 h, a constant dehydrochlorination yield of about 46% was reached at 190°C. The rapid dehydrochlorination resulted probably in the coverage of the PVC surface by MBS, likely preventing the penetration by the solution. Figure 10 shows the effect of the temperature on the substitution of Cl by SCN and the elimination of HCl in SCN/DEG and SCN/TEG solutions with a molar SCN/Cl ratio of 4. The substitution yield for DEG was 5.3 and 21% at 150 and 190°C, respectively, resulting in a substitution/dehydrochlorination ratio of 0.39 and 0.22. For TEG, the substitution yield was slightly lower at 150°C with 4.2%, and

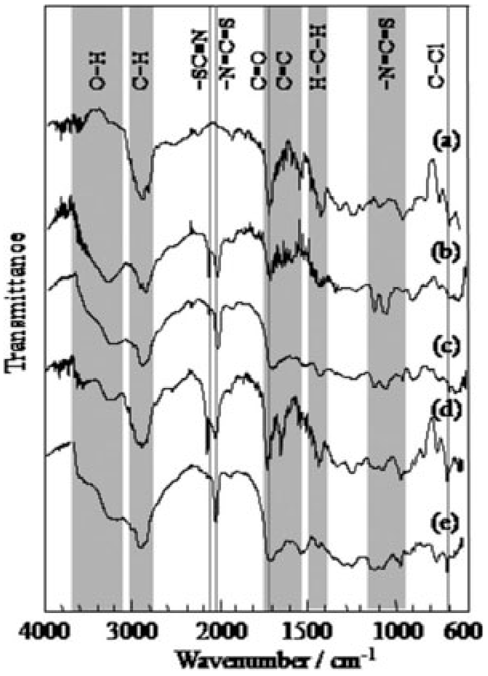


Figure 11 FTIR spectra of (a) rigid PVC and the products, obtained from the reaction of rigid PVC in SCN/DEG or SCN/TEG solutions with a molar SCN/Cl ratio of 4. SCN/DEG: (b) 150°C, 12 h (c) 190°C, 4 h. SCN/TEG: (d) 150°C, 12 h (e) 190°C, 3 h.

strongly reduced at 190°C with 6.9% because of the hindered penetration of the PVC particles by MBS, accompanied by lower substitution/dehydrochlorination ratios of 0.25 and 0.15, respectively. It should be noted that the substitution/dehydrochlorination ratio increased with decreasing temperature. The comparison with the results for EG (Fig. 5) show a decreasing substitution/dehydrochlorination ratio in the order of EG (0.24) > DEG (0.22) > TEG (0.15) at 190°C because of the change in the polarity of the solvent. The polar activated complex of the S_N2 mechanism is stabilized best by a polar solvent such as EG, whereas the E2 mechanism is favored with less polar solvents such as TEG.

The color of the white PVC changed to brown in all cases, suggesting the presence of conjugated C—C double bonds in the products, obtained from the dehydrochlorination by an E2 mechanism. Figure 11 shows the FTIR spectra of rigid PVC and products, obtained from the reaction of rigid PVC in SCN/DEG or SCN/TEG solutions with a molar SCN/Cl of 4 at 150 and 190°C. The peaks, corresponding to the C=O stretching vibrations of MBS (around 1730 cm^{-1}), were still visible at least for the products obtained at 150°C [Fig. 11(b–e)], suggesting that MBS remained in the particle. The FTIR spectra of the products obtained at 150°C show also the absorption bands of the C=C stretching vibrations (1653 cm^{-1}), confirming the elimination of HCl by an E2 mechanism. The FTIR spectra for the products also confirm the substitution of Cl in by SCN by an S_N2 mechanism. The FTIR spectra of the products at 150°C, shown in Figure 11(b,d), show both isomeric forms of the thiocyanate, the $-S-C\equiv N$ group (2154 cm^{-1}) and the $-N=C=S$ group (around 2055 cm^{-1}). Both isomers were still visible at 190°C in the presence of DEG [Fig. 11(c)], whereas only $-N=C=S$ group was observed in the presence of TEG.

CONCLUSIONS

The reaction of rigid PVC in Nu/EG solution was found to result in the substitution of Cl by different nucleophiles in addition to the elimination of HCl, leading to the dehydrochlorination of the rigid PVC. During the reaction, MBS was dissolved by EG at 190°C, however, remained in the particle, when other solvents of conditions were used. SCN^- and N_3^- were effective nucleophiles because of the high substitutions yield observed. However, the N_3-group owns a high reactivity, which may result in various unexpected reactions. Therefore, the chemical modification of the rigid PVC by the substitution with SCN^- was examined in detail. In the SCN/EG solution, the substitution/dehydrochlorination ratio increased with decreasing temperature. The product at 150°C revealed the mixed structure of thiocyanate and isothiocyanate, whereas the product contained only isothiocyanate groups at 190°C. This is attributed to the isomerization of the $-S-C\equiv N$ group, forming $-N=C=S$ groups at high temperatures. The dehydrochlorination yield increased with increasing the molar SCN/Cl ratio, and a high molar SCN/Cl ratio was found to favor the substitution over the elimination. Besides EG, DEG, and TEG were also examined as solvents for the reaction of rigid PVC with SCN^-. The dehydrochlorination preceded in DEG more rapid than in EG. It is considered that the solvent owns a higher compatibility with PVC, making the penetration of the PVC particle easier, and leading to the acceleration of the dehydrochlorination. In opposite to EG and DEG, the larger TEG molecules were not able to penetrate the PVC surface covered with MBS, preventing the PVC from dehydrochlorination. The substitution/dehydrochlorination ratio decreased in the order of EG > DEG > TEG due to the decreasing polarity of the solvents, resulting in a reduced stabilization of the activated S_N2 complex.

References

1. Vinyl Environmental Council, Available at http://www.vec.gr.jp/main.html. (accessed July 23, 2009).
2. Scheirs, J. In Feedstock Recycling and Pyrolysis of Waste Plastics, Scheirs, J., Kaminsky, W., Eds.; Wiley: London, 2006. pp 678–695.
3. Winkler, D. E. J Polym Sci 1959, 35, 3.
4. Kise, H. J Polym Sci 1982, 20, 3189.
5. Montaudo, G.; Puglisi, C. Polym Degrad Stab 1991, 33, 229.
6. Yoshioka, T.; Akama, T.; Uchida, M.; Okuwaki, A. Chem Lett 2000, 29, 322.
7. Guo, L.; Shi, G.; Liang, Y. Polymer 2001, 42, 5581.
8. Mio, H.; Saeki, S.; Kano, J.; Saito, F. Environ Sci Technol 2002, 36, 1344.
9. Yoshinaga, T.; Yamaye, M.; Kito, T.; Ichiki, T.; Ogata, M.; Chen, J.; Fujino, H.; Tanimura, T.; Yamanobe, T. Polym Degrad Stab 2004, 86, 541.
10. Yoshioka, T.; Saitoh, N.; Okuwaki, A. Chem Lett 2005, 34, 70.
11. Yoshioka, T.; Imai, S.; Ieshige, M.; Okuwaki, A. In Feedstock Recycling of Plastics. Muller-Hagedorn, M., Bockhorn, H., Eds.; Universitatsverlag Karlsruhe: Germany, 2005. pp 147–52.
12. Scheirs, J. In Feedstock Recycling and Pyrolysis of Waste Plastics. Scheirs, J., Kaminsky, W., Eds.; Wiley: London, 2006; pp 498–502.
13. Yoshioka, T.; Yasuda, S.; Kawamura, K.; Sato, T.; Okuwaki, A. Nippon Kagaku Kaishi 1992, 1992, 534.
14. Yoshioka, T.; Furukawa, K.; Sato, S.; Okuwaki, A. Energy Resour 1995, 16, 165.
15. Yoshioka, T.; Furukawa, K.; Okuwaki, A. Polym Degrad Stab 2000, 67, 285.
16. Yoshioka, T.; Furukawa, K.; Sato, S.; Okuwaki, A. J Appl Polym Sci 1998, 70, 129.
17. Shin, S-M.; Watanabe, S.; Yoshioka, T.; Okuwaki, A. Nippon Kagaku Kaishi 1997, 1997, 64.
18. Shin, S-M.; Yoshioka, T.; Okuwaki, A. Polym Degrad Stab 1998, 61, 349.
19. Shin, S-M.; Yoshioka, T.; Okuwaki, A. J Appl Polym Sci 1998, 67, 2171.

20. Yoshioka, T.; Kameda, T.; Imai, S.; Okuwaki, A. Polym Degrad Stab 2008, 93, 1138.
21. Marian, S.; Levin, G. J Appl Polym Sci 1981, 26, 3295.
22. Lopez, D.; Mijangos, C. Colloid Polym Sci 1994, 272, 159.
23. Reinecke, H.; Mijangos, C. Polym Bull 1996, 36, 13.
24. Martinez, G.; Millan, J. Macromol Chem Phys 2000, 201, 1709.
25. Lide, D. R., Ed. Handbook of Chemistry and Physics, 76th ed; CRC Press: Boca Raton, 1995–1996; pp 8–43.
26. Behnisch, J.; Zimmermann, H. Inter J Polym Mater 1992, 16, 143.
27. Lu, J.; Ma, S.; Gao, J.; Freitas, J. C. C.; Bonagamba, T. J. J Appl Polym Sci 2003, 90, 3252.
28. Pearson, R. G., Sobel, H.; Songstad, J. J Am Chem Soc 1968, 90, 319.
29. Kameda, T.; Ono, M.; Grause, G.; Mizoguchi, T.; Yoshioka, T. Polym Degrad Stab 2009, 94, 107.
30. Grulke, E. A. Polymer Handbook. Brandrup, J.; Immergut, E. H., Grulke, E. A., Ed.; Wiley: New York, 1999 pp VII-675–VII-714.