Synthesis and characterization of vinyl silane modified imidazole copolymer as a novel corrosion inhibitor

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Summary

For a novel corrosion inhibitor for copper, the free radical copolymerization of vinyl imidazole(VI) and vinyl trimethoxy silane(VTS) was carried out in benzene at 68 ℃ using azobisisobutyronitrile(AIBN) as an initiator. The reactivity ratios of the two monomers were determined from instantaneous composition diagram: r_{VI} = 3.22 and r_{VTS} = 0. Thermal stability of poly(VI-co-VTS) depended on VTS mole fraction in the feed rather than the molecular weight of the copolymer, due to the disiloxane bond linkages formed during heating.

Introduction

Protective organic coatings on copper surface are necessary to protect its surface in corrosive environments. Imidazole and its derivatives have been known as effective corrosion inhibitors for copper and its alloy.(1-5) However, imidazole derivatives can not inhibit the corrosion of copper surface in humid conditions due to its poor interfacial adhesion strength between copper and organic film.(2-5) Jang et al. introduced a silane coupling agent into polyvinylimidazole(1) to improve the adhesion between the polymer film and copper surface.(6,7) Silane modified PVI could suppress the corrosion of copper surface at 360 ℃ for 15 min and at 80 ℃ with 100% relative humidity for 24 hr due to the strong adhesion at the copper/polymer interface, but thermal degradation of polymer might lead to the cuprous oxide formation on copper surface above 360 ℃. Therefore, silane modified PVI with higher thermal stability is necessary to suppress the copper oxidation at higher temperature.

In this paper, poly(VI-co-VTS) was synthesized from VI and VTS as a novel corrosion inhibitor, and the relative reactivities of the two monomers were determined to understand the copolymerization process. In addition, thermal behaviors of the copolymers with different mole fractions were investigated using thermogravimetric and spectroscopic analysis, and their intrinsic viscosities were measured using Ubbelohde capillary viscometer.
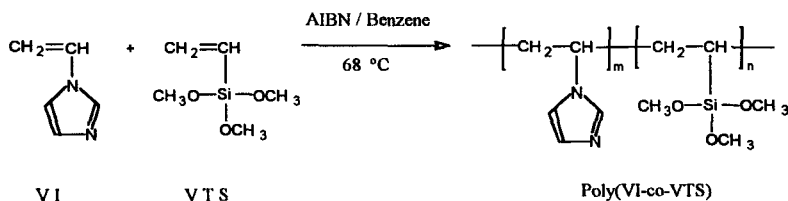
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Figure 1. The copolymerization scheme of VI and VTS.

Experimental

VI and VTS were purchased from Aldrich Chemical Co., and distilled in vacuo to yield pure and colorless liquids. AIBN from Wako Pure Chemical Industries, Ltd. was dissolved in warm methanol(35℃), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature for two days. Poly(VI-co-VTS)s were synthesized by free radical copolymerization using AIBN as an initiator. VI and VTS were copolymerized in benzene at 68℃ with stirring in argon atmosphere. The total monomer concentration was 2M, and the initiator concentration was fixed at 2×10^{-3}M. The copolymerization scheme of VI and VTS is shown in Figure 1.

For the purpose of the determination of the reactivity ratios of the two monomers, instantaneous copolymers were obtained during the copolymerization. After the reaction period required(45-90min) for copolymerization, the contents were pippeted, immediately cooled and precipitated by a large volume of n-hexane. The precipitated copolymers were collected by filtration, washed with benzene and finally dried in a vacuum oven at room temperature for two days. In addition, copolymers were synthesized for 24 hr in the same condition as instantaneous copolymers.

The compositions in instantaneous copolymers were determined by carbon, hydrogen and nitrogen analysis using YANACO MT-2 elemental analyzer. The column temperature was maintained at 850℃ during the combustion, and at 550℃ during the reduction. He and O_2 were used as carrier gases and the detector temperature was 55℃. Fourier transform infrared(FT-IR) transmission spectroscopy was used to characterize poly(VI-co-VTS). The spectrometer was continuously purged with nitrogen gas to remove water vapor and atmospheric CO_2. Spectra were obtained using Bomem MB-100 spectrometer at a resolution of 4 cm^{-1} and 16 scans were collected. Thermal behaviors of the copolymers were investigated by using a Perkin-Elmer TGA7 thermogravimetric analyzer at a heating rate of 10℃ /min in air atmosphere.

Results and discussion

Figure 2 demonstrates FT-IR transmission spectra of the two monomers and poly(VI-co-VTS). Figure 2(A) shows the characteristic peaks of VI at 3114 cm^{-1}, 1498 cm^{-1}, 1282 cm^{-1}, and 1230 cm^{-1}. Figure 2(B) shows the characteristic peaks of VTS at 2945 cm^{-1}, 2842 cm^{-1}, and 1194 cm^{-1}. In Figure 2(C) the band around
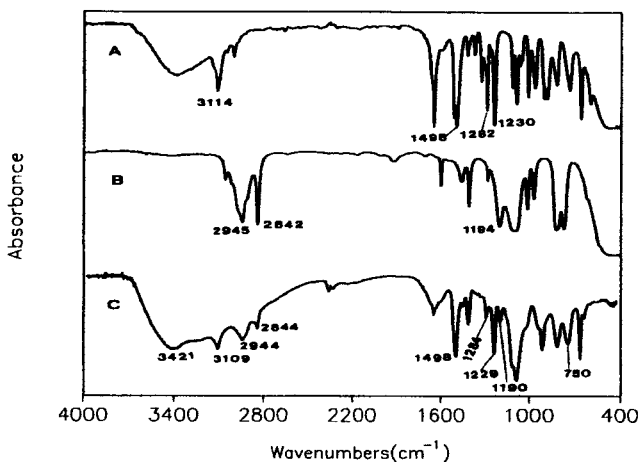
Figure 2. FT-IR spectra of (A) VI, (B) VTS, and (C) poly(VI-co-VTS).

3421 cm^{-1} is assigned to the O-H stretching mode due to the water overtone. The broad feature in the 3700-2800 cm^{-1} region is due to the hydrogen bond of the residual water bound in the imidazole ring.(3,10) The peak at 3109 cm^{-1} originates from the C=C-H/N=C-H stretching in the imidazole ring, and the peak at 1498 cm^{-1} is due to the C=C/C=N stretching in the imidazole ring. The two peaks at 1229 cm^{-1} and 1284 cm^{-1} represent the ring vibration of VI, and the

Table 1 Tentative band assignments of poly(VI-co-VTS)

Band positions (cm^{-1})	Tentative assignments
3421	O-H from residual water
3109	C=C-H/N=C-H stretching
2944	CH$_3$ asymmetric stretching from Si-O-CH$_3$
2844	CH$_3$ symmetric stretching from Si-O-CH$_3$
1649	O-H deformation(water)/C=N stretching
1498	C=C/C=N stretching
1451	CH$_2$ bending(mostly) + ring stretching
1415	CH$_2$ bending(mostly) + ring stretching
1284	Ring vibrations
1229	Ring vibrations
1190	CH$_3$ rocking from Si-O-CH$_3$
1109	CH in-plane bending
1083	CH in-plane bending + Si-O-C asymmetric stretching
915	CH out-of-plane bending
816	CH out-of-plane bending + Si-O-C symmetric stretching
750	CH$_2$ bending
664	Ring torsion
638	C=C-H/N=C-H wagging

Table 2 Data for the elemental analysis and the copolymer compositions

Feed ratio (VI:VTS)	C (wt%)	H (wt%)	N (wt%)	VI (mol%)	VTS (mol%)	Conversion (%)
90:10	58.6	6.82	27.0	96.26	3.74	9.4
85:15	57.6	7.21	26.2	95.10	4.90	9.2
70:30	56.6	7.11	23.4	90.65	9.35	8.2
50:50	51.3	6.92	17.8	79.70	20.30	7.3
30:70	41.8	5.72	10.6	59.34	40.66	5.6

peak at 750 cm^{-1} is designated to the CH_2 rocking. The characteristic peaks of VTS unit are observed at 2944 cm^{-1}, 2844 cm^{-1}, and 1190 cm^{-1}. The peak at 2944 cm^{-1} is due to the CH_3 asymmetric stretching from $Si-O-CH_3$, and the peak at 2844 cm^{-1} is designated to the CH_3 symmetric stretching from $Si-O-CH_3$. The peak at 1190 cm^{-1} is attributed to the CH_3 rocking from $Si-O-CH_3$. The details for the peak assignments of poly(VI-co-VTS) are represented in Table 1.

The copolymer compositions were calculated by elemental analysis to determine the reactivity ratios of the two monomers. The data for the elemental analysis and the calculated copolymer compositions are given in Table 2. The conversions in all copolymerization process were kept below 10%, and the copolymer compositions could be calculated on the basis of nitrogen contents in the elemental analysis data. The reactivity ratios of the two monomers were obtained from instantaneous composition diagram. First of all, the reactivity ratio of VTS is equal to zero because it does not homopolymerize due to a bulky side group. Now that r_{VTS} is zero instantaneous composition diagram could be obtained from data in Table 2 using a curve fitting method. r_{VI} was determined from the slope where the mole fraction of VI in the feed is 1. This slope corresponds to the reciprocal of r_{VI} (8), and r_{VI} is 3.22. Instantaneous composition diagram with r_{VTS} = 0 is shown in Figure 3.

Judging from the data r_{VI} > 1 and r_{VTS} = 0, VI prefers homo-propagation to cross-propagation. Since VTS does not homopolymerize, an alternating copolymer is formed when VTS is in large excess. These results for the relative reactivities of the two monomers in the copolymerization process can be explained by steric hindrance and resonance stabilization of radical.(9) From the viewpoint of steric hindrance, both VI and VTS prefer VI to VTS because VTS has a bulky side group. The formation of VI radical is encouraged by resonance stabilization through π-electron in the imidazole ring. Consequently, VI enters preferentially into copolymer chain. In addition, in the initial stage of copolymerization the mole fraction of VTS in the copolymer is lower than that in the feed due to r_{VTS} = 0 However, the mole fraction of VTS in the copolymer increases with reaction time because the mole fraction of VTS in unreacted monomers increases as the reaction proceeds. In the later stage of the reaction most copolymers are

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

The mole fraction of VI in the copolymer

Slope = $1/r_{VI}$

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

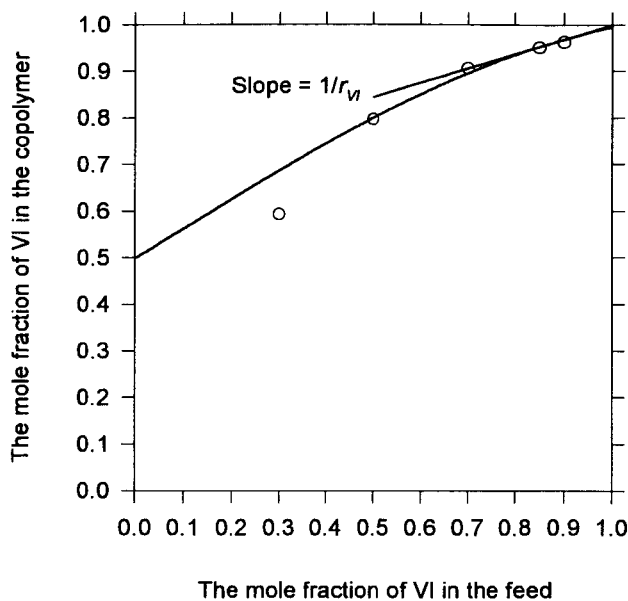The mole fraction of VI in the feed

Figure 3. Instantaneous composition diagram with $r_{VTS} = 0$.

terminated with VTS and unreacted VTS remains in the reactor because VTS does not homopolymerize due to its steric hindrance. Therefore, copolymerization system contains VTS-terminated poly(VI-co-VTS) and unreacted VTS in spite of enough reaction time. As the mole ratio of VTS in the feed increases, the amount of unreacted VTS increases and the molecular weight of the copolymer decreases.

Table 3 represents the intrinsic viscosities of poly(VI-co-VTS)s with different mole ratios in the feed. As the mole fraction of VTS increases in the feed, the value of the intrinsic viscosity of the copolymer decreases gradually. This fact means that as the VTS mole fraction increases in the feed the molecular weight of the copolymer decreases.

Table 3 Intrinsic viscosities of poly(VI-co-VTS)s with different mole ratios

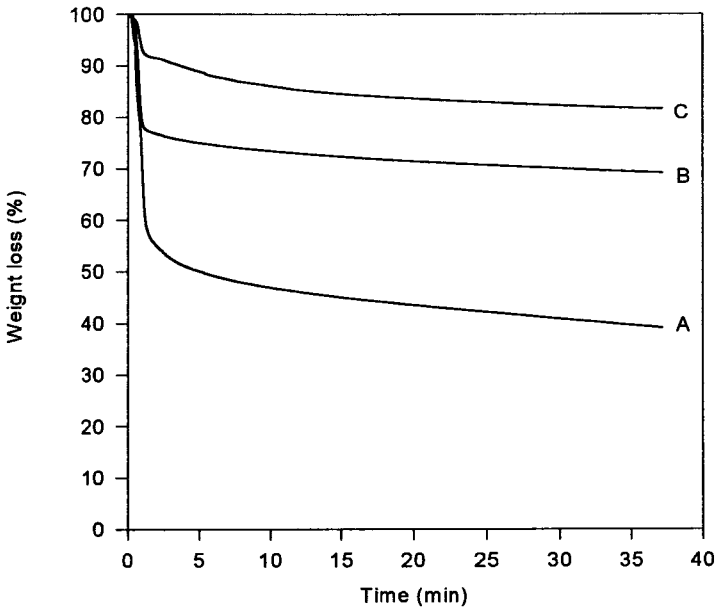| Mole ratio (VI:VTS)	90:10	85:15	70:30	50:50	30:70
Intrinsic Viscosity (cm^3/g)	9.7101	9.3611	8.8378	7.3842	6.9772

Figure 4. TGA curves of the copolymers with the different mole ratios as a function of heating time at 360℃ in air : (A) VI:VTS = 85:15, (B) VI:VTS = 50:50, and (C) VI:VTS = 30:70.

In order to investigate the thermal behaviors of the copolymers with different mole fractions, thermogravimetric analysis was performed in air atmosphere. Figure 4 shows the weight losses with different mole fractions as a function of heating time at 360℃ in air. As the VTS mole fraction in the feed increases, the thermal stability of the copolymer increases in spite of the decrease of the molecular weight of the copolymer. This suggests that thermal stability of the copolymer depends on VTS mole fraction in the copolymer rather than molecular weight of the copolymer. This result is due to the condensation reaction between the Si-O-CH$_3$ groups hydrolyzed by the vaporized water during heating.(10) Therefore, as VTS mole fraction of the copolymer increases, the Si-O-Si bond increases in number and the copolymer becomes thermally more stable. The initial drastic weight losses are due to the degradation of VI part in the copolymer,(10) and it

Table 4 The weight loss of the copolymers after heating in air

Mole ratio(VI:VTS)	90/10	85/15	70/30	30/70
Weight loss(%)	18.3	25.4	39.7	74.1

becomes larger as the VI mole fraction increases.   Table 4 represents the weight loss of the copolymers with different mole fractions after heating in air. Temperature was changed from room temperature to 600 °C at a heating rate of 1 0 °C/min.   As VTS mole fraction increases, the weight loss becomes lower due to Si-O-Si bond formation.

Figure 5 shows FT-IR transmission spectra of the copolymer(VI:VTS = 30:70) heated in air. In spectrum A, the peak at 3622 cm^{-1} is due to the Si-OH group, and the peak at 1030 cm^{-1} corresponds to the Si-O-Si linkage. The peaks at 2945 cm^{-1} and 2845 cm^{-1} are assigned to the Si-O-CH$_3$ group and the peaks at 1720 cm^{-1} and 1620 cm^{-1} are designated to the oxidation peaks of the copolymer. The small peak at 1270 cm^{-1} results from the VI unit in the copolymer. This suggests that most of VI units in the copolymer were oxidized, and that Si-O-CH$_3$ groups of VTS unit were partially hydrolyzed and condensed to form Si-O-Si linkage. In spectrum B, the peaks from Si-O-CH$_3$ group have disappeared, and the peaks from copolymer oxidation decreased in intensity. However, the peak at 1030 cm^{-1} increased in intensity due to the increased Si-O-Si bond formation. Spectrum C
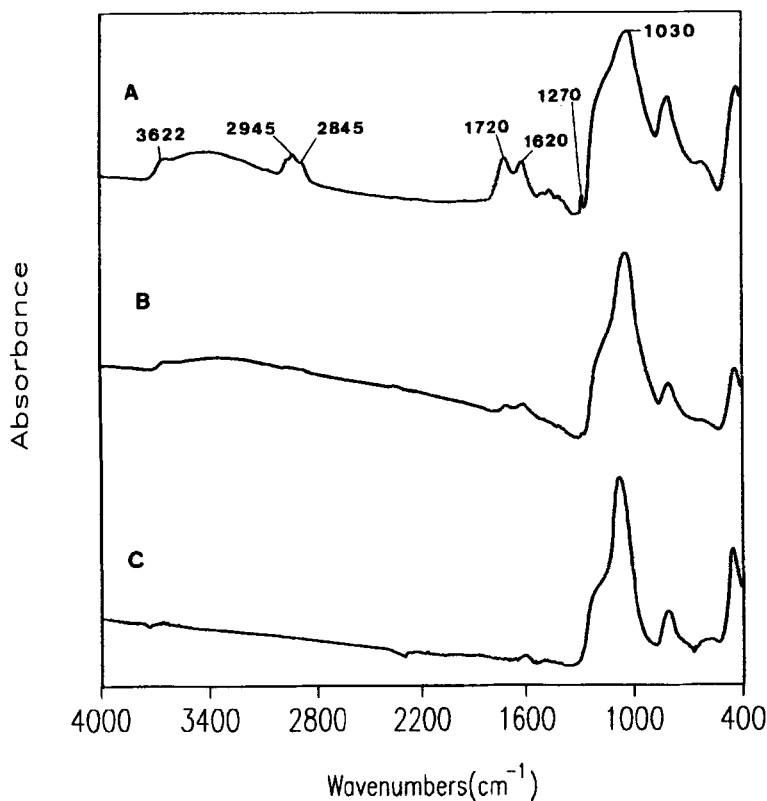

Figure 5. FT-IR transmission spectra of the copolymer(VI:VTS = 30:70) heated in air : (A) heated at 360 °C for 10min, (B) heated at 360 °C for 30min, and (C) heated from room temperature to 600 °C at a heating rate of 10 °C/min.

shows a similar feature to spectrum B. Thermally stable Si-O-Si linkage remained still in spite of heating up to 600℃. This result is in good accordance with TGA results.

Conclusion

Poly(VI-co-VTS) was synthesized as a novel corrosion inhibitor for copper. The reactivity ratios of the two monomers were determined: $r_{VI} = 3.22$ and $r_{VTS} = 0$. As VTS mole fraction in the feed increased, the molecular weight of the copolymer decreased and the thermal stability of the copolymer increased.

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