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Radical copolymerization of 1-vinylimidazole and methacryl- or styryl-functional silane coupling agents

Masashi Kumagai, Katsuyuki Tsuchida and Yukio Ogino
Nippon Mining Co., Ltd, 3-17-35 Niizo-Minami, Toda-shi, Saitama, Japan

and Joan Hansen and Hatsuo Ishida*
NSF Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA
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For the purpose of developing an effective surface finish for copper, imidazole–silane copolymers were synthesized by radical copolymerization of 1-vinylimidazole and methacryl or styryl silane coupling agents. It was found that the reactivity of 1-vinylimidazole was very low as in the case of the copolymerization with styrene or other vinyl monomers. Monomer reactivity ratios obtained from Kelen–Tüdüs plots were 0.079 (r_1; imidazole) and 1.39 (r_2; methacryl silane), and 0.002 (r_1; imidazole) and 6.9 (r_2; styryl silane). According to the reactivity ratios, it was presumed that the imidazole moiety was sandwiched between the silane groups in the early stage of the copolymerization.

(Keywords: radical copolymerization; 1-vinylimidazole; silane coupling agent)

INTRODUCTION

It was previously reported that poly(*N*-vinylimidazole) and poly(4-vinylimidazole) could be effective anticorrosion agents for copper at elevated temperatures[1-3]. As in the case of other polymers[4], the poly(vinylimidazole)s were degraded by the catalytic effect of cupric ions to produce α,β-unsaturated keto, then α,β-unsaturated cyano and finally carbodiimide structures due to imidazole ring cleavage and ladder structure formation. In spite of these observed structural changes, oxidation of copper at elevated temperatures was suppressed compared with other inhibitors such as benzotriazole and undecylimidazole. This thermal stability was thought to be mainly due to the high chelating ability of the polymeric structure to copper, coupled with low volatility of the polymer. Furthermore, in an industrial sense, these polymers seemed to be very promising because of their water solubility, which makes water-based coating formulations possible. On the other hand, the high water solubility could be a disadvantage when used in a humid environment. Unfortunately, pure poly(*N*-vinylimidazole) exhibited a weak anticorrosion effect in a humid environment[5]. To solve this problem, novel polymeric anticorrosion agents which had the imidazole backbone modified with silane were proposed[6]. In this paper, the synthesis and characterization of the proposed polymers are described. It will be very important to take into account the sequences of the obtained copolymers if there are any chemical interactions between imidazole and silane moieties as in the case of some esterolytic enzymes and the model systems[7-11]. The interactions between the two moieties will be discussed elsewhere with respect to thermal stability of these copolymers.

EXPERIMENTAL

Reagents

Reagents used in the copolymerization are shown in *Figure 1*. The styryl-functional silane coupling agents were synthesized by a Grignard reaction[12] and purified by vacuum distillation. *N*-vinylimidazole was purified by vacuum distillation over calcium hydride. The methacryl-functional silane coupling agents were purchased from Toshiba Silicone and purified by column chromatography using a mixture of benzene and acetonitrile as the mobile phase and silica gel as the packing material.

Instrumentation

The ^{1}H n.m.r. spectra were obtained using a 270 MHz Jeol GSX-270. The *FT*i.r. spectra were obtained using a Bomem Michelson MB110 FT-IR spectrometer, which was coupled with a mercury–cadmium telluride (MCT) detector. The specific detectivity, D^*, of the detector was 1.0×10^{10} cm Hz$^{0.5}$ W^{-1}. G.p.c. chromatograms were obtained using a Shimazu LC-3A gel permeation chromatograph.

Copolymerization

The typical copolymerization involved the dissolution of the silane compound (0.02 mol), 1-vinylimidazole (0.02 mol) and azobisisobutyronitrile (AIBN; 13.1 mg,

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* To whom correspondence should be addressed

0.2 mol%) in benzene (200 ml). The solution was stirred at 60°C for 24 h under argon. Next, the solution was condensed by a rotary evaporator and poured into an excess amount of dry hexane to form a precipitate. This precipitation process was repeated until the residual monomers became negligible in the g.p.c. chromatograms. The obtained copolymers were dried at ambient temperature in a vacuum oven overnight.

RESULTS AND DISCUSSION

Copolymerization of γ-MPDMMS and 1-vinylimidazole

The conditions and the results of the copolymerization are summarized in *Table 1*. In order to obtain monomer reactivity ratios r_1 and r_2 (1 and 2 refer to the imidazole and the silane, respectively), the yields were controlled down to 10% by reducing the amount of AIBN and/or the reaction time. In the case that the monomer feed ratio was 90 mol% imidazole and 10 mol% silane, a white precipitate appeared after 4 h. The reacted solutions remained transparent for runs 3 and 4 in *Table 1*; however, the obtained copolymers could not be redissolved in the same solvent (benzene) after they were precipitated out of solution. The precipitates became soluble in protonic polar solvents such as methanol. This was probably due to the fact that the imidazole moieties in the copolymer backbone absorbed water to form strong hydrogen bonds. The absorbed water could be identified by the broad peaks around 3400 cm^{-1} in the *FT*i.r. spectra of the poly(vinylimidazole)s[1–3]. Also, Overberger and Vorchheimer[7] reported that poly(vinylimidazole)s absorbed water strongly. Although some of the synthesized copolymers were powder-like substances, they eventually became viscous by absorbing water. The copolymers obtained here became gels when kept as solids in a few hours, but remained stable for a long time when kept in solution. It was presumed that the imidazole moieties, which were hydrogen-bonded by water molecules, accelerated the hydrolysis reaction of the silane alkoxy moieties, eventually forming the siloxane bonds by a condensation reaction. This presumption was supported by the fact that the corresponding silane homopolymer did not become a gel after a long period of time. Actually, an *FT*i.r. reflection–absorption spectroscopic study showed that this type of copolymer had a higher hydrolysis rate than the homopolymer as coated films on copper surfaces[13]. Furthermore, it is well known that the imidazolyl group of histidine forms a portion of the catalytic site of several hydrolytic enzymes. Plueddemann[14] also recommended the use of amine compounds as hydrolysis catalysts for silane coupling agents.

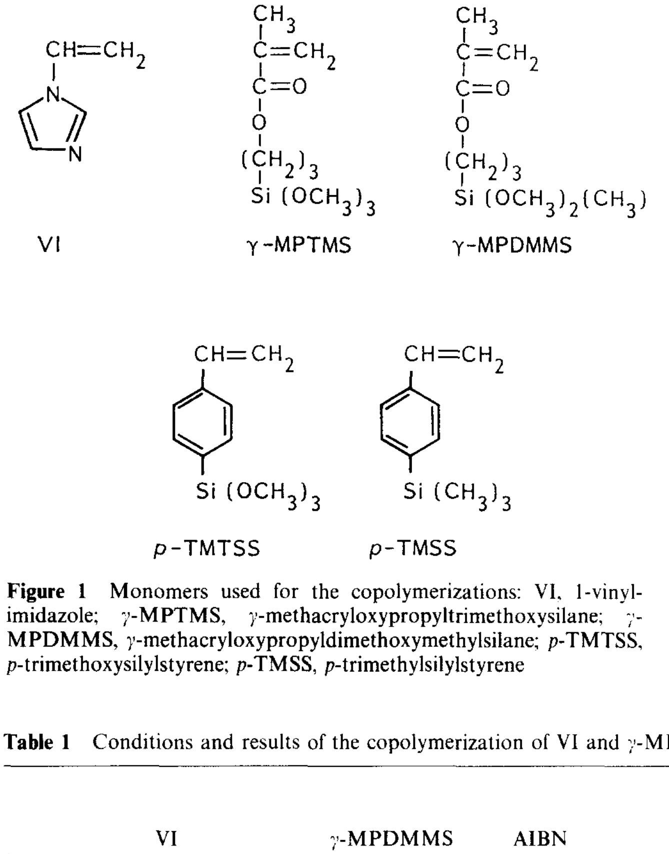

Figure 1 Monomers used for the copolymerizations: VI, 1-vinylimidazole; γ-MPTMS, γ-methacryloxypropyltrimethoxysilane; γ-MPDMMS, γ-methacryloxypropyldimethoxymethylsilane; *p*-TMTSS, *p*-trimethoxysilylstyrene; *p*-TMSS, *p*-trimethylsilylstyrene

The i.r. spectra of the copolymers and the corresponding homopolymers are given in *Figure 2*. It is obvious from *Figure 2* that the bands arising from imidazole moieties become more intense as the reaction time increases. On the other hand, the bands from silane moieties can be seen clearly, even at the early stage of copolymerization. These experimental results imply that the reactivity of the silane compound for radical polymerization is much higher than that of the imidazole. Actually, it was already reported that the reactivity of vinyl imidazole towards other vinyl monomers such as styrene, vinyl acetate and others in radical polymerization was very low[15]. By using the Kelen–Tüdüs plot shown in *Figure 3*, the monomer reactivity ratios were calculated to be 0.079 (r_1; imidazole) and 1.39 (r_2; silane, γ-MPDMMS). The contents of each moiety in the copolymers were obtained by elemental analysis, which agreed well with the findings obtained from ^{1}H n.m.r. spectra. As a result, it was concluded that the imidazole moiety was sandwiched between the silane

Table 1 Conditions and results of the copolymerization of VI and γ-MPDMMS

Run	VI (g)	γ-MPDMMS (g)	AIBN (mg)	Time (h)	Yield (%)	Copolymer composition d(VI): d(γ-MPDMMS) (mol%)	Intrinsic viscosity, [η]
1	3.38	0.928	131.2	24	97.7		
2	3.38	0.928	131.2	6	37.4		
3	3.38	0.928	131.2	3	23.4		
4	3.38	0.928	13.1	3	7.4	71.5:28.5	0.4
5	3.01	1.86	13.1	2	8.2	54.0:41.0	
6	2.63	2.76	13.1	2	4.8	40.1:59.9	
7	1.13	6.44	13.1	2	3.4	20.9:79.1	

All copolymerizations carried out in benzene (200 ml)

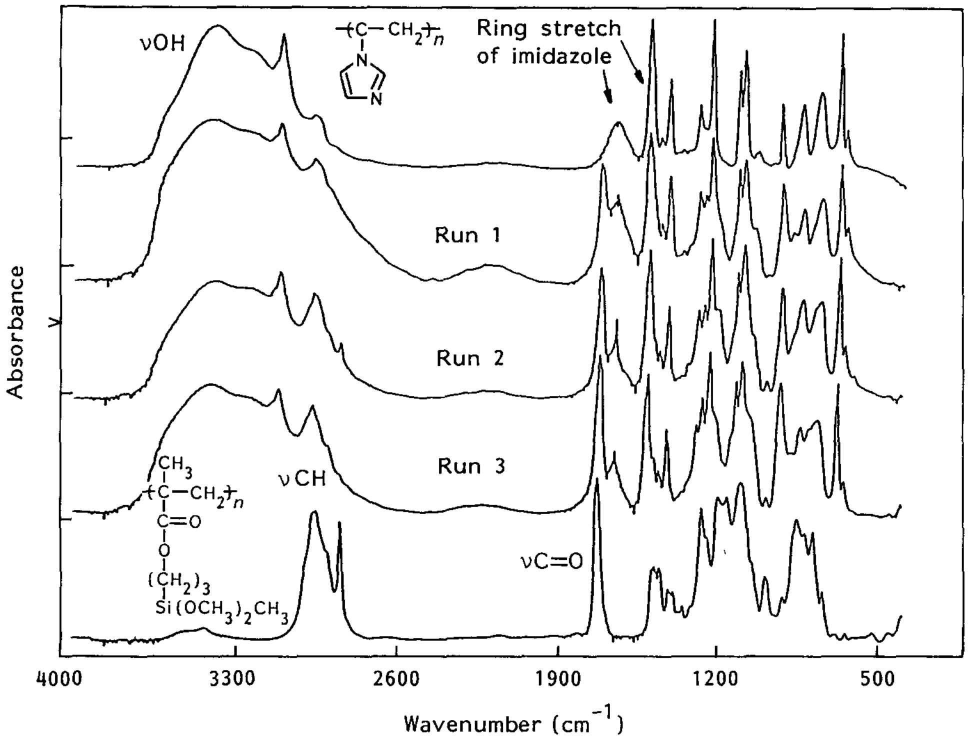

Figure 2 I.r. spectra of runs 1–3 and corresponding homopolymers

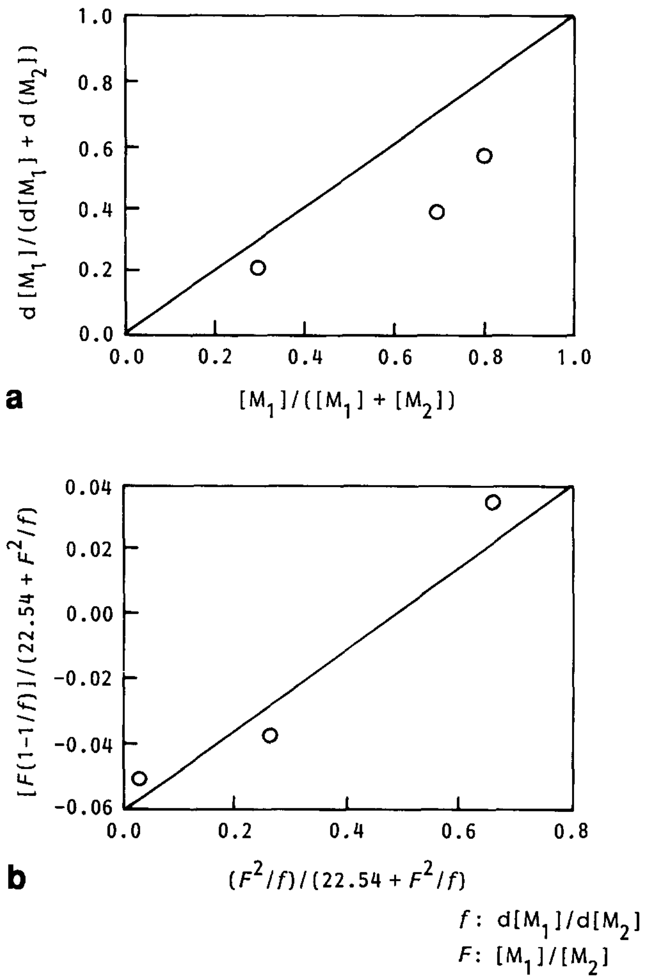

Figure 3 (a) Copolymer compositions and (b) Kelen–Tüdüs plot for runs 5–7

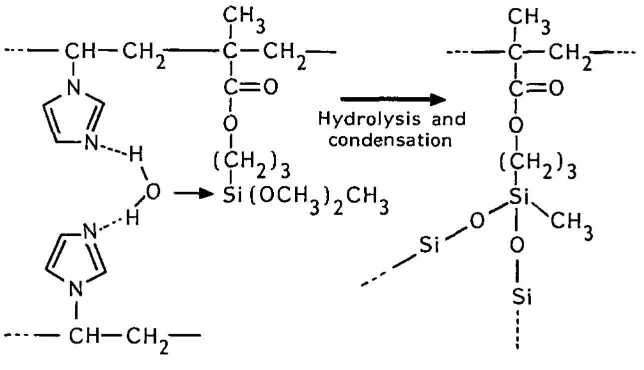

Figure 4 Acceleration effect of imidazole moieties on the hydrolysis of silane groups

groups in the early stage of the copolymerization. It was very probable that this copolymer's sequence favoured the acceleration effect of the imidazole moieties for the hydrolysis reaction of the silane groups (*Figure 4*). The ^{1}H n.m.r. and *FT*i.r. spectra of run 4 are shown in *Figures 5* and *6*, respectively. The intrinsic viscosity of run 4 was calculated to be approximately 0.4 by means of Huggins–Kramer plots, which meant that polymerization actually took place.

Copolymerization of p-*TMTSS and 1-vinylimidazole*

The conditions and the results of the copolymerization are given in *Table 2*. No precipitate formed during these reactions and the solutions remained transparent. The Kelen–Tüdüs plot (*Figure 7*) gave the monomer reactivity ratios $r_1 = 0.002$ and $r_2 = 6.9$, which also indicated that the imidazole moiety was sandwiched between the silane groups. Since imidazoles have a chelating ability with

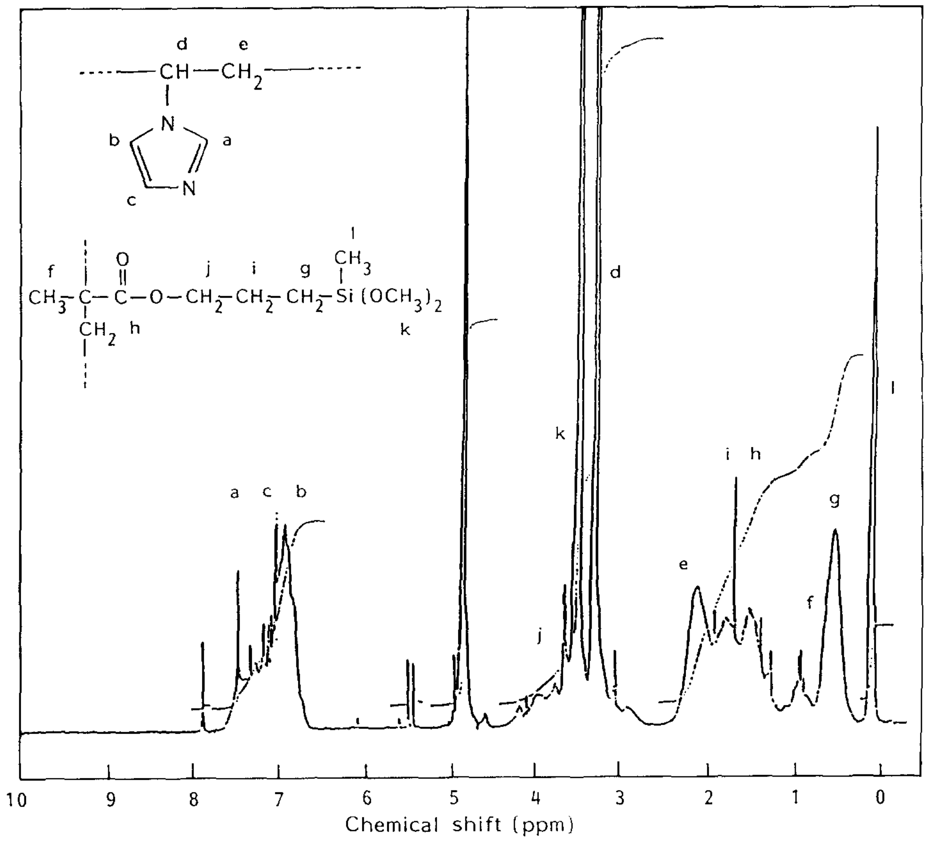

Figure 5 ^1H n.m.r. spectrum of run 4

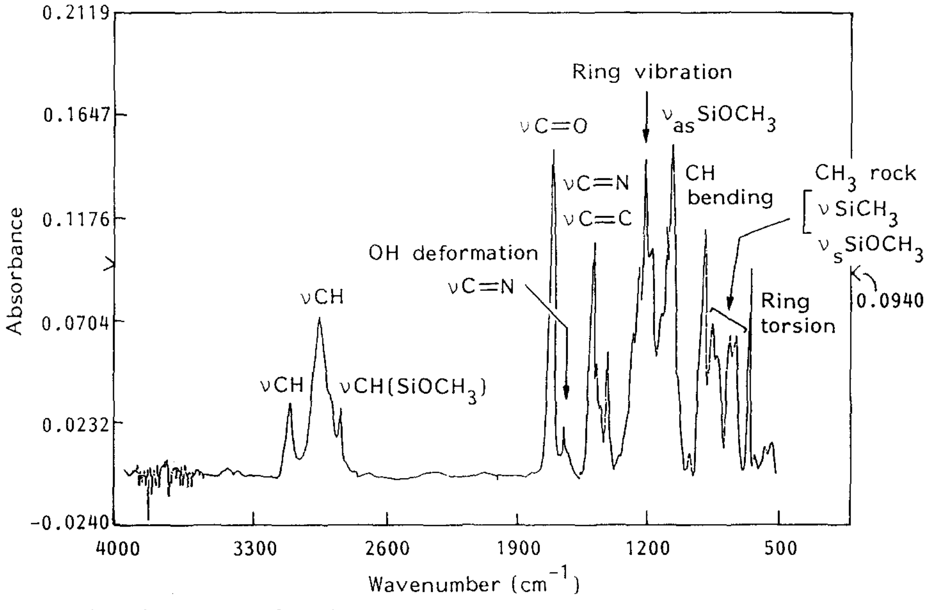

Figure 6 *FT*i.r. spectrum of run 4

Table 2 Conditions and results of the copolymerization of VI and *p*-TMTSS

Run	VI (g)	*p*-TMTSS (g)	AIBN (mg)	Time (h)	Yield (%)	Copolymer composition d(VI): d(*p*-TMTSS) (mol%)	Molecular weight	
							M_w	M_n
8	1.88	3.91	131.2	3	8.7	11.5:88.5		
9	2.63	2.37	131.2	3	6.6	19.9:80.1		
10	1.13	5.53	131.2	3	9.2	5.5:94.5		
11	1.88	3.96	131.2	24	24.0	12.2:87.8	7300	4800

All copolymerizations carried out in benzene (200 ml)

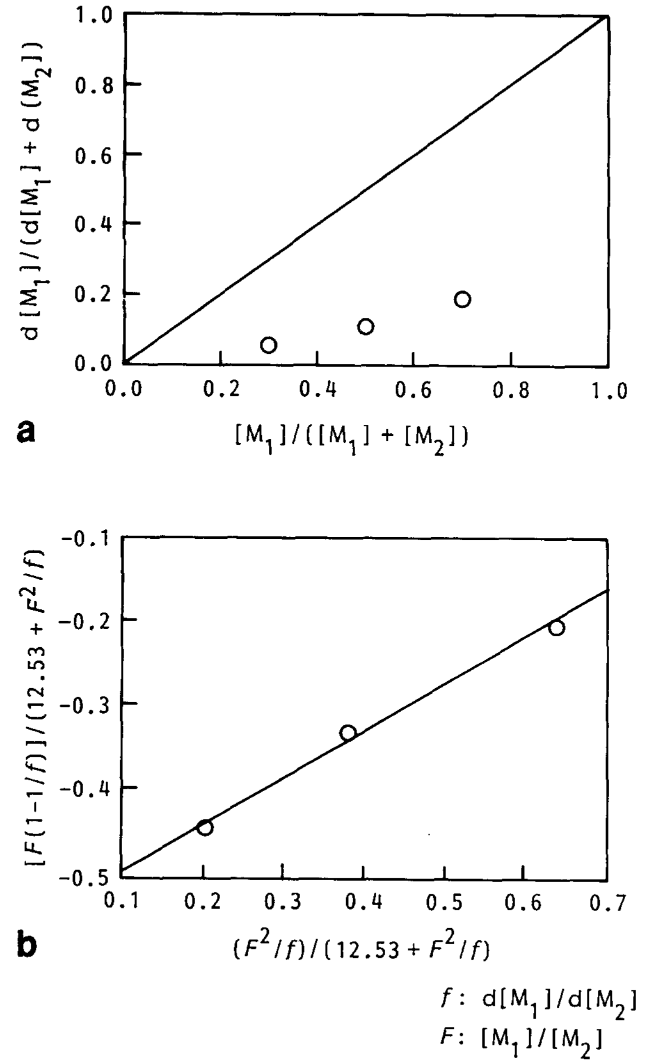

Figure 7 (a) Copolymer compositions and (b) Kelen–Tüdüs plot for runs 8–10

metals and are hydrophilic in nature, and silanes have a high thermal stability and are hydrophobic due to siloxane bond formation, it may be possible to obtain a self-curable polymer which can be applied as adhesives, primers, coupling agents or other applications which involve the surface modification of metals. In *Figures 8* and *9*, the ^{1}H n.m.r. spectrum and the *FT*i.r. spectrum of run 11 are shown, respectively. The obtained copolymers were white solids and soluble in benzene, tetrahydrofuran and chloroform.

Copolymerization of p-*TMSS*, *γ-MPTMS and 1-vinylimidazole*

The copolymerization conditions and the results are listed in *Table 3*. The ^{1}H n.m.r. and the *FT*i.r. spectra of the copolymers obtained are shown in *Figures 10–13*. The

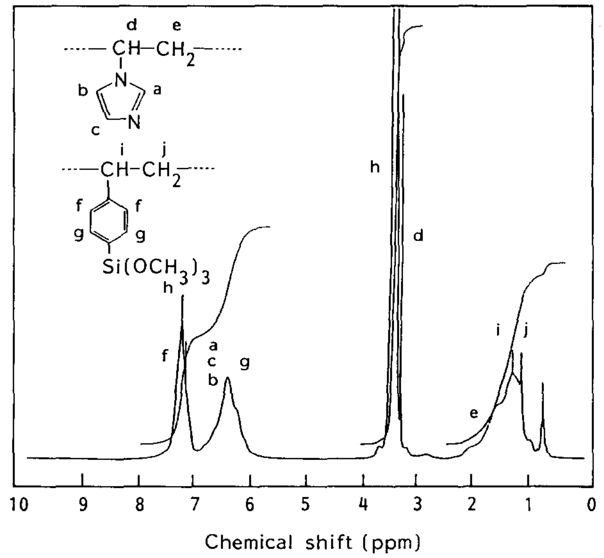

Figure 8 ^{1}H n.m.r. spectrum of run 11

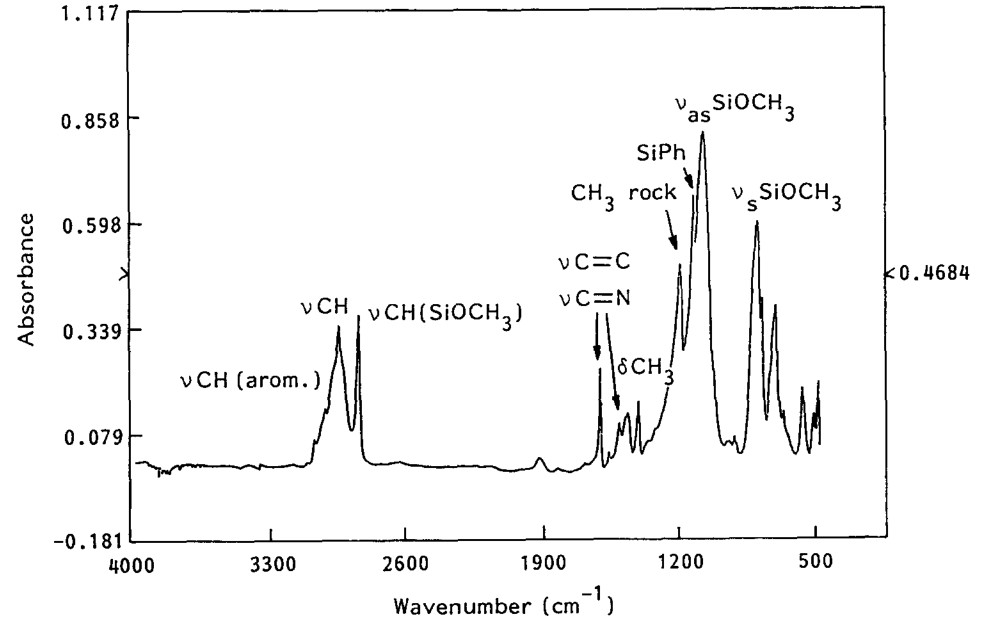

Figure 9 *FT*i.r. spectrum of run 11

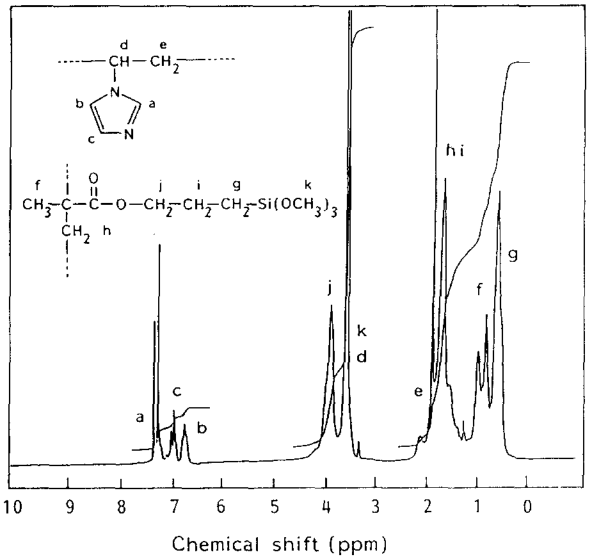

Figure 10 ^{1}H n.m.r. spectrum of run 12

copolymers were soluble in benzene, tetrahydrofuran and chloroform. The acceleration effect of the imidazole moiety for the hydrolysis of the silane groups could be seen for the methacryl-functional copolymer; however, the styryl-functional copolymer did not show such behaviour due to the lack of the hydrolysable group in the silane moieties. The copper surface coated by the styryl-functional copolymer exhibited high hydrophobicity due to the trimethylsilyl group[16]. The sequences of the copolymers are expected to be like a sandwiched structure, as seen in the other copolymers synthesized in this paper.

CONCLUSIONS

For the purpose of developing a novel surface finish for copper, methacryl- and styryl-functional silane–imidazole copolymers were synthesized by radical copolymerization. Characterization of the copolymers obtained was done using ^{1}H n.m.r., *FT*i.r. and g.p.c. According to the

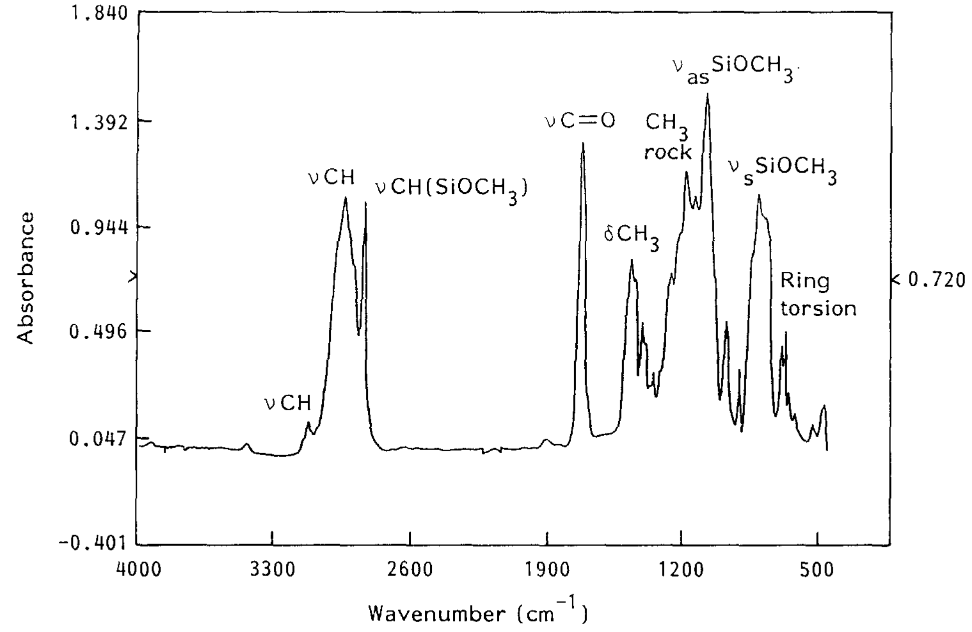

Figure 11 *FT*i.r. spectrum of run 12

Table 3 Conditions and results of the copolymerization of VI and γ-MPTMS or *p*-TMSS

Run	VI (g)	γ-MPTMS (g)	AIBN (mg)	Time (h)	Yield (%)	Copolymer composition d(VI): d(γ-MPTMS) (mol%)	Molecular weight	
							M_w	M_n
12	1.88	4.97	131.2	24	75.5	34.0:66.0	9300	1700
13	1.88	4.97	13.1	24	34.0	26.2:73.8	18700	9200

Run	VI (g)	*p*-TMSS (g)	AIBN (mg)	Time (h)	Yield (%)	Copolymer composition d(VI): d(*p*-TMSS) (mol%)	Molecular weight	
							M_w	M_n
14	1.88	4.97	131.2	24	4.9	7.3:92.7	8300	6600

All copolymerizations carried out in benzene (200 ml)

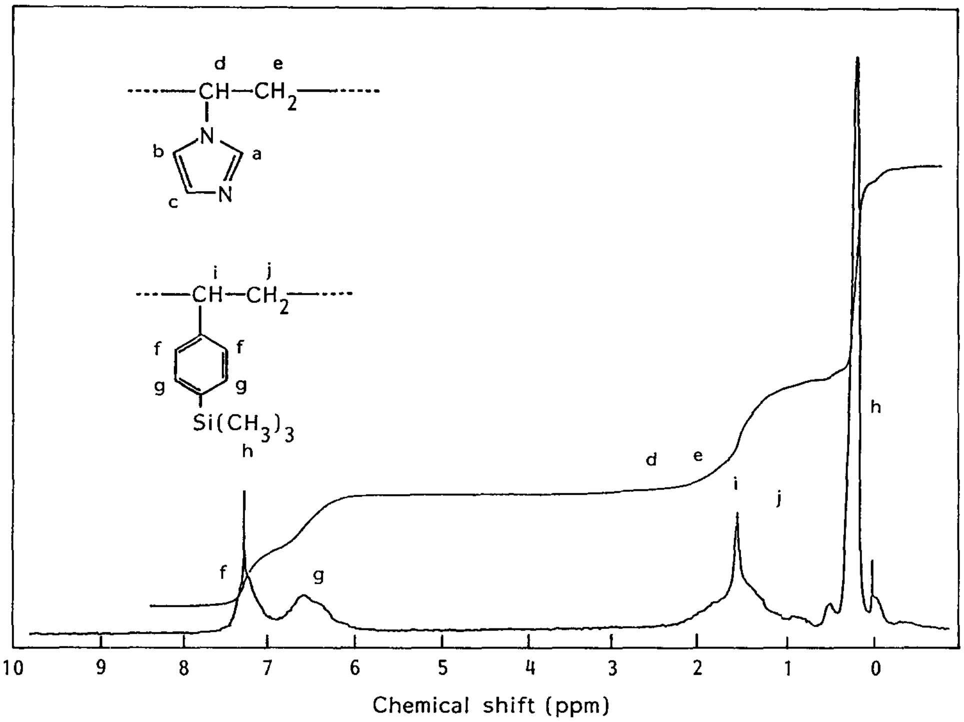

Figure 12 ^{1}H n.m.r. spectrum of run 14

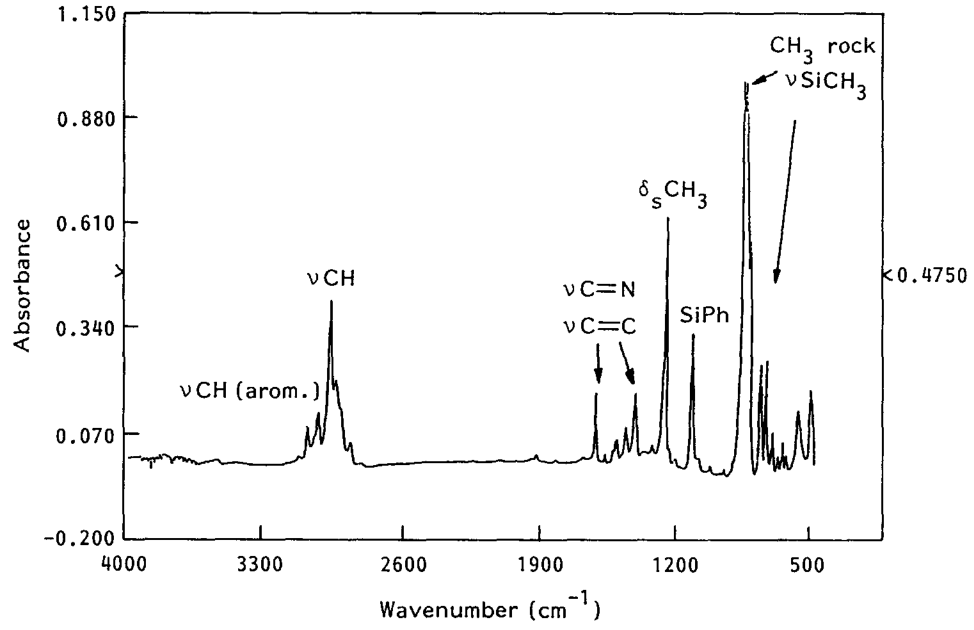

Figure 13 *FT*i.r. spectrum of run 14

monomer reactivity ratios r_1 and r_2, it was presumed that the imidazole moiety was sandwiched between the silane groups in the early stage of the copolymerization. It was found that the copolymers which had hydrolysable silane moieties became gels when kept as solids in a few hours or so. This phenomenon could not be seen in the case of the corresponding homopolymers. Therefore, it was concluded that the imidazole moieties, which were hydrogen-bonded by water molecules and were sandwiched between the silane moieties, accelerated the hydrolysis reaction of the silane moieties. This hydrolysis reaction was followed by a condensation reaction to form the crosslinked structures.

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