



Synthesis and Decrosslinking of Networked Polymers Having Zwitterion Structure Consisted by Cyclic Amidine and Isothiocyanate

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ABSTRACT: We have already found that the polymers, which are obtained by the polymerization of 4-vinylphenyl isothiocyanate after the zwitterion formation with cyclic amidines, are networked through the ionic interaction among the zwitterions becoming insoluble to various solvents. We report here on the results of the reaction of nucleophilic reagents such as amines and alcohols with the zwitterionic adduct to investigate about the decrosslinking through the resolution of ionic interactions. In the model reactions of amines and alcohols with the zwitterion compounds, which were consisted of the phenyl isothiocyanate and cyclic amidines, the reaction of nucleophilic

reagents and zwitterionic adducts having methyl group at the 2-position of the amidine proceed quantitatively. Based on the model reaction, such nucleophilic addition was applicable to decrosslinking reaction of the networked polymers containing the zwitterion structure in the side-chain. © 2019 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 2131–2137

KEYWORDS: zwitterion structure; decrosslinking reaction; polymer reaction; radical polymerization; copolymer; zwitterion adduct; crosslinking; decrosslinking; thiourea; thiourethane

INTRODUCTION Zwitterions, unlike normal ions, characteristically possess covalently bonded pair of cation and anion in their structure and stay stable without getting affected by harsh environments such as the graded electrical field under the electrophoresis.^{1–3} The polymers that possess zwitterion structure also display such characteristics as high polarity and electrical neutrality despite their high polarity and possession of ion pair, and thus they are expected to be useful as antibacterial material, flame-resistive material, lubricant, emulsifier, anti-freeze material, and electrical material.^{4–6} To the present authors' knowledge, however, the hitherto published reports are overwhelmed by those related with betaines and few works have been done on other zwitterion structures. Present authors have reported on the basis of the synthesizability of novel zwitterion structured materials by way of the 1:1 reaction of highly nucleophilic cyclic amidines with isothiocyanates which are heterocumarenes having cumulative double bond, that the polymers which possess novel zwitterions on their side chain can be synthesized by way of the radical polymerization of the zwitterion compounds that possess vinyl group.⁷ The synthesized polymers form strongly crosslinked structure through the parallel ionic interaction among zwitterions and improvement on thermal stability and solvent resistivity resulted. The cyclic amidines that the authors used to form zwitterions are known to function as the catalyst in the synthesis of thiourea and/or thiocarbamate via

the reaction of isothiocyanate with amines or alcohols,⁸ and the zwitterion compounds that are synthesized from the cyclic amidines and isothiocyanate described above can be considered as the intermediate compounds in the reaction of isothiocyanate where cyclic amidines are used as catalyst. Thus, the authors consider that the changes in the side chain to thioureas and/or thiocarbamates are made possible to the polymers that have zwitterions consisted of cyclic amidines and isothiocyanates. Accordingly, the bridge structures of the polymer, with the bridge being formed via the ionic interaction among zwitterions, are debridged accompanying the polymer reaction. In view that a large number of study is under way, with the environmental load in mind, of reversible and/or irreversible and thermal and/or optical processes of decrosslinking, and here-reported way of decrosslinking should be worthy of attention.^{9–12} The work reported here aimed to the decrosslinking, by way of the polymer reaction, in the polymers possessing zwitterions consisted by cyclic amidines and isothiocyanates in the side chain. The study, as the model of the polymer reaction, of the reaction of amines and alcohols onto simple zwitterion structures, was followed by the detailed examination of the reaction behavior therein, and then the attempt was made to decrosslink via polymer reaction in the homopolymers and the styrene-copolymers thereof to achieve the decrosslinking.

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EXPERIMENTAL

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JME-ECS 400 instrument (JEOL, Tokyo, Japan) using tetramethyl silane as an internal standard (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). The infrared absorption (FTIR) spectra were measured by using Nicolet iS10 spectrometer (Thermo Fisher Scientific, Tokyo, Japan).

Materials

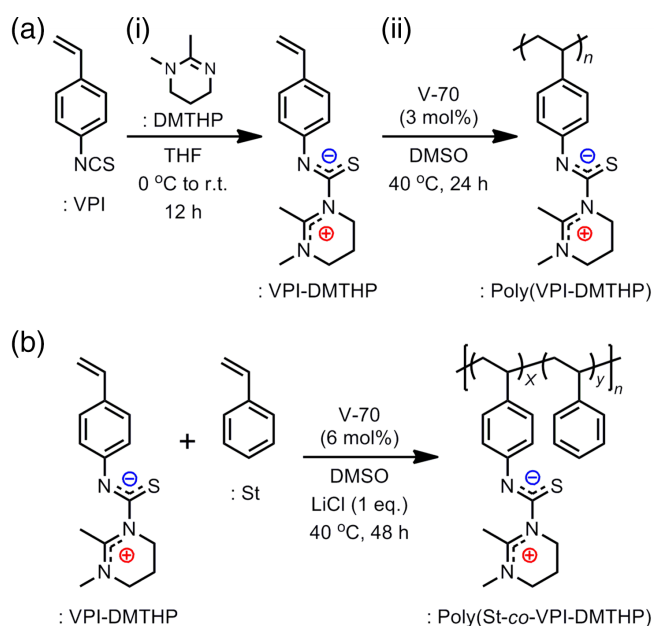
Phenyl isothiocyanate (PI), lithium chloride (LiCl), trifluoroacetic acid (CF_3COOH), 1-butyl-3-methylimidazolium hexafluorophosphate (IL), and 2,2'-azobis(2,4-dimethyl-4-methoxy)valeronitrile (V-70) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Styrene (St), aniline (An), *n*-hexylamine (HA), piperidine (Pi), benzyl alcohol (BA), isopropyl alcohol (IPA), dimethyl sulfoxide (DMSO), and acetonitrile (MeCN) were purchased from Wako Pure Chemical Industries (Osaka, Japan). *N*-methyltetrahydropyrimidine (MTHP), 1-methyl-2-methyltetrahydropyrimidine (DMTHP), 4-vinylphenyl isothiocyanate (VPI), and the zwitterion compound from PI with MTHP or DMTHP (PI-MTHP or PI-DMTHP) were synthesized according to the reported procedures.^{7,13–15} The zwitterion compound, which consisted of DMTHP and VPI (VPI-DMTHP), was polymerized by using V-70 as radical initiator (poly(VPI-DMTHP)). The VPI-DMTHP and St were also polymerized by using V-70 as radical initiator (poly(St-co-VPI-DMTHP)). These synthetic procedures were summarized in the Supporting Information and shown in Scheme 1.⁷

Synthesis of 1,3-Diphenyl-2-Thiourea by the Reaction of PI-DMTHP and Aniline

After placing PI-DMTHP (0.023 g, 0.09 mmol) and dehydrated acetonitrile (0.5 mL) into a two-necked round bottom flask with a three-way stopcock, aniline (0.008 g, 0.09 mmol) was added at room temperature under nitrogen. After stirring for 2 h at room temperature, the solvent was removed using a rotary evaporator and the residue was purified by silica gel column chromatography (hexane/ethyl acetate with v/v of 92/8), and white solid of 1,3-diphenyl-2-thiourea was obtained with the yield of 84% (0.018 g, 0.076 mmol). ^1H NMR (CDCl_3): δ 7.18–7.44 (m, 6H) ^{13}C NMR (CDCl_3): δ 180.09, 137.12, 129.72, 127.26, 125.37 FTIR (neat): 3263, 3092, 3057, 1601, 1590, 1552, 1498, 1451, 1399, 1347, 1318, 1309, 1297, 1244, 1182, 1071, 1029, 1001, 931, 761, 749, 705, 699 cm^{-1} .

Synthesis of *N*-Phenylthiocarbamic Acid Benzyl Ether by the Reaction of PI-DMTHP and Benzyl Alcohol

After placing PI-DMTHP (0.023 g, 0.09 mmol) and dehydrated acetonitrile (0.5 mL) into a two-necked round bottom flask with a three-way stopcock, benzyl alcohol (0.012 g, 0.09 mmol) was added at room temperature under nitrogen. After stirring for 2 h at room temperature, the solvent was removed using a rotary evaporator and the residue was purified by silica gel column chromatography (hexane/ethyl acetate with v/v of 92/8), and white solid of *N*-phenylthiocarbamic acid benzyl ether was obtained with the



SCHEME 1 Synthesis of (a) poly(VPI-DMTHP) and (b) poly(St-co-VPI-DMTHP). [Color figure can be viewed at wileyonlinelibrary.com]

yield of 77% (0.017 g, 0.07 mmol). ^1H NMR (CDCl_3): δ 7.21–7.36 (m, 10H, Ph), 4.66 (d, $J = 2.7$ Hz, 2H, $\text{S}=\text{C}-\text{CH}_2-\text{Ph}$). ^{13}C NMR (CDCl_3): δ 140.95, 135.38, 131.32, 129.63, 128.64, 127.71, 127.39, 127.07, 125.83, 65.37 FTIR (neat): 3126, 3029, 2974, 2160, 1972, 1593, 1541, 1494, 1405, 1333, 1309, 1286, 1221, 1187, 1075, 1052, 1016, 967, 920, 904, 850, 836, 815, 748, 732, 684 cm^{-1} .

Polymer Reactions by Nucleophilic Reagents onto Poly(St-co-VPI-DMTHP), a Typical Example

After placing poly(St-co-VPI-DMTHP) (0.014 g, 0.09 mmol, St/VPI-DMTHP = 70/30) and dehydrated DMSO (0.5 mL) into a two-necked round bottom flask with a three-way stopcock, amines (3 equiv) or alcohols (5 equiv) were added. After stirring for 24 h at room temperature, the objective adducts were obtained by reprecipitation in acetonitrile.

Poly(St-co-VPI-An)

From aniline (0.007 g, 0.08 mmol), yield: 94% (0.013 g, 0.08 mmol), FTIR (neat): 3267, 2918, 1651, 1593, 1510, 1493, 1435, 1312, 1258, 1199, 1015, 950, 872, 831, 756, 699 cm^{-1} .

Poly(St-co-VPI-HA)

From *n*-hexylamine (0.008 g, 0.08 mmol), yield: 89% (0.011 g, 0.07 mmol), FTIR (neat): 3289, 3024, 2921, 2848, 1651, 1597, 1511, 1493, 1436, 1415, 1312, 1259, 1195, 950, 798, 756, 699 cm^{-1} .

Poly(St-co-VPI-Pi)

From piperidine (0.007 g, 0.08 mmol), yield: 90% (0.007 g, 0.05 mmol), FTIR (neat): 3273, 3024, 2920, 2849, 1651, 1593, 1511, 1493, 1435, 1309, 1259, 1198, 1016, 951, 872, 831, 757, 699 cm^{-1} .

Poly(St-co-VPI-BA)

From benzyl alcohol (0.015 g, 0.14 mmol), yield: 90% (0.006 g, 0.04 mmol), FTIR (neat): 3266, 3025, 2919, 2850, 1648, 1593, 1510, 1492, 1451, 1433, 1416, 1373, 1330, 1308, 1259, 1197, 1109, 1018, 950, 872, 832, 749, 699 cm^{-1} .

Poly(St-co-VPI-IPA)

From isopropyl alcohol (0.008 g, 0.14 mmol), yield: 93% (0.007 g, 0.05 mmol), FTIR (neat): 3280, 3024, 2923, 2850, 1651, 1598, 1509, 1492, 1434, 1379, 1333, 1309, 1259, 1197, 1017, 952, 872, 820, 802, 758, 699 cm^{-1} .

RESULTS AND DISCUSSION

The authors first examined the nucleophilic reaction of aniline (An) and zwitterion adduct (PI-MTHP), which was composed of MTHP and phenyl isothiocyanate (PI) as the model reaction for the polymer reaction. Thus, 1 equiv of An was added as nucleophilic reagent to the PI-MTHP and the reaction was carried out at ambient temperature for 2 h [Scheme 1(a-i)]. The ^1H NMR spectrum (Fig. 1) of the resulted crude mixture indicated that the mixture is a complicated mixture and thus the occurrence of the reactions other than the intended one took place. Specifically, characteristic peaks are observed at around 8 ppm, and as we know that the amidine we used in the reaction undergoes in basic condition the ring opening and results in formamide derivative under ambient moisture [Fig. 1(a)].¹⁴ As the peak of the formamide generated by this ring opening was observed in ^1H NMR spectrum [Fig. 1(b)], the occurrence of ring opening of the amidine ring is suggested to take place in the reaction with aniline.

Accordingly, 1 equiv of aniline was added to PI-DMTHP and then the mixture was stirred for 2 h at room temperature [Scheme 2(a)]. The solvent was removed and the resulted crude mixture was examined by ^1H NMR, which showed the presence of the intended thiourea compound and DMTHP by

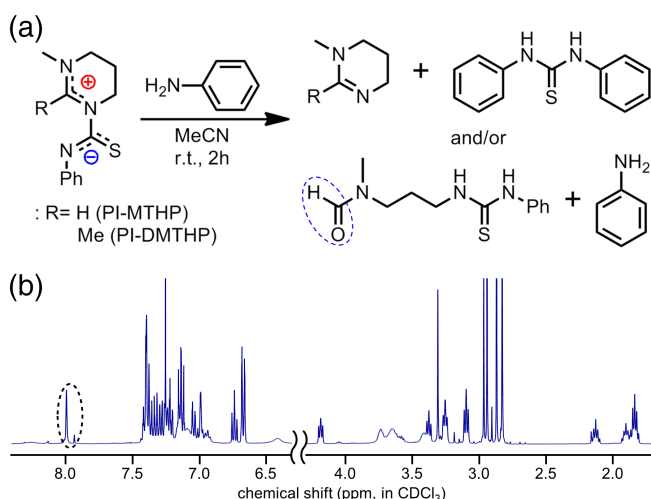
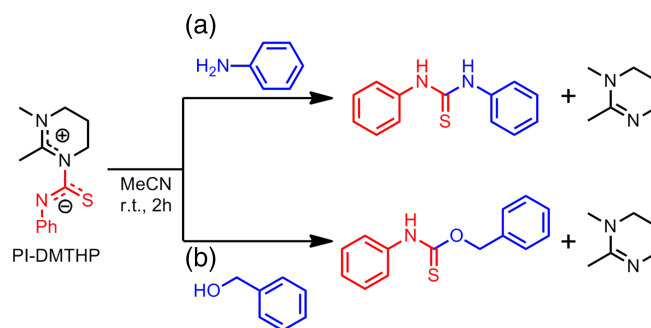


FIGURE 1 (a) Reaction of zwitterionic adduct and aniline. (b) ^1H NMR Spectrum of crude product obtained from PI-MTHP and An. [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 2 (a) Synthesis of 1,3-diphenyl-2-thiourea from PI-DMTHP and aniline. (b) Synthesis of *N*-phenylthiocarbamic acid benzyl ether from PI-DMTHP and benzyl alcohol. [Color figure can be viewed at wileyonlinelibrary.com]

the ratio of 1:1 indicating that the reaction took place quantitatively [Fig. 2(a)]. It was confirmed that the isolation of the thiourea compound can be achieved by the yield of 84% after the purification using silica gel column chromatography. The reaction using benzyl alcohol (BA) was examined in a similar way. BA was added by 1 equiv to PI-DMTHP in acetonitrile and then the mixture was stirred for 2 h at room temperature [Scheme 2(b)]. The ^1H NMR spectrum of the resulted mixture showed that the mixture was composed of the DMTHP and the intended thiocarbamate compound alone proving that is the reaction to proceed quantitatively like the one for aniline [Fig. 2(b)]. The authors achieved the isolation of the thiocarbamate compound with 77% yield by way of the silica-gel column chromatography.

The synthesis of thiourea and thiocarbamate from PI-DMTHP is explained by two kinds of routes, which are reaction of the dissociated isothiocyanate from zwitterion adduct and nucleophiles (route i) and the direct reaction of zwitterion adduct and nucleophiles (route ii). We have already demonstrated that the zwitterion adduct was decomposed by heating at 60 °C. Based on the previous report, we measured ^1H NMR of PI-DMTHP before and after heating to investigate the reversible reaction of PI and DMTHP (Supporting Information Fig. S1). The spectrum of PI-DMTHP after heating showed the complicated signals in the aromatic region around 7.5--7.0 ppm, whereas the signals arisen from DMTHP were clearly observed [Supporting Information Fig. S1(c)]. Next, the crude mixture after heat treatment was reacted again at room temperature for 24 h. However, ^1H NMR spectrum after re-reaction almost agreed with that after heat treatment [Supporting Information Figs. S1(c) and S1(d)]. These results indicated that not only reversible reaction of PI and DMTHP but also direct reaction of PI-DMTHP and nucleophiles did not proceed at all because the dissociated isothiocyanate from zwitterion adduct was degraded and/or inactive. Therefore, the authors inferred the ring-opening mechanism of PI-MTHP as shown in Figure 3(a). As the first step, the nucleophilic aniline attacks the 2-position of MTHP because the imine carbon is fairly electrophilic than the carbon of thiocarbonyl group. Then, the ring opening takes place when the hydrolysis of the

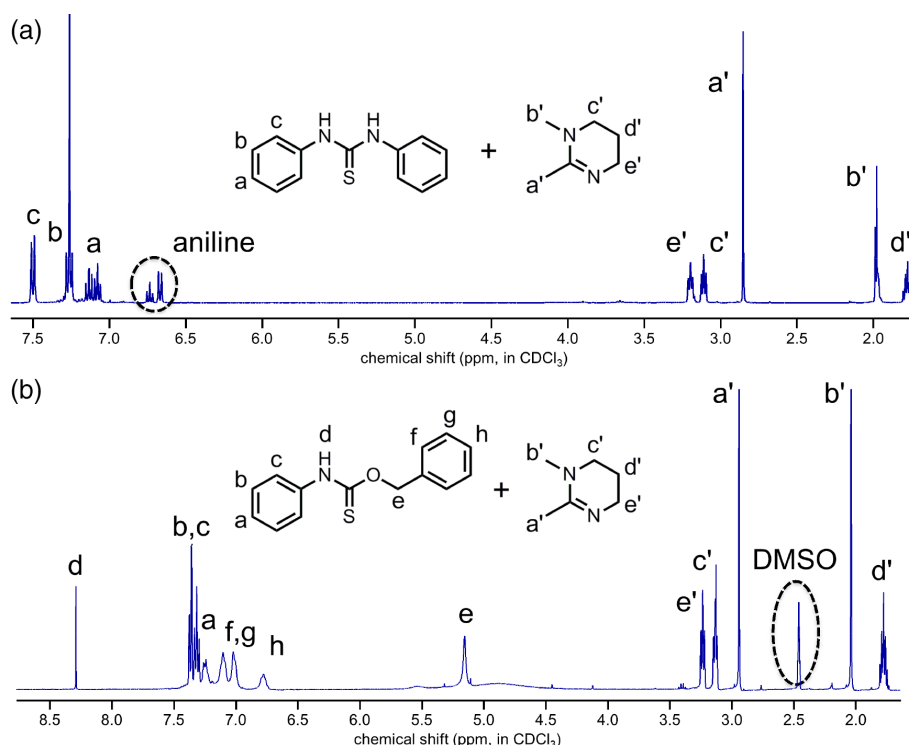


FIGURE 2 ^1H NMR spectra of the crude product of the reaction of (a) PI-DMTHP and aniline, and (b) that of the reaction of PI-DMTHP and benzyl alcohol. [Color figure can be viewed at wileyonlinelibrary.com]

amidine occurs resulting in the generation of formamide under ambient moisture. On the other hand, the nucleophilic addition of aniline takes place on the thiocarbonyl carbon of PI-DMTHP, resulting in the occurrence of thiourea compound and its source compound of cyclic amidine structure, because the nucleophilic attack of aniline to the position-2 of amidine is inhibited owing to the steric hindrance of methyl group. [Fig. 3(b)].

As we verified by using cyclic amidine having methyl group at 2-position that the model reaction proceeded quantitatively, the reaction of amines and alcohols with the polymer bearing a zwitterion moiety on its side-chain (poly(VPI-DMTHP)), which was obtained by the polymerization of 4-vinylphenyl isothiocyanate after the zwitterion formation with cyclic amidine having methyl group at 2-position (DMTHP), was investigated next. The polymer reaction using aniline was first examined; 1 equiv of aniline with respect to the amount of zwitterion was added and let the reaction proceed in DMSO for 24 h. Incidentally, poly(VPI-DMTHP) is insoluble to DMSO and the experiment was carried out in the polymer dispersion. The system remained nonuniform after 24 h of reaction and the inspection using the FTIR spectra measured prior to and after the reaction indicated that the polymer did not undergo the reaction at all (Supporting Information Fig. S2). All of the supplemental experiments, that is, raise in the reaction temperature to 50°C , addition of 5 equiv of aniline instead of 1 equiv, the use of aniline as solvent, and so on, failed to make the reaction proceed (Table 1). The authors infer as the

reason of this failure that bridge structure that is formed via ionic interaction among the zwitterions is very dense and thus the dissipation of the reagent aniline into the polymer network is inhibited.

Briefly stated, poly(VPI-DMTHP), which is the polymer having the zwitterion structure consisted of cyclic amidine and isothiocyanate did not undergo the polymer reaction to debridge, presumably because the bridging through ionic interaction among the zwitterions is so dense. We then inferred that the polymer reaction in the system with decreased density of the zwitterion, namely the reaction in general-purpose polymer may proceed as expected because the relative density of the bridging is lower. The copolymer obtained by the copolymerization of VPI-DMTHP and styrene (St) display strong bridging arising from ionic interaction even when the content of the vinyl monomer having the zwitterion structure is as low as 5 mol % and is known to give out the polymer which has the network and is insoluble to various solvents. Namely, the authors conferred that the decrease in the density of the bridge structure with respect to that in the homopolymer may allow for the polymer reaction with aniline enabling the polymer reaction that accompany the decrosslinking reaction. Two types of the polymer obtained by the copolymerization of the monomers with the ratios of St:VPI-DMTHP = 50:50 and 70:30 were examined for their polymer reaction (Scheme 3); 1 equiv. of aniline was added to the DMSO solutions of the two types of poly(St-co-VPI-DMTHP) and let the reaction go for 24 h. The result for the 50:50 copolymer was similar to

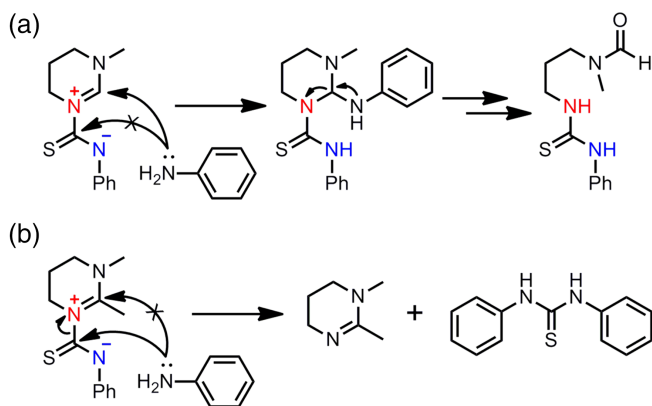


FIGURE 3 Proposed mechanism of nucleophilic addition of aniline into (a) PI-MTHP and (b) PI-DMTHP. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Reaction of Poly(VP-DMTHP) and An

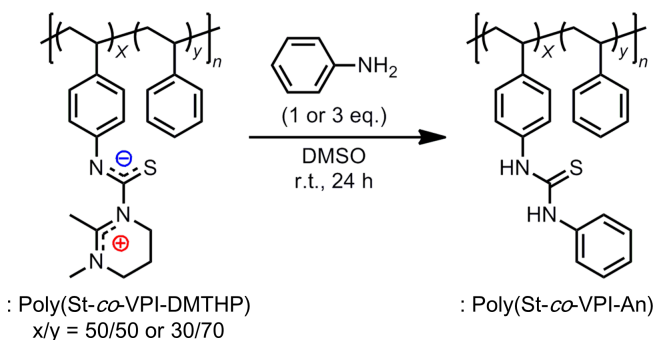
Entry ^a	Aniline	Temperature	Result ^b
1	1.0 equiv	50 °C	No reaction
2	5.0 equiv	r.t.	No reaction
3	5.0 equiv	50 °C	No reaction
4	Excess ^c	r.t.	No reaction
5	Excess ^c	50 °C	No reaction

^a Condition: in DMSO for 24 h.

^b Determined by FTIR measurement.

^c Aniline was used as solvent.

the one obtained for the homopolymer as revealed by the FTIR spectrum measured after the reaction, and thus the reaction did not proceed at all [Fig. 4(a)]. The copolymer that was synthesized by the monomer ratio of 30:70, on the other hand, the reaction system changed from heterogeneous to homogeneous after the reaction and the FTIR spectrum of the resultant displayed the near-disappearance of the peaks that sit near those arising from the isothiocyanate part of the zwitterion. Furthermore, the reaction with the increase of the aniline quantity to 3 equiv with respect to that of the zwitterion gave the product in which the FTIR peak due to the isocyanate



SCHEME 3 Polymer reaction of poly(St-co-VPI-DMTHP) and aniline. [Color figure can be viewed at wileyonlinelibrary.com]

disappeared completely [Fig. 4(b)]. The polymer obtained by the reaction looked as being dissolved in DMSO, but the GPC and/or NMR measurements failed to give any significant signal at all and thus the formation of adducts by way of hydrogen bond is suggested. Thus, the homopolymer and copolymers of 4-vinylphenyl isothiocyanate without the zwitterion moiety were utilized as alternative polymers to estimate the molecular weight and dispersity of polymers containing the zwitterion structure, which exhibited $M_n = 6,500$ ($M_w/M_n = 1.5$) and $M_n = 12,000$ ($M_w/M_n = 1.5$), respectively (Supporting Information Table S1).

Next, the reaction of poly-(St-co-DMTHP), (St/VP-DMTHP = 70/30) with 3 equiv of benzyl alcohol was carried out in DMSO for 24 h at room temperature. The comparison of the FTIR

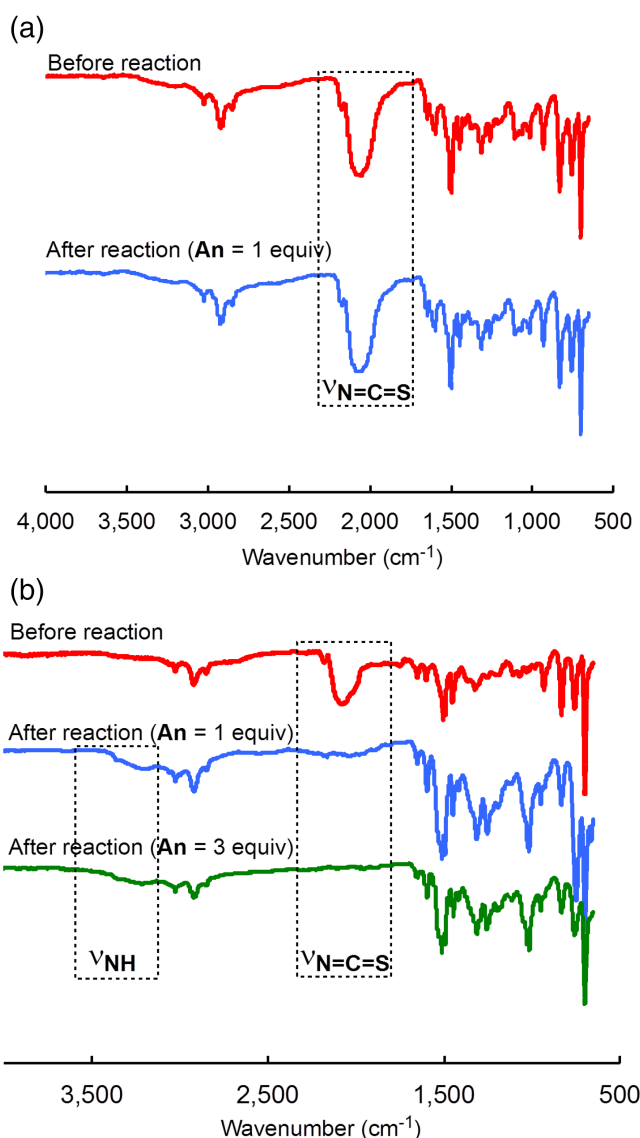


FIGURE 4 FTIR spectra of the polymer reaction of poly(St-co-VPI-DMTHP) and aniline, (a) $x/y = 50/50$ and (b) $x/y = 30/70$. [Color figure can be viewed at wileyonlinelibrary.com]

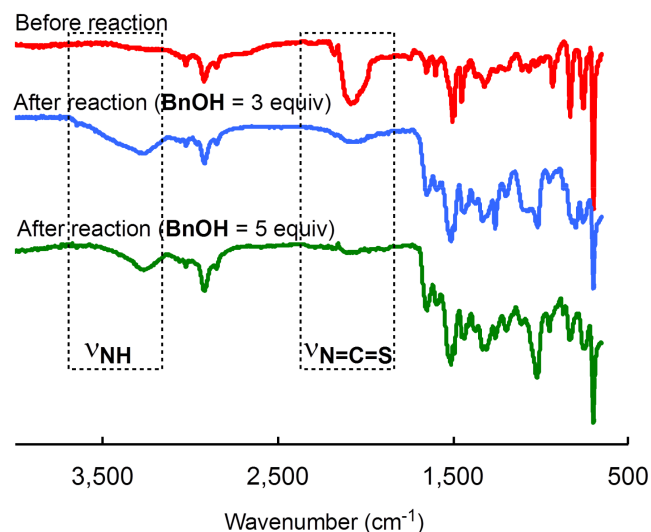


FIGURE 5 FTIR spectra of the polymer reaction of poly(St-co-VPI-DMTHP). [Color figure can be viewed at wileyonlinelibrary.com]

spectrum measured after the reaction with that taken beforehand showed the decrease in the intensity of the peaks arising from the isothiocyanate, but the existence of remnant zwitterion was suggested by the residual intensity of the absorption peak. The remnant peak disappeared when reaction was performed by increasing the amount of benzyl alcohol to 5 equiv indicating the quantitiveness of the reaction (Fig. 5). The polymer derived here has thiocarbamate group deriving from the reaction with benzyl alcohol and it also appeared to be dissolved in DMSO, significant signals were not obtained on the results of both GPC and NMR measurements suggesting the occurrence of the association through hydrogen bonding. The polymers after reprecipitation were completely insoluble in not only typical solvents but also high polar solvents, acidic solution, and ionic liquid, whereas the polymers containing ratio of St/VP-DMTHP = 70/30 before and after nucleophilic

TABLE 2 Reaction of Poly(VP-DMTHP) and An

Solvent	A	B	C	D	E
DMF	X	X	X	X	X
DMF(10%LiCl)	X	X	X	X	X
H ₂ O	X	X	X	X	X
CF ₃ COOH	X	X	X	X	X
1.0 M HCl _{aq} .	X	X	X	X	X
DMSO	X	X	O	O	O
DMSO (100 °C)	X	X	O	O	O
IL	X	X	X	X	X

A: poly(VPI-DMTHP).

B: poly(St(50)-co-VPI-DMTHP(50)).

C: poly(St(30)-co-VPI-DMTHP(70)).

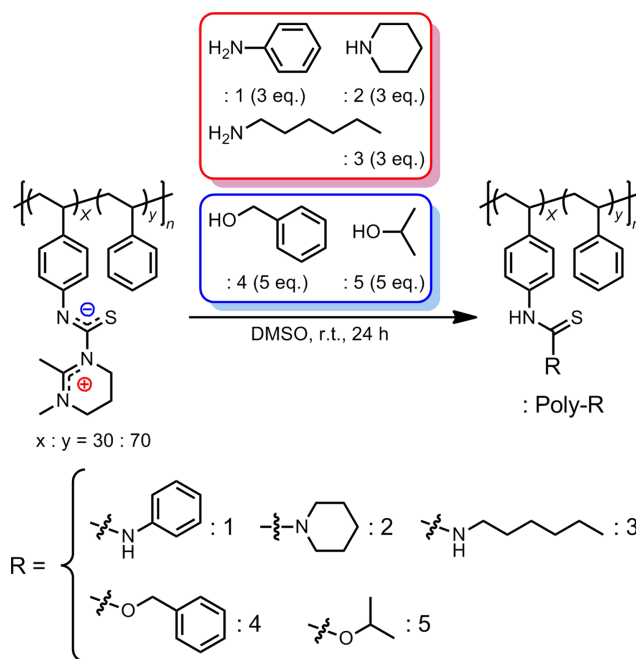
D: poly(St-co-VPI-An).

E: poly(St-co-VPI-BA).

IL: 1-butyl-3-methylimidazolium hexafluorophosphate.

O: partly soluble.

X: completely insoluble.



SCHEME 4 Polymer reaction of poly(St(30)-co-VPI-DMTHP(70)) and various nucleophiles. [Color figure can be viewed at wileyonlinelibrary.com]

addition with aniline and benzyl alcohol were partly soluble and swelling in DMSO (Table 2).

The last system reported in this article is the polymer reaction of the amines and alcohols of different kind with poly(St-co-VPI-DMTHP) containing ratio of St/VP-DMTHP = 70/30. The examined amines are hexyl amine (HA) which is aliphatic amine and piperidine (Pi) which is secondary amine. Also, the examined alcohols are isopropanol which is bulky secondary alcohol and benzyl alcohol which is aromatic alcohol (Scheme 4). The reaction conditions are like the ones used in the aforementioned systems; 3 equiv of amine or 5 equiv of alcohol was added, DMSO was used as solvent, and reactions were carried out at room temperature for 24 h. Then, the reaction solutions became homogeneous after 24 h and the FTIR spectra indicated that the reaction proceeded quantitatively. Thus, quantitative procedure of the reaction was revealed even for sluggish nucleophilic agents owing to their bulky substituents such as secondary amines and secondary alcohols.

CONCLUSIONS

The authors reported in this article the study of the decrosslinking in the networked polymer by the polymer reaction of the polymers having the zwitterion structure formed by cyclic amidines and heterocumurenes in their side chains and the nucleophilic reagents such as amines and alcohols. The model reaction of aniline and the zwitterion compound which composed by phenyl isothiocyanate and cyclic amidine demonstrates the importance of the presence of methyl group

on the 2-position of the amidine. The decrosslinking reaction of the homopolymer having the zwitterion structure in the side chain did not proceed at all. On the other hand, the decrosslinking reaction of styrene copolymer containing the zwitterion structure of 30% units in the side chain was achieved quantitatively in DMSO. The polymer reaction proceeded quantitatively even when the bulky secondary amines or secondary alcohols were used as the nucleophilic reagents. Therefore, these findings prove that the procedure, which has wide-ranged application, has been established herewith from the viewpoint of the functionalization of polymer materials, too.

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