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A Novel De-Cross-Linking System from Cross-Linked Polymer to Linear Polymer Utilizing Pressure or Visible Light Irradiation

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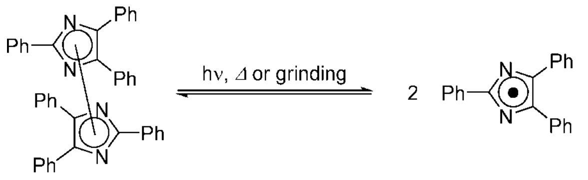
ABSTRACT: A monomer having a 2,4,5-triphenylimidazole moiety was prepared by the reaction of benzoin and 3-vinylbenzaldehyde with ammonium acetate and 1-butylimidazolium tetrafluoroborate in moderate yield. The radical copolymerization of the obtained monomer and MMA were carried out at 60 °C for 24 h by using AIBN (5 mol %) as an initiator to give a copolymer in good yield. The cross-linking reaction of the obtained copolymer proceeded with $K_3[Fe(CN)_6]$ and KOH. The obtained cross-linked polymer was de-cross-linked by visible light or pressure. The signal of imidazolyl radical was detected by ESR spectroscopy. This signal showed that a linear polymer was generated.

Introduction

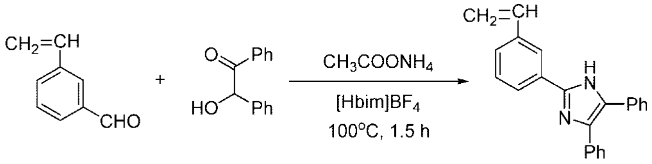
Recyclable polymers are expected to be candidate polymers for overcoming a serious problem such as environmental protection. Chemical recycling is the most important and substantial target among a few recycling methods of used polymers such as thermal, material, and chemical recycling. Recent studies on chemical recycling have been reported concerning poly(vinyl chloride),[1] polyamides,[2] poly(ethylene terephthalate),[3] polyurethanes,[4] and poly(cyclic orthoesters).[5] However, new chemical recycling should be further developed for polymers because valuable chemicals can be produced. On the other hand, polymer materials which have been prepared by a cross-linking reaction or compositization are difficult to recycle because such materials are very stable chemically, thermally and mechanically. Therefore, recycle use of cross-linked polymers is regarded as an urgent problem that needs to be resolved because of its technological difficulty. Moreover, research on the use of more sustainable materials that are friendly to the environment must take into account the need for an efficient end-of-life disposal. To overcome these obstacles, we have proposed a possible approach which consists of the introduction of a de-cross-linking system through the use of weak covalent bonding into chemical recycling of cross-linked polymers.

Hexaarylbiimidazole (HABI), having weak covalent bonding, was first synthesized by Hayashi and Maeda in 1960.[6] HABI has two kinds of 2,4,5-triphenylimidazole dimers which are prepared by oxidation of 2,4,5-triphenylimidazole. One of them exhibits photochromism and thermochromism with irradiation and change of temperature.[7,8] The other exhibits piezochromism on grinding.[9] It was shown that the photochromic compound is a HABI dimer and that photo-, thermo-, and piezochromism of the two compounds are due to reversible dissociation of the dimers into an imidazolyl radical which is shown by the reversible reaction (Scheme 1). The photochromic and piezochromic dimers are isomeric dimers which differ in their positions of combination of the 2,4,5-triphenylimidazolyl radicals and are at equilibrium with the radical in solution.[10] HABI derivatives are readily cleaved under mild conditions such as visible light irradiation and pressure. In this article, we demonstrate cross-linking−de-cross-linking of a polymer having a HABI moiety in the cross-linkage moiety.

Scheme 1. Reversible Dissociation of HABI into Imidazolyl Radical



Scheme 2. Synthesis of Monomer 1



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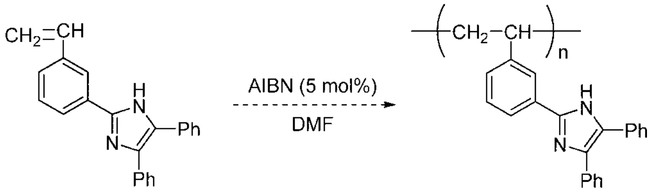
Scheme 3. Radical Homopolymerization of 1



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Experimental Section

Materials. 1-Butylimidazolium tetrafluoroborate ([Hbim]BF_4) was prepared by a reported procedure.[17] Dehydrated *N,N*-dimethylformamide (DMF) and dehydrated ethanol were purchased from Wako Pure Chemical Industries, Ltd. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Methyl methacrylate (MMA) was distilled and stored under nitrogen. The other solvents and reagents were used as supplied.

Measurements. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-500 spectrometer. IR spectra were measured on a Shimadzu IR Prestige-21 spectrometer. Gel permeation chromato-

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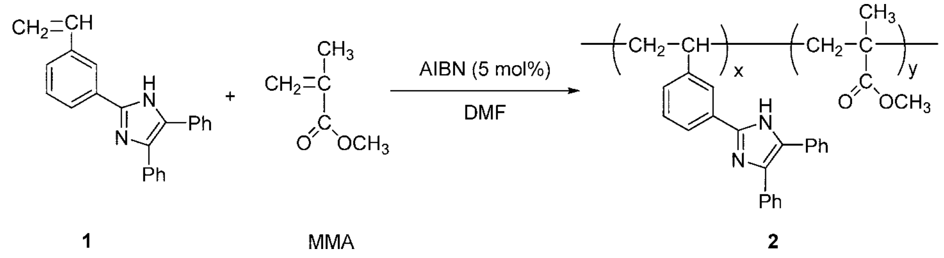
10.1021/ma801298e CCC: $40.75

Scheme 4. Radical Comopolymerization of 1 and MMA



graphic analyses were carried out on a Tosoh Co. HLC-8020 GPC system (TSK-GEL G3000XL, THF as eluent, and an ultraviolet (UV) detector) using polystyrene as a standard. The high resolution fast atom bombardment mass spectrum (FAB-MS) was recorded by using a JEOL JMS-HX110A spectrometer, whereby a mixture of a sample and *m*-nitrobenzyl alcohol on a standard FAB target was subjected to a beam of xenon atoms. The ESR spectra were observed with 100 kHz field modulation using a JEOL JES-RE3X spectrometer (X-band). De-cross-linked polymer was purified by a Japan Analytical Industry recycling preparative HPLC system (LC908-C60) equipped with polystyrene gel columns (JAIGEL-1H and JAIGEL-2H) using chloroform as eluent.

Synthesis of Monomer 1. A mixture of benzoin (1.609 g, 7.58 mmol), 3-vinylbenzaldehyde (1.002 g, 7.58 mmol), ammonium acetate (5.838 g, 75.74 mmol) and [Hbim]BF_4 (1.603 g, 7.56 mmol) was heated at 100 °C with good stirring for 1.5 h. After the reaction, the reaction mixture was diluted with water. The solid product was washed with water and dried. The obtained solid was purified by column chromatography on silica gel with hexane/ethyl acetate (from 9/1 to 8/2, v/v). The obtained solid was further purified by recrystallization from methanol-dichloromethane.

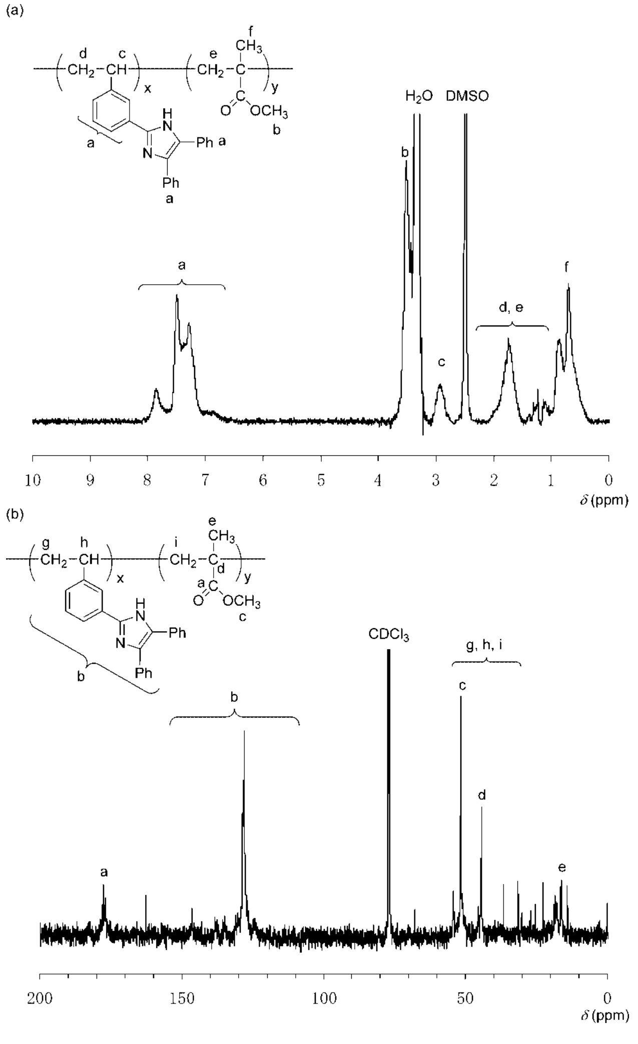


Figure 1. ^1H NMR (DMSO-d_6) (a) and ^{13}C NMR ($CDCl_3$) (b) spectra of copolymer **2**.

Yield: 45%.

IR (KBr): 3061, 3038, 3030, 3007, 2967, 2926, 2853, 1603, 1504, 1483, 766, 698 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz) δ: 5.34 (d, CH_2=CH− *cis*, J_{BX} =10.0 Hz, 1H), 5.94 (d, CH_2=CH− *trans*, J_{AX} =15.0 Hz, 1H), 6.81 (dd, CH_2=C*H*−, J_{AX} = 15.0 Hz, J_{BX} =10.0 Hz, 1H), 6.9−7.7 (m, Ph−*H*, 14H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz) δ: 114.9, 112.6, 124.8, 126.2, 127.2, 127.8, 128.4, 128.7, 129.0, 130.5, 136.5, 137.5, 145.2 ppm.

High-resolution FAB-MS $[M + H]^+$: found, 322.1468; calcd for $C_{23}H_{18}N_2$, 322.4025.

Radical Homopolymerization of 1 (Typical Procedure). Monomer **1** (100 mg, 0.31 mmol) and AIBN (2.6 mg, 5 mol %) were dissolved into DMF (3.1 mL) in a test tube, which was then degassed and sealed *in vacuo*. After being stirred at 60 °C for 14 h, the mixture was poured into a large amount of water, and the obtained solid was dried *in vacuo*. However, the expected homopolymer could not be obtained from the reaction mixture. The ^1H NMR spectrum of the obtained solid showed monomer **1**. Recovery: 99%.

Radical Copolymerization of 1 and MMA. Monomer **1** (61.7 mg, 0.19 mmol), MMA (85.2 mg, 0.85 mmol) and AIBN (8.2 mg, 5 mol %) were dissolved in DMF (1.0 mL) in a test tube, which was then degassed and sealed *in vacuo*. After 24 h at 60 °C, the reaction mixture was poured into a mixed solvent of hexane and diethyl ether (v/v, 6/4), and the precipitated polymer was dried *in vacuo*.

Yield: 94%. GPC (eluent: THF): M_n = 9900 (M_w/M_n = 3.69).

IR (KBr): 2949, 2936, 2859, 1732, 1605, 1448, 768, 700 cm^{-1}.

^1H NMR (DMSO-d_6, 500 MHz) δ: 0.49−1.50 (m, $-CH_2-C(CH_3)-$, 3H × 0.76), 1.50−2.20 (m, $-CH_2-C(CH_3)-$, 2H × 0.76 and $-CH_2-CH(Ph)-$, 2H × 0.24), 2.93 (s, $-CH_2-CH(Ph)-$, 1H × 0.24), 3.51 (s, $-CO-CH_3$, 3H × 0.76), 6.50−7.90 (m, Ph−*H*, 14H × 0.24) ppm.

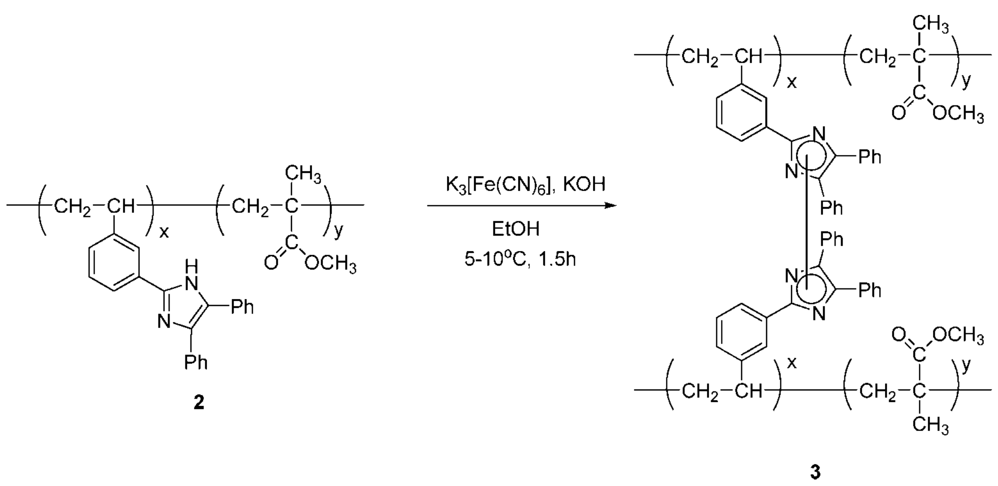
^{13}C NMR ($CDCl_3$, 125 MHz) δ: 0.14.01, 16.25, 17.81, 18.17, 18.63, 22.60, 25.54, 26.85, 30.22, 31.39, 31.53, 36.46, 44.41, 44.78, 45.60, 51.76, 54.27, 124.55, 126.85, 127.92, 128.34, 130.10, 134.94, 138.21, 146.40, 176.88, 178.78 ppm.

Cross-Linking Reaction of Copolymer 2. A cold 1% aqueous solution of potassium ferricyanide (3.4 mL) was added slowly to a solution of copolymer **2** (14.7 mg) dissolved in a mixed solvent of ethanol (0.8 mL) and THF (1.0 mL) containing potassium hydroxide (104.1 mg). During addition the reaction mixture was maintained at 5 to 10 °C and vigorously stirred. After the addition was completed (1.5 h) the obtained cross-linked polymer was collected by using a Hitachi centrifuge CT4 (3000 rpm, 15 min). Inorganic reagents were removed by centrifugation/washing (7 times) with distilled water and methanol. Then, the obtained cross-linked polymer **3** was dried *in vacuo*.

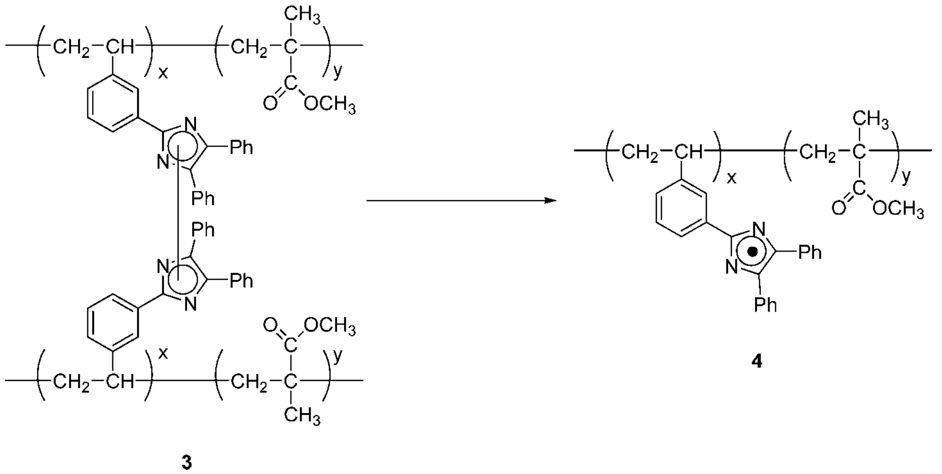
Yield: 57%.

IR (KBr): 2987, 2948, 1728, 1604, 1446, 768, 700 cm^{-1}.

Scheme 5. Cross-Linking Reaction of 2



Scheme 6. De-Cross-Linking Reaction of 3



De-Cross-Linking of Cross-Linked Polymer under Visible Light Irradiation. The cross-linked polymer **3** was dispersed in chloroform. The suspension of **3** was transferred to the ESR tube. The ESR measurements were carried out under visible light irradiation using a desk lamp (HITACHI RS3205, 34W).

De-Cross-Linking of Cross-Linked Polymer under Pressure. The cross-linked polymer **3** was pressurized by an agate mortar and pestle. After being pressurized, the cross-linked polymer **3** was transferred to the ESR tube. The ESR measurements were carried out at atmospheric pressure.

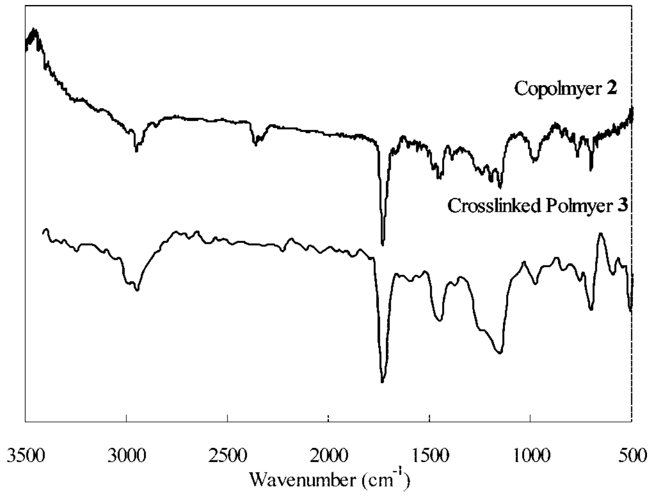


Figure 2. IR spectra of copolymer **2** and cross-linked polymer **3**.

GPC Analysis of De-Cross-Linked Polymer. The cross-linked polymer **3** (15 mg) was pressurized by an agate mortar and pestle. After being pressurized, chloroform (3 mL) as a solvent and 1-dodecanethiol (24 μL, 97 μmol) as a radical scavenger were added into the agate mortar. The reaction mixture was filtered and dried *in vacuo*. The resulting mixture was purified by recycling preparative HPLC (eluent: chloroform) to afford 4.2 mg of de-cross-linked polymer. The obtained de-cross-linked polymer was subjected to GPC analysis.

GPC (eluent: THF): $M_n = 6400$ ($M_w/M_n = 2.21$).

Results and Discussion

Synthesis of Monomer 1. Monomer **1** was synthesized by means of Siddiqui's protocol.[12] Concretely, monomer **1** was prepared by a one-step reaction from benzoin, 3-vinylbenzaldehyde, ammonium acetate, and [Hbim]BF_4 in a moderate yield (Scheme 2). Monomer **1** was well characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Its high-resolution FAB-MS spectrum was in conformity with its structure.

Radical Homopolymerization of 1. The radical homopolymerization of **1** was carried out at 60 °C for 14 h using a radical polymerization initiator (5 mol %) such as AIBN (Scheme 3). However, the homopolymerization of **1** did not proceed under the usual radical polymerization conditions. As a result, monomer **1** was recovered in a 99% yield. Moreover, the homopolymerization of **1** was carried out at 80 or 120 °C

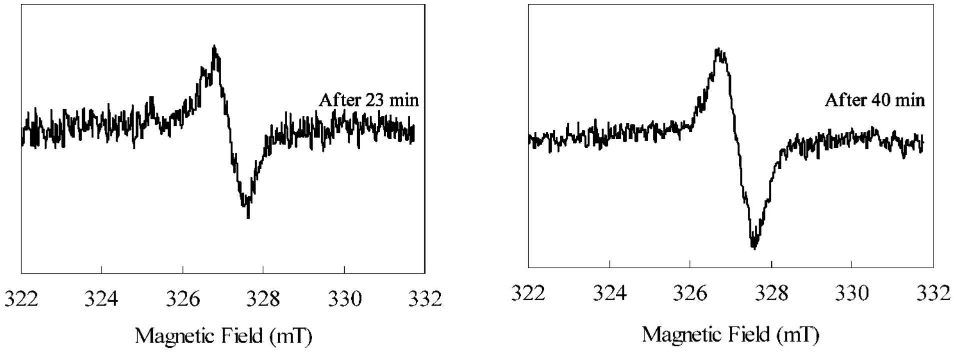


Figure 3. ESR spectra of **4** under visible light irradiation.

Table 1. Spin Concentration of 4 in the Dark[a]

shading time (min)	spin concn (spin/mg) × 10^{17}
0	2.41
8	2.11
20	2.03
40	1.94

[a] $g = 2.003$.

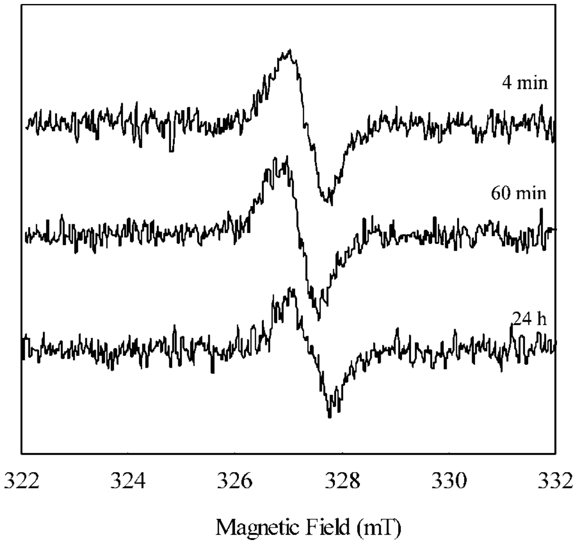


Figure 4. ESR spectra of **4** after pressurization.

Table 2. Spin Concentration of 4 under Pressure[a]

standing time (min)	spin concn (spin/mg) × 10^{16}
4	3.49
60	3.49
1440	3.55

[a] $g = 2.003$.

by use of benzoyl peroxide or di-*t*-butyl peroxide as an initiator. However, the homopolymer was not obtained in these conditions. We ascribed the unsuccessful radical homopolymerization of **1** to the very sterically demanding substituent of **1** consisting of four aromatic rings.

Radical Copolymerization of 1 and MMA. The radical copolymerization of **1** and MMA was carried out at 60 °C for 24 h using AIBN as an initiator (Scheme 4). The copolymerization proceeded homogeneously. Copolymer **2** was obtained in 94% yield as a mixed solvent of hexane and diethyl ether (v/v, 6/4) insoluble part. The obtained copolymer **2** was soluble in tetrahydrofuran, dimethylsulfoxide, and *N*,*N*-dimethylformamide. From GPC analysis, the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of **2** were estimated to be 9900 and 3.69, respectively. The copolymer composition was determined by its ^{1}H NMR spectra (Figure 1a). As a result, the unit ratio was determined to be x:y = 24:76 from the integral ratio between c and f in the aliphatic region. The ^{13}C NMR spectrum of **2** is shown in Figure 1b. The signals ascribable to the aryl imidazole moiety (x unit) were observed at δ 124−147 ppm. Furthermore, the signals ascribable to the MMA moiety (y unit) were observed at 44, 52, and 178 ppm. The ^{13}C NMR spectrum of **2** also supported the fact that **1** undertook the radical copolymerization process.

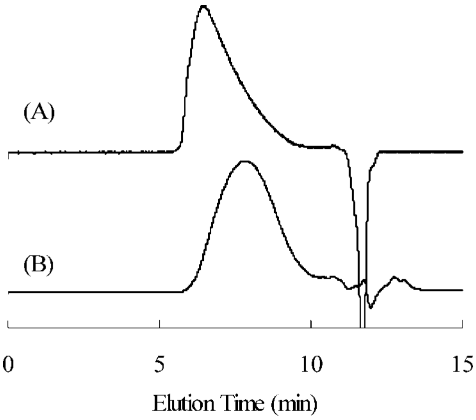


Figure 5. GPC profiles of before cross-linking and after de-cross-linking: (A) before cross-linking (copolymer **2**); (B) after de-cross-linking of cross-linked polymer **3**.

Cross-Linking Reaction of Copolymer 2. The cross-linking reactions of **2** followed a procedure reported in the literature.[13] To the solution of **2** in a solution of potassium hydroxide in a mixed solvent of ethanol and THF, a cold ethanol 1% potassium ferricyanide aqueous solution was added during a period of 1.5 h with vigorous stirring at 5−10 °C (Schemes 5 and 6). The precipitated polymer was collected by centrifugation at 3000 rpm. The precipitated polymer was washed with distilled water repeatedly and then washed with methanol. The obtained cross-linked polymer **3** was dried *in vacuo*. The obtained cross-linked polymer **3** was insoluble in tetrahydrofuran, dimethylsulfoxide, and *N*,*N*-dimethylformamide.

We tried to characterize the cross-linked polymer **3**. In the case of dimerization of 2,4,5-triphenylimidazole, White et al. reported that six dimer structures are possible when the imidazole rings are linked together *via* bonds between various combinations of the nitrogen atoms and the C_2 and C_4 carbon atoms.[13] Furthermore, these structures can be differentiated by the characteristic infrared absorptions of arylimidazoles in the 1625 to 1475 cm^{-1} region.[14] The IR spectra of copolymer **2** and cross-linked polymer **3** are shown in Figure 2. In the IR spectrum of **3**, the signals ascribable to the ester group were observed at 1728 and 1604 cm^{-1}, similar to those observed in the case of the corresponding copolymer **2**. Unfortunately, in the case of **3**, the strong absorption bands ascribable to the MMA moiety were observed in this region. Therefore, the bond-structure of the cross-linking site derived from the arylimidazole moiety was not clarified.

On the other hand, White et al. also reported that the C−H out-of plane deformations for unsubstituted phenyl groups usually occur at 765 and 695 cm^{-1} in arylimidazole compounds.[14] In the case of **3**, the absorption bands were observed at 768 and 700 cm^{-1}, respectively. Consequently, the cross-linkable moiety would be included in the cross-linked polymer **3** at least.

De-Cross-Linking of Cross-Linked Polymer 3 under Visible Light Irradiation. The cross-linked polymer **3** was insoluble in chloroform. Therefore, **3** was compulsorily dispersed in chloroform. The suspension of **3** was transferred to the ESR tube in which ESR measurements were carried out under visible light irradiation using a desk lamp. Before irradiation, **3** was ESR inactive. After irradiation for 23 min, the pattern of **4** had a single peak with a width of 7.6 G and a *g* value of 2.003 (Figure 3). Hayashi and Maeda reported that the ESR pattern of cleaved imidazolyl radical exhibited a single peak with a width of 7.5 G and a *g* value of 2.003. The spin concentration was about 10^{18} spins/cc immediately after irradiation of a 0.1% solution in benzene by direct sunlight.[15] Since our results were near to Hayashi and Maeda's results, we supposed that the de-cross-linking reaction of **3**, which was a dissociation of the bisarylimidazolyl moiety, proceeded by the irradiation of visible light. Consequently, it was clarified that the arylimidazolyl radical **4** was generated from the cross-linkage moiety of **3**. The intensity of the ESR signal was 1.56×10^{17} spins/mg under visible light irradiation for 23 min. After 40 min under visible light irradiation, the intensity of the ESR signal increased with time (2.41×10^{17} spins/mg). After visible light irradiation, the suspension of **3** turned into a clear solution. On the other hand, after stopping the irradiation with visible light, the signal of the arylimidazolyl radicals **4** gradually decreased with time in the dark (Table 1). Maeda et al. reported that the fading behavior of 2,4,5-triphenylimidazole radicals such as the model compound **4** could be studied by UV and ESR spectra.[16] They described that the single peak signal of 2,4,5-triphenylimidazole radicals gradually decreased with time in the dark. It can be seen from Hayashi and Maeda's report that our results were reasonable.

De-Cross-Linking of Cross-Linked Polymer 3 under Pressure. The cross-linked polymer **3** was ground manually in an agate mortar with a pestle at room temperature. After being pressurized, the powder of the cross-linked polymer **3** was transferred to an ESR tube. The ESR measurements were carried out at atmospheric pressure. After 4 min, the ESR pattern of **4** exhibited a single peak with no structure, a width of 7.5 G, and a *g* value of 2.003 (Figure 4). The spin concentration of **4** was 3.49×10^{16} spins/mg immediately after being pressurized. In the case of a dispersion liquid of **3**, the signal of **4** gradually decreased with time after stopping the irradiation with visible light. However, in the solid state, the signal of **4** did not decrease with time after being pressurized (Table 2). Since no solvents existed in the solid state, the generated radicals could not be diffused. Consequently, the lifetime of the generated radicals might be prolonged. Hasegawa et al. reported that the mechano-radicals generated from quartz and quartz glass were measured by an ESR spectrometer. From the observed ESR spectra, the lifetime of mechano-radicals produced from ground quartz and quartz glass was confirmed to be longer than about 3800 h in an inert condition.[17] Their report may support our results.

The GPC analysis of de-cross-linked polymer from **3** was carried out in THF using polystyrene as the standard. The GPC profiles before cross-linking and after de-cross-linking confirmed the de-cross-linking of **3** (Figure 5). In conclusion, the de-cross-linking of cross-linked polymer **3** were accomplished by pressure.

Conclusion

Under radical polymerization conditions, monomer **1** prepared from benzoin and 3-vinylbenzaldehyde with ammonium acetate and 1-butylimidazolium tetrafluoroborate and MMA were found to undergo radical copolymerization. The cross-linking reaction of copolymer **3** proceeded with $K_3[Fe(CN)_6]$ and KOH. The de-cross-linking reaction of **3** proceeded by visible light or pressure. The signal of imidazolyl radical **4** was detected by ESR spectroscopy. This signal showed that a linear polymer was generated. From an environmental science viewpoint, controls of cross-linkage moieties such as arylimidazole moiety are applicable to polymer recycling.

References and Notes

(1) Blazevska-Gilev, J.; Spaseska, D. *J. Univ. Chem. Technol Met.* **2007**, *42*, 29–34.
(2) Kanazawa, H.; Higuchi, M.; Yamamoto, K. *Macromolecules* **2006**, *39*, 138–144.
(3) Paszum, D.; Spychaj, T. *Ind. Eng. Chem. Res.* **1997**, *36*, 1373–1383.
(4) Kacperski, M.; Spychaj, T. *Prog. Rubber Plast. Technol.* **2000**, *16*, 61–68.
(5) Yoshida, K.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *25*, 2551–2558.
(6) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 565–566.
(7) Hayashi, T.; Maeda, K.; Morinaga, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1563–1564.
(8) Hayashi, T.; Maeda, K.; Kanaji, T. *Bull. Chem. Soc. Jpn.* **1965**, *387*, 857.
(9) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 685–686.
(10) White, D. M.; Sonnenberg, J. *J. Am. Chem. Soc.* **1966**, *88*, 3825–3829.
(11) Palimkar, S. S.; Siddiqui, S. A.; Rajgopal; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *J. Org. Chem.* **2003**, *68*, 9371–9378.
(12) Siddiqui, S. S.; Narkhede, U. C.; Palimkar, S. S.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron* **2005**, *61*, 3539–3546.
(13) White, D. M.; Sonnenberg, J. *J. Am. Chem. Soc.* **1966**, *88*, 3825–3829.
(14) White, D. M.; Sonnenberg, J. *J. Org. Chem.* **1964**, *29*, 1926–1930.
(15) Hayashi, T.; Maeda, K. *J. Chem. Phys.* **1960**, *32*, 1568.
(16) Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 429–438.
(17) Hasegawa, M.; Ogata, T.; Sato, M. *Powder Technol.* **1995**, *85*, 269–274.

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