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Thermal Latent Reductants for Controlled Degradation of Polyperoxides and Their Application to High Performance Dismantlable Adhesives

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ABSTRACT

1-Phenyl-3-pyrazolidone (PhP) having an active hydrogen was blocked by phenyl isocyanate derivatives to reduce its nucleophilicity, and the potential of the blocked PhP as a thermal latent reductant generating the organic reducing agent, PhP, was revealed for the first time. The degree of dissociation of the blocked PhP during heating in solution can be controlled by the steric hindrance of the isocyanate-blocking agents. The thermal latency of the blocked PhP for the sorbic ester-based polyperoxides, which undergo a serious reductive decomposition by PhP even at 30 °C, was investigated in order to accelerate the decomposition of the polyperoxides only at elevated temperatures. It was revealed that the stability of the polyperoxides was not significantly affected at 30 °C and marked reductive decomposition of the polyperoxides together with thermal decomposition took place at elevated temperatures. For the block PhPs, which are highly compatible with the polyperoxides, the decomposition promotion effect increased with increasing the steric hindrance of the blocking agents, and the controlled decomposition of the polyperoxides was successfully achieved. Moreover, the addition of the blocked PhP resulted in the complete solubilization of sorbic ester-based cross-linked polyperoxides by heating, which was not able to be achieved without the blocked PhP. The performance of the debondable adhesive using the sorbic ester-based cross-linked polyperoxides was improved by the addition of the blocked PhP, although hazardous isocyanate formation during the activation process may limit the practical application. Specifically, a faster decrease in the lap-shear adhesion strength by heating was accomplished. Furthermore, the same level of dismantlability was achieved in the wide range of heating temperatures and time, which is an

important requirement for polyperoxides undergoing significant exothermic decomposition bringing about undesired temperature rise.

Keywords: degradable polymer, network polymer, polyperoxide, redox reaction, deprotection, thermal latency, dismantlable adhesive

INTRODUCTION

Thermal latent reagents including catalysts, initiators, and curing agents are inactive at ambient temperature, but are activated at elevated temperatures.¹⁻³ In the other words, in addition to an Arrhenius type temperature dependence, the reaction rate constants are also increased by the activation of thermal latent reagents. As a result, the reactions are only started at elevated temperatures without adding additional reagents, while maintaining a sufficient stability at ambient temperature. In the other word, thermal latent reagents are useful in the achievement of discontinuous acceleration of reactions with increasing temperature. Various molecular designs to provide a thermal latency have been reported. For example, increasing solubilities of dicyandiamide⁴ and dihydrazides⁵ in epoxy resin, deprotection of blocked reagents,³ acid formation from the corresponding ester compounds by heterolytic cleavage of the ester carbon-oxygen bond,^{6, 7} increasing the nucleophilicity of imidazole derivatives by the cleavage of intramolecular hydrogen bonding,⁸ and release of amines from intercalated layered compounds⁹ were used as a trigger to activate the thermal latent reagents.

Blocked isocyanates are one of the most well-established thermal latent curing agents and widely used for one-component type polyurethane synthesis.^{2, 3, 10} As blocking agents, compounds having an active hydrogen are used and the activation temperatures of the blocked isocyanates can be controlled by the chemical structures of the blocking agents and isocyanates. Generally speaking, aromatic isocyanates exhibit lower dissociation temperatures than aliphatic isocyanates, and a large steric hindrance around an isocyanate group lowers the dissociation temperatures. Blocked isocyanates have also attracted attention not only in polyurethane synthesis, but also in other applications such as post polymerization¹⁰ and self-healing materials.¹¹

We recently found that 1-phenyl-3-pyrazolidone (PhP), which has an active hydrogen, shows an interesting redox reaction behavior for the conjugated diene-based polyperoxides.¹² That is, the reducing ability of PhP toward the polyperoxides strongly depends on the regiospecificity of the diene monomers during the polymerization (Scheme 1(a) and (b)). The polyperoxides are degradable polymers having a peroxy bond as a repeating unit of the polymer main-chain, and undergo decomposition by heating, UV irradiation, and a redox reaction.¹³⁻¹⁸ The polyperoxides are synthesized by the alternating radical copolymerization of conjugated diene monomers and oxygen,^{13, 19} and it was revealed that sorbic esters generate the polyperoxides exclusively consisting of 5,4-structures, whereas conjugated hydrocarbon dienes, such as 2,4-hexadiene (HD), generate the polyperoxides consisting of 2,3- and 2,5-structures.^{20, 21} In our recent report, it was found that the redox reaction of PhP with the sorbic ester-based polyperoxides proceeds

Scheme 1. Reactivity of (a) sorbic ester-based polyperoxide and (b) HD-based polyperoxide in the presence of PhP (previous work), and (c) aimed reactivity of sorbic ester-based polyperoxide in the presence of blocked PhP in this work.

even at room temperature and the molecular weight of the polyperoxide decreased (Scheme 1(a)).¹² In the case of the conjugated hydrocarbon diene-based polyperoxides, a decrease in the molecular weight by the redox reaction with PhP is negligible at 30 °C, but significantly occurs at 100 °C together with the thermal decomposition of the polyperoxides (Scheme 1(b)).

Such an acceleration of the decomposition only at elevated temperatures without affecting the stability of the polyperoxides at room temperature will be useful to improve the performance of degradable functional materials using polyperoxides. Various degradable functional materials utilizing the degradability of polyperoxides, i.e., dismantlable (debondable) adhesives,²²⁻²⁶ biocompatible degradable materials,^{27, 28} and property changeable thin films,^{25, 29, 30} have been reported. We should note that a number of the degradable functional materials have used sorbic ester-based polyperoxides rather than conjugated hydrocarbon dienes because of the easy introduction of functional groups as the ester groups. As already mentioned, since the reducing ability of PhP for sorbic ester-based polyperoxides is too strong, the reduction proceeds not only at elevated temperatures but also at ambient temperature. We then conceived that providing reductants with a thermal latency can allow reductive decomposition only at an elevated temperature without reducing the stability of the sorbic ester-based polyperoxides at room temperature (Scheme 1(c)). Such thermal latent reductants will increase the dismantlability of the adhesives utilizing cross-linked sorbic-ester based polyperoxides during heating without disturbing the stability at room temperature. Although we have already reported that the adhesion strength of the cross-linked sorbic-ester based polyperoxides decreases even by simple heating without a thermal latent reductant, 2-h heating at 110 °C was necessary to reach the minimum adhesion strength.²² Considering practical applications, the time required for dismantling should be shortened without decreasing the stability at room temperature. The

cross-linked polyperoxides in combination with thermal latent reductants will be one of the promising materials to achieve the requirement. In fact, we reported that the promotion of the polymer reactions by photoacid generators, can achieve the thermal stability of the pressure-sensitive type of dismantlable adhesives in the dark and their rapid dismantling after photo irradiation with subsequent heating.³¹⁻³⁴ Sasaki et al. also reported that the use of a photobase generator attained the thermal stability of poly(olefin sulfone) in the dark and decrease in the adhesion strength after photo irradiation in conjunction with heating.³⁵ These systems using photolabile catalysts are useful as long as light reaches the adhesive polymers sufficiently, but they are difficult to be applied for opaque adherends and adherends with depth such as screw holes. On the other hand, in the case of the thermal latent reductants proposed in this study, various adherends can be used and the application range will be expanded. Other various stimuli-responsive materials, such as photoresponsive azobenzene derivatives,^{36, 37} photoresponsive liquid crystals,³⁸ photo- and thermo- responsive supramolecular polymers,^{39, 40} shape memory materials,⁴¹ and polyzwitterion brushes on an adherend,⁴² were reported as dismantlable adhesives. Each material exhibits characteristic properties, such as the applicable adherend or external stimulus, adhesion strength, reversibility, and environmentally friendliness. The advantage of the sorbic ester-based polyperoxides being investigated in this paper is that the concentration optimization of the cross-linker allows to change the property from a pressure-sensitive adhesive to adhesive with remaining dismantlability.²²

It was mentioned that PhP blocked by phenyl isocyanate acts as an acid-sensitive organic reducing agent,⁴³ however, to the best of our knowledge, the simple thermal activation of a blocked PhP has not been reported. In this study, four types of PhPs blocked by the substituted phenyl isocyanates having a different steric hindrance were newly synthesized, and the thermal

latent properties of the blocked PhP (B(PhP,Ix)) and their addition effect for sorbic ester-based polyperoxides were investigated for the first time (Scheme 2). Furthermore, the addition effects of the blocked PhP on the performance of dismantlable adhesives utilizing sorbic ester-based cross-linked polyperoxides were examined in detail. Although the generation of hazardous isocyanates during the activation of the thermal latent reductants may limit application, the concept of a thermal latent reductant presenting in this study will provide new aspect.

Scheme 2. Thermal latent reductants.

EXPERIMENTAL SECTION

Materials. PhP (Tokyo Chemical Industry Co., Ltd., >98%), phenyl isocyanate (Ia, Wako Pure Chemical Industries, Ltd., >98%), *o*-tolyl isocyanate (Ib, Tokyo Chemical Industry Co., Ltd., >98%), 2,6-dimethylphenyl isocyanate (Ic, Wako Pure Chemical Industries, Ltd., >97%), 2-*tert*-butylphenyl isocyanate (Id, Sigma-Aldrich, >98%), 2-ethyl-6-methylphenyl isocyanate (Ie, Sigma-Aldrich, >98%), and polystyrene (PS, Wako Pure Chemical Industries, Ltd., $M_n=7.9 \times 10^4$, $M_w/M_n=2.2$) were used as received. Methyl sorbate (MS, Tokyo Chemical Industry Co., Ltd., >97%,) was distilled under reduced pressure (85 °C/2 mmHg). 2,2'-Azobis (4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was recrystallized from methanol. Dichloromethane and 1,2-

dichloroethane were purified by distillation. All other reagents and chemicals were used without purification.

Measurements. The ^1H NMR spectra were obtained using a Bruker AV300N spectrometer at r.t. in deuterated chloroform or $\text{DMSO-}d_6$, and at 100 °C in deuterated toluene. Electrospray ionization high resolution mass spectra (ESI-HRMS) were obtained by a JEOL AccuTOF LC-plus JMS-T100LP spectrometer. The number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC), a Tosoh CCPD RE-8020 system, using tetrahydrofuran (THF) as the eluent with the calibration curves obtained by standard polystyrenes. The thermogravimetric and differential thermal analyses (TG/DTA) were performed using a Seiko TG/DTA6200 at the heating rate of 10 °C/min under N_2 at the flow rate of 220 mL/min. The FT-IR spectra were recorded on a JASCO FT/IR-410.

Synthesis of the blocked PhP. In a typical experiment, 0.5 g of Ix was dissolved in 15 mL of dichloromethane, and the solution was dropwise added to 15 mL of a dichloromethane solution containing 2 equivalents of PhP (relative to Ix) followed by stirring at room temperature. In the case of B(PhP,Ie), 5 equivalents of PhP dissolved in 30 mL of dichloromethane was used. The consumption of Ix was monitored by the antisymmetric stretching vibration of the isocyanate group near 2260 cm^{-1} in the IR spectrum (Figure S1). In the cases of B(PhP,Ic) and B(PhP,Id), the isocyanate peak did not disappear even after 7 days of stirring, then another 2 equivalents of PhP in dichloromethane (15 mL) were added. After the completion of the protection, dichloromethane was removed by distillation, and the products were purified by silica gel column chromatography using acetone/dichloromethane = 1/4 (vol/vol) for B(PhP,Ia) and B(PhP,Ib), acetone/dichloromethane = 1/5 (vol/vol) for B(PhP, Ic), and dichloromethane/ethyl acetate = 9/1 (vol/vol) for B(PhP,Id) and B(PhP,Ie).

B(PhP,Ia). 82% yield; white solid; ^1H NMR (300 MHz, CDCl_3) δ 10.18 (broad, CONH , 1H), 7.57-7.02 (aromatic protons, 10H), 4.00 (t, $J = 7.2$ Hz, N-CH_2 , 2H), 2.81 (t, $J = 7.2$ Hz, $\text{CH}_2\text{-CO}$, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.4, 149.6, 147.0, 137.1, 129.4 (2C), 129.0 (2C), 124.2, 124.1, 119.8 (2C), 117.5 (2C), 54.2, 31.5; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_2$ 282.1243; found 282.1235.

B(PhP,Ib). 84% yield; white solid; ^1H NMR (300 MHz, CDCl_3) δ 10.13 (broad, CONH , 1H), 8.05 (d, $J = 8.7$ Hz, NH-C=CH , 1H), 7.31-7.03 (aromatic proton, 8H), 4.02 (t, $J = 7.2$ Hz, N-CH_2 , 2H), 2.82 (t, $J = 7.2$ Hz, $\text{CH}_2\text{-CO}$, 2H), 2.38 (s, Ar-CH_3 , 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.5, 149.7, 147.0, 135.6, 130.3, 129.3 (2C), 127.6, 126.8, 124.3, 124.1, 121.0, 117.5 (2C), 54.2, 31.5, 18.0; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}_2$ 296.1399; found 296.1398.

B(PhP,Ic). 90% yield; white solid; ^1H NMR (300 MHz, CDCl_3) δ 9.46 (broad, CONH , 1H), 7.34-7.03 (aromatic proton, 8H), 4.03 (t, $J = 7.2$ Hz, N-CH_2 , 2H), 2.83 (t, $J = 7.2$ Hz, $\text{CH}_2\text{-CO}$, 2H), 2.30 (s, Ar-CH_3 , 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.4, 149.9, 147.6, 135.4 (2C), 132.9, 129.3 (2C), 128.2 (2C), 127.3, 124.0, 117.6 (2C), 54.3, 31.4, 18.6 (2C); HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_2$ 310.1556; found 310.1562.

B(PhP,Id). 81% yield; white solid; ^1H NMR (300 MHz, CDCl_3) δ 9.88 (broad, CONH , 1H), 7.59 (d, $J = 8.1$ Hz, NH-C=CH , 1H), 7.58-7.03 (aromatic proton, 8H), 4.03 (t, $J = 7.2$ Hz, N-CH_2 , 2H), 2.83 (t, $J = 7.2$ Hz, $\text{CH}_2\text{-CO}$, 2H), 1.47 (s, $\text{C(CH}_3\text{)}$, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.3, 149.7, 147.9, 142.9, 134.0, 129.3 (2C), 127.7, 126.6, 126.5, 126.1, 124.1, 117.6 (2C), 54.3, 34.6, 31.5, 30.5 (3C); HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_2$ 338.1869; found 338.1878.

B(PhP,Ie). 43% yield; white solid; ^1H NMR (300 MHz, CDCl_3) δ 9.49 (broad, CONH , 1H), 7.41-7.01 (aromatic proton, 8H), 4.03 (t, $J = 7.4$ Hz, N-CH_2 , 2H), 2.83 (t, $J = 7.4$ Hz, $\text{CH}_2\text{-CO}$,

2H), 2.67 (q, $J=7.6$ Hz, Ar-CH₂, 2H), 2.30 (s, Ar-CH₃, 3H), 1.22 (t, $J=7.6$ Hz, CH₂-CH₃, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 175.4, 149.9, 147.9, 141.0, 135.9, 132.2, 129.2 (2C), 128.3, 127.6, 126.4, 124.1, 117.6 (2C), 54.3, 31.4, 25.1, 18.6, 14.6; HRMS (ESI-TOF) m/z : [M + H]⁺ calcd. for C₁₉H₂₂N₃O₂ 324.1712; found 324.1703.

Synthesis of polyperoxides. 2-Hydroxyethyl sorbate (HES) was synthesized as described in the literature.⁴⁴ In a typical polymerization, 5.0 g of a sorbic ester monomer (HES or methyl sorbate) and 0.10 g of AMVN were dissolved in 5.0 g of 1,2-dichloroethane, and the dissolved air in the solution was replaced by oxygen. The solutions were placed in a water bath at 30 °C for 6 h, and the resulting polymers were purified by three reprecipitations using a mixture of diethyl ether/hexane (1/1 vol/vol) for the polyperoxide of HES (PP-HES), and hexane for the polyperoxide of MS (PP-MS) as the precipitants. The formation of the alternating copolymers of the sorbic ester monomers with oxygen was confirmed by ¹H NMR.^{13, 44} The values of M_n and M_w/M_n were determined by GPC for PP-HES (M_n = 2,800-3,500, M_w/M_n = 1.7-1.9) and PP-MS (M_n = 4,200-5,400, M_w/M_n = 1.5-1.7).

Addition effects of B(PhP,Ix) on the decomposition of PP-MS. PP-MS (0.1 g) and B(PhP,Ix) were dissolved in 2 mL of chloroform ([-O-O- in PP-MS] : [B(PhP,Ix)] = 1 : 0.3), and the solvent was removed at room temperature under reduced pressure for 1 h. The dried samples were stored at 30 °C or 100 °C for a predetermined time, then the GPC measurement was carried out to determine the number average molecular weight of PP-MS in the presence of B(PhP,Ix) ($M_n(\text{red.})$). The number average molecular weight of PP-MS in the absence of B(PhP,Ix) ($M_n(\text{none})$) was similarly determined, and the ratio, $M_n(\text{red.})/M_n(\text{none})$, was calculated.

Addition effects of B(PhP,Ix) on the decomposition of cross-linked PP-HES. PP-HES (0.1 g), TDI as a cross-linker, and B(PhP,Ix) ([-O-O- in PP-HES] : [TDI] : [B(PhP,Ix)] = 1: 0.17: 0.38)

were dissolved in THF (0.5 wt% solution of PP-HES). The solution was placed on a Teflon plate and the crosslinking reaction was carried out at 30 °C under atmospheric pressure for 18 h and under reduced pressure for 12 h. The gel fraction of the cross-linked PP-HES was calculated after immersion in THF for 3 h. B(PhP,Ix) is soluble in THF, thus the converted gel fraction was used, in which the weight of B(PhP,Ix) was excluded from the calculation. The cross-linked PP-HES without B(PhP,Ix) was similarly prepared.

Lap-shear Adhesion Test. Aluminum adherends (10 mm × 100 mm × 1.0 mm) were ultrasonically cleaned in acetone for 15 min, isopropanol for 15 min, and air dried before use. Typically, 30 mg of PP-HES (1.6×10^{-4} mol of OH unit), 14 mg of TDI (8.0×10^{-5} mol) as a cross-linker, and B(PhP,Ix) ($[\text{-OH in PP-HES}] / [\text{-NCO}] / [\text{B(PhP,Ix)}] = 1.0 / 1.0 / 0.38$) were dissolved in acetone (0.1 mL), and about one-third of the solution was applied on a predetermined area (10 mm x 10 mm) of two pieces of aluminum adherend. After removal of the acetone under reduced pressure for 1 h, the two adherends were combined, clamped, and cured at 30 °C in the dark for 12 h under reduced pressure. For the dismantling treatments, the bonded lap-shear test joint was placed in a preheated oven for a predetermined time, then allowed to cool to room temperature. The lap-shear adhesion strength was measured using a universal testing machine, i.e., SHIMADZU autograph AGS-1 kNX equipped with a 1 kN load cell, by referring to ASTM D1002. The measurement was carried out at 1 mm/min at room temperature, and the average value of three measurements was used.

RESULTS AND DISCUSSION

Thermal dissociation behavior of the blocked PhP in solution. PhP was protected by five phenyl isocyanate derivatives (Ix) having different steric hindrances around the isocyanate group

to generate the blocked PhP (B(PhP,I_x)) (Scheme 2 and Figure S1). All five types of the blocked PhPs were stable at room temperature and were successfully isolated. In order to compare the degree of dissociation of B(PhP,I_x), the ¹H NMR measurements of the toluene-*d*₈ solutions of B(PhP,I_x) ([B(PhP,I_x)] = 0.02 mol/L) were carried out at 100 °C and the degree of dissociation was plotted versus time (Figure 1). The values of the degree of dissociation at equilibrium are indicated on the right of the plots in Figure 1. B(PhP,I_a) and B(PhP,I_b) reached equilibrium in approximately 60 min, and the degree of dissociation of B(PhP,I_b) having the *o*-methyl group (= 0.28) was higher than that of B(PhP,I_a) without a substituent (= 0.16). B(PhP,I_c) and B(PhP,I_e) having two substituents at the *o,o'*-positions did not reach equilibrium in 100 min, and the degrees of dissociation were determined to be 0.63 and 0.65, respectively, after approximately 160-min of heating. B(PhP,I_d) having a *tert*-butyl group at the *o*-position showed a very similar dissociation behavior to B(PhP,I_e) up to 100 min, and the degree of dissociation in equilibrium is expected to be similar to that of B(PhP,I_e). The degree of dissociation at equilibrium in the toluene solution is in the order of B(PhP,I_c) ~ B(PhP,I_d) ~ B(PhP,I_e) >> B(PhP,I_b) > B(PhP,I_a),

Figure 1. Degree of dissociation vs time plots of B(PhP,I_a) (●), B(PhP,I_b) (○), B(PhP,I_c) (●), B(PhP,I_d) (▲), and B(PhP,I_e) (△) determined by ¹H NMR in toluene-*d*₈ at 100 °C ([B(PhP,I_x)] = 0.02 mol/L). The solid lines are drawn as a visual guide. The numerical numbers on the right of the plots indicate the degree of dissociation at equilibrium.

reflecting the steric hindrance around the isocyanate group.

Controlled decomposition of sorbic ester-based polyperoxides by the blocked PhP. The five types of B(PhP,Ix)s were added to PP-MS, and the stabilities of PP-MS after holding at 30 °C for 12 h and at 100 °C for 1 h were evaluated by the $M_n(\text{red.})/M_n(\text{none})$ values (Figure 2). Not only the reductive decomposition of the polyperoxides, but also the thermal decomposition of the polyperoxides occurred, and the relative M_n in the presence of B(PhP,Ix) to that in the absence of additives was used to evaluate the solo effect of the reductive decomposition on the decrease in M_n .¹² When the value of $M_n(\text{red.})/M_n(\text{none})$ equals unity, a decrease in M_n by the reductive decomposition is negligible, and the contribution of the reductive decomposition increases with the decreasing $M_n(\text{red.})/M_n(\text{none})$ values. When the mixture of PP-MS and free-PhP was stored at 30 °C for 12 h, the $M_n(\text{red.})/M_n(\text{none})$ value significantly decreased from unity (= 0.56).¹² Whereas, as clearly seen in Figure 2, the $M_n(\text{red.})/M_n(\text{none})$ values in the presence of B(PhP,Ia), B(PhP,Ib), or B(PhP,Id) at 30 °C were close to unity indicating that reductive decomposition hardly proceeded. In the case of B(PhP,Ic) and B(PhP,Ie), the $M_n(\text{red.})/M_n(\text{none})$ values were

Figure 2. $M_n(\text{red.})/M_n(\text{none})$ values of PP-MS containing 0.3 equivalents of B(PhP,Ix) (based on the peroxy bond in PP-MS) after storing at 30 °C for 12 h (gray solid bar) and at 100 °C for 1 h (red open bar). The values in the bar graphs are the $M_n(\text{red.})/M_n(\text{none})$ values.

0.87 and 0.83, respectively, and slightly lower than unity, but they are obviously higher than the case of PhP. These results clearly demonstrated that the nucleophilicity of the blocked PhP was sufficiently decreased by the protection of PhP with the isocyanates.

When the mixture of PP-MS and B(PhP,Ix) was stored at 100 °C for 1 h, the $M_n(\text{red.})/M_n(\text{none})$ values obviously became lower than those at 30 °C for B(PhP,Ia), B(PhP,Ib) and B(PhP,Ie). These results are attributed to the promoted decomposition of PP-MS by the redox reaction and agree with the order of the degree of dissociation in the toluene solution. On the contrary, in the case of B(PhP,Ic) and B(PhP,Id), no or a very small promotion effect at 100 °C was observed despite having a relatively high degree of dissociation in the toluene solution. It should be noted that when one polymer chain is completely converted to low molecular weight degradation products, the degradation is not reflected in the $M_n(\text{red.})$ value, which does not include the low molecular weight fraction. To avoid such cases, the amount of the residual polymer was estimated by the peak areas of the GPC elution curves of PP-MS, which were normalized by using the PS peak as an internal standard. As the representative data,

Figure 3. GPC elution curves of PP-MS containing 0.3 equivalents of B(PhP,Ix) (based on the peroxy bond in PP-MS) after storing at 100 °C for 1 h in the presence of PS as an internal standard; no additive (black solid line), B(PhP,Ia) (red dashed line), B(PhP,Ib) (blue dotted line), B(PhP,Ic) (green dashed dotted line), B(PhP,Ie) (orange dashed double-dotted line), and PhP (gray solid line).

the normalized GPC curves for PP-MS and PP-MS containing B(PhP,Ia), B(PhP,Ib), B(PhP,Ic), B(PhP,Ie), or PhP after storing at 100 °C for 1 h are shown in Figure 3. The peak areas, i.e., the amount of the residual polymer, decreased in the order of PP-MS without additives, PP-MS with B(PhP,Ia), B(PhP,Ib), B(PhP,Ie), and PhP in agreement with the degree of dissociation in toluene and the $M_n(\text{red.})/M_n(\text{none})$ values. The results clearly show that the decomposition of PP-MS was accelerated at elevated temperatures and the extent of the acceleration can be controlled by the isocyanates as the blocking agents. However, in the case of B(PhP,Ic), the largest peak area, i.e., the largest amount of the residual polymer, was observed. Both the $M_n(\text{red.})/M_n(\text{none})$ value and the residual amount of the polymer indicated that B(PhP,Ic) did not show the promotion effect on the decomposition of PP-MS at 100 °C. This result is inconsistent with the degree of dissociation in the toluene solution. A similar trend was also observed for B(PhP,Id), that is the acceleration effect evaluated by the residual amount of PP-MS was in agreement with the value of $M_n(\text{red.})/M_n(\text{none})$ and in disagreement with the degree of dissociation in toluene (Figure S3). It seems that there are other factors than the degree of dissociation to determine the overall acceleration effect.

Dissociation behavior of neat B(PhP,Ix). The dissociation behavior of the blocked isocyanates is known to be significantly affected by the polarity of the solvents.⁴⁵ In order to exclude the effect of the polarity difference between toluene and PP-MS, the dissociation behavior of neat B(PhP,Ix) was investigated by TG/DTA. The TG/DTA curves of B(PhP,Ia) are shown in Figure 4 together with those of Ia and PhP. In Figure 4, the endothermic DTA peaks, B_I, A_P and C_P, correspond to the vaporization of Ia, melting of PhP, and vaporization of PhP, respectively. The DTA curve of B(PhP,Ia) showed three endothermic peaks, A, B, and C. Since no peak corresponding to peak B_I was observed in the temperature range lower than the peak A, it is

Figure 4. DTA and TG curves of Ia (black dashed line), PhP (blue dotted line), and B(PhP,Ia) (red solid line).

suggested that the dissociation of B(PhP,Ia), i.e., the formation of Ia and PhP, did not take place below the temperatures of peak A. Therefore, the sharp endothermic peak A is attributable to the melting of B(PhP,Ia). Peak C then appeared in the temperature range close to that of the peak C_P results from the vaporization of PhP, which was generated by the thermal dissociation of B(PhP,Ia). Finally, the remaining peak B was assigned to the vaporization of Ia, which was generated by the dissociation of B(PhP,Ia). Peak B appeared in a much higher temperature range than B_I, and it is considered that the dissociation of B(PhP,Ia) proceeds at a temperature around peak B. In the DTA curve for B(PhP,Ia), the dissociation of B(PhP,Ia) seems to hardly take place at 100 °C, whereas the dissociation of B(PhP,Ia) in toluene took place (the degree of dissociation = 0.16) as shown in Figure 1. The apparent discrepancy is due to the difference in molecular mobility between solid and solution states, and surrounding polarity.

All the DTA curves were similarly analyzed and are shown in Figure 5, where peaks A, B, and C correspond to the melting of B(PhP,I_x), vaporization of I_x, and vaporization of PhP, respectively. In the case of B(PhP,I_a), B(PhP,I_b), and B(PhP,I_e), peaks A and B are sufficiently separated, and it is shown that their dissociation takes place at around peak B, which occurs significantly higher than the melting point of each B(PhP,I_x). On the other hand, in the case of B(PhP,I_c) and B(PhP,I_d), peaks A and B overlapped each other showing that the dissociation proceeded almost simultaneously with melting. In other words, it is presumed that below the melting points of B(PhP,I_c) and B(PhP,I_d), their dissociation is suppressed. This consideration is also supported by the analysis of the differential TG (DTG) curves (Figure S2). The melting

Figure 5. DTA curves of B(PhP,I_x) (red solid line) and I_x (black dashed line): (a) $x=a$, (b) $x=b$, (c) $x=c$, (d) $x=d$ and (e) $x=e$.

points of B(PhP,Ic) and B(PhP,Id) are 169 °C and 167 °C, respectively, and they are much higher than the temperature where the promotion effect of the PP-MS decomposition was examined. Therefore, when the compatibility of B(PhP,Ic) and B(PhP,Id) with PP-MS is poor, they exist in PP-MS as a crystal and the same suppression of the dissociation observed for the neat blocked PhP will occur. In fact, the cast films of PP-MS containing B(PhP,Ic) and B(PhP,Id) resulted in an obvious phase separation, i.e., precipitation, whereas almost transparent cast films were obtained for B(PhP,Ia), B(PhP,Ib), and B(PhP,Ie) (Figure S4). Therefore, the suppression of the dissociation of B(PhP,Ic) and B(PhP,Id) in the incompatible polymer matrix, i.e., PP-MS, is the reason for the apparent inconsistency between the degree of dissociation in the toluene solution (Figure 1) and the promotion effect for the decomposition of PP-MS (Figure 2).

Promoted decomposition of cross-linked polyperoxides by the blocked PhP The decomposition promotion effect of the blocked PhP on the cross-linked polyperoxides was investigated considering the improvement of the dismantlability of the cross-linked polyperoxides-based dismantlable adhesive.²² As the representative blocked PhP, B(PhP,Ib) and B(PhP,Ie) were selected because they showed a high decomposition promotion effect at 100 °C for the non-cross-linked PP-MS. The cross-linked PP-HES was synthesized in the absence and presence of B(PhP,Ib) or B(PhP,Ie), and the gel fractions were measured. The cross-linked PP-HES prepared in the presence of B(PhP,Ib) resulted in the same level of the gel fraction (75 wt%) as the cross-linked PP-HES prepared in the absence of additives (71 wt%) showing that B(PhP,Ib) does not inhibit the cross-linking reaction. In contrast, when B(PhP,Ie) was added, the gel fraction decreased to 32%. There are two possible explanations for this observation. One is that a small amount of PhP generated by the dissociation of B(PhP,Ie), which has the higher degree of dissociation than B(PhP,Ib) in toluene, decomposes PP-HES by a redox reaction

during the crosslinking reaction at 30 °C. The other is that an isocyanate exchange reaction takes place between B(PhP,Ie) and TDI resulting in the formation of the mono-isocyanate, Ie, the reaction of which with PP-HES decreases the number of cross-linking points. It was confirmed that the reductive decomposition of PP-HES was not observed in the presence of B(PhP,Ie) under the conditions of the cross-linking reaction, i.e., at 30 °C for 30 h (Figure S5). Therefore, the former, i.e., the decomposition of PP-HES, is not the reason for the low gel fraction in the presence of B(PhP,Ie). Next, in order to confirm whether the isocyanate exchange reaction proceeds, the mixture of B(PhP,Ie) and TDI was held at 30 °C for 30 h in DMSO-*d*₆ or toluene-*d*₈, and the ¹H NMR spectra before and after the holding were measured. The expected exchange reaction products are shown in Scheme 3. In DMSO-*d*₆, the ¹H NMR peaks assignable to B(PhP,Ie), TDI, and Ie were confirmed, but no peak due to the free-PhP was observed (Figure S6). In addition, the consumption of TDI was confirmed. The ¹H NMR observations indicated

Scheme 3. Expected products for the isocyanate exchange reaction between B(PhP,Ie) and TDI.

that the isocyanate exchange reaction occurred. However, the ^1H NMR peaks due to the products of the exchange reaction (B(PhP,TDI1), B(PhP,TDI2) and B(PhP,TDI3)) were not clearly assigned probably because of the side reactions of the isocyanates with a trace amount of water. In order to suppress the side reactions and confirm the exchange reaction products, the same reaction was carried out in toluene- d_8 as toluene is less polar than DMSO and the reaction temperature was raised to 100 °C to promote the reaction. After the retention at 100 °C for 30 h, the peaks due to B(PhP,Ie) completely disappeared, and the three exchange reaction products in Scheme 3 were assigned (Figure S7). Therefore, it is concluded that the decrease in the gel fraction of the crosslinked PP-HES in the presence of B(PhP,Ie) is attributed to the progress of the isocyanate exchange reaction.

The decomposition promotion effect on the cross-linked PP-HES was examined using B(PhP,Ib), which did not inhibit the cross-linking reaction. The gel fractions before and after heating are summarized in Table 1. The cross-linked PP-HES without additives generated an insoluble residue in THF after heating at 100 °C for 60 to 120 min, and the larger gel fraction was obtained after heating at 120 °C for 120 min. The TG/DTA data of the insoluble fraction demonstrated that the insoluble fraction does not contain a peroxide bond (Figure S8), and a similar result was reported for the thermal decomposition of the PP-HES gel.⁴⁴ In the presence of B(PhP,Ib), the cross-linked PP-HES was completely solubilized at both 100 °C and 120 °C. These facts show that the thermal decomposition of the cross-linked PP-HES brings about the formation of non-degradable cross-linked polymers being different from the cross-linked PP-HES, and the addition of B(PhP,Ib) well suppresses the formation of such a non-degradable cross-linked polymer. When cross-linked PP-HES is applied to dismantlable adhesives, the formation of non-degradable cross-linked polymers during thermal decomposition makes it

difficult to remove adhesive residue from adherends.²² The current result shows that the addition of the blocked PhP enables complete removal of cross-linked PP-HES by solvent wash after thermal dismantling.

Table 1. Gel fractions of the cross-linked PP-HES containing B(PhP,Ib) before and after thermal treatment.

	Gel fraction (wt%)	
	no additive	B(PhP,Ib)
untreated	71	75 ^a
100 °C, 60 min	9	0
100 °C, 120 min	trace	n.d. ^b
120 °C, 120 min	13	0

^aConverted gel fraction. ^bNot determined.

The possible reactions for the formation of non-degradable cross-linked polymers include hydrogen abstraction of the oxygen-center radicals, which are generated by the decomposition of a peroxy bond in cross-linked PP-HES, and the subsequent recombination of the resulting carbon-center radicals to form stable C-C bonds. In the presence of B(PhP,Ib), these side reactions were suppressed and thus the cross-linked PP-HES is successfully solubilized by heating. PhP is known to act as a radical scavenger,⁴⁶ and it is expected that PhP generated by the dissociation of B(PhP,Ib) contributed to the suppression of the side reactions involving oxygen-center radicals. In addition, it is proposed that the reaction of secondary amines and peroxides occurs via a non-radical process,⁴⁷ and it is considered that the redox decomposition of the cross-linked PP-HES with PhP, which is a secondary amine, may proceed via non-radical

process. Redox decomposition of the cross-linked PP-HES without radical formation also suppresses the side reactions.

Addition effects of the blocked PhP on cross-linked polyperoxides-based dismantlable adhesives. B(PhP,Ib) was examined as a dismantlability improving agent on cross-linked PP-HES-based dismantlable adhesives.²² Aluminum was chosen as an adherend because applicability to opaque adherends is one of the important characteristics of this system using the thermal latent reductants. The adhesion properties in the absence and presence of B(PhP,Ib) were compared. In the presence of B(PhP,Ib), the lap-shear adhesion strength was 7.2 ± 0.6 MPa (the cohesive failure) and adhesion properties were comparable to those in the absence of B(PhP,Ib) (7.7 ± 0.2 MPa, the mixture of cohesive and adhesive failures) (The stress-strain curves are shown in Figure S9). Moreover, the absolute value of the lap-shear adhesion strength is sufficiently high compared to the commercially available epoxy-based adhesives for household use, which is mentioned as one of easily understandable examples.⁴⁸ Since temporary bonding, which does not generally require very high adhesion strength, is one of the promising applications of the cross-linked polyperoxide-based dismantlable adhesives, the lap-shear adhesion strength seems to be enough considering practical application. Furthermore, the failure mode of the cross-linked PP-HES containing B(PhP,Ib) was a cohesive failure showing that the interfacial interaction between the adhesive polymer layer and the aluminum adherend is significant. These results clearly demonstrated that the addition of B(PhP,Ib) to the cross-linked PP-HES based adhesive did not affect the adhesion properties.

The dismantling behavior after heating under various conditions was then compared in the absence and presence of B(PhP,Ib). The lap-shear adhesion strength after heating relative to that before heating is shown in Figure 6, in which a lower relative strength corresponds to a better dismantlability. When the heating temperature was changed, at 90 °C, the relative strength in the presence of B(PhP,Ib) ($= 0.18 \pm 0.1$) was slightly lower than that in the absence of B(PhP,Ib) ($= 0.23 \pm 0.03$), and the difference increased with the increasing dismantling temperature to 120 and 130 °C (Figure 6(a)). At 130 °C, the relative strength in the presence of B(PhP,Ib) ($= 0.23 \pm 0.03$) is almost the same as that at 90 °C, whereas in the absence of B(PhP,Ib), the relative

Figure 6. Relative lap-shear adhesion strength after heating under various conditions to that before heating; (a) heating at 90, 120, and 130 °C for 2 h; cross-linked PP-HES (gray solid bar) and cross-linked PP-HES containing B(PhP,Ib) (red striped bar), and (b) heating at 130 °C for 5, 10, and 120 min; cross-linked PP-HES (left) and cross-linked PP-HES containing B(PhP,Ib) (right).

strength ($= 0.48 \pm 0.05$) was twice that at 90 °C. The improvement of the dismantlability in the presence of B(PhP,Ib), especially at the higher temperatures, is due to the suppression effect of the aforementioned side reactions by B(PhP,Ib). The dissociation of B(PhP,Ib) forming PhP is significantly promoted by the increasing temperatures, and the suppression effect is also more pronounced at higher temperatures. The effect of the heating time was further investigated at 130 °C. The relative lap-shear adhesion strength after heating for 5, 10 and 120 min are shown in Figure 6(b). In the absence of B(PhP,Ib), it took 10 min to reach the minimum relative adhesion strength ($= 0.32 \pm 0.05$) and the relative adhesion strength increased again after a 120-min heating. In stark contrast, in the presence of B(PhP,Ib), the relative strength decreased to the minimum value ($= 0.25 \pm 0.08$) in 5 min, and the longer heating did not cause an increase in the relative strength. These results demonstrated that the addition of B(PhP,Ib) succeeded in reducing the strength in a shorter time. In addition, in the absence of B(PhP,Ib), it is necessary to stop the heating at the optimal time, but in the presence of B(PhP,Ib), an excessive heating does not cause problems and the relative strength can be reduced to the minimum value. Polyperoxides undergo significant exothermic decomposition by heating, and an unexpected increase in the temperature of the polyperoxides occurs during thermal decomposition.¹³ Therefore, the fact that similar decrease in the lap-shear adhesion strength can be achieved in the wide range of heating temperatures and time is an important finding considering practical application. Although the release of low-molecular-weight isocyanate is not preferred considering a practical application, the replacement of the isocyanate with non-volatile polymeric isocyanates is one of the solutions. For some limited applications such as temporal bonding in manufacturing process, which is one of the most promising applications of

polyperoxide-based dismantlable adhesives, well-vented working atmosphere can be provided and the release of low-molecular-weight isocyanate may be acceptable.

CONCLUSIONS

Four types of blocked PhPs with substituted phenyl isocyanates were newly synthesized and successfully isolated due to their stability at room temperature. The degree of dissociation of the blocked PhP in a toluene solution at 100 °C increased with the increasing steric hindrance around the isocyanate group, i.e., $B(\text{PhP}, \text{Ia}) < B(\text{PhP}, \text{Ib}) \ll B(\text{PhP}, \text{Ic}) \sim B(\text{PhP}, \text{Id}) \sim B(\text{PhP}, \text{Ie})$. The stability of PP-MS containing the blocked PhP was not affected at 30 °C, whereas PP-MS containing the free-PhP underwent a significant reductive decomposition even at 30 °C. The decomposition of PP-MS containing the blocked PhP at 100 °C was promoted compared to that in the absence of the blocked PhP, because reductive decomposition by the thermally regenerated PhP proceeds together with the thermal decomposition of PP-MS. When the blocked PhP was compatible with the polyperoxides, the acceleration effect of decomposition at elevated temperatures increased with increasing the steric hindrance of the blocking agent. The addition of the blocked PhP, such as $B(\text{PhP}, \text{Ib})$, to the dismantlable adhesives based on the cross-linked PP-HES shortened the dismantling time without reducing the adhesion properties at ambient temperature. Moreover, the significant decrease in the lap-shear adhesion strength was achieved in the wide range of temperatures and excess heating did not give an adverse effect. This is important finding for polyperoxide-based functional materials because the sample temperature sometimes unexpectedly rises due to the exothermic decomposition. It was clearly demonstrated that the blocked PhP can be used as a thermal latent reductant and is useful to promote the decomposition of the sorbic ester-based polyperoxides only at elevated temperatures. In addition

to the application to polyperoxides, the thermal latent reductants developed in this study can be applied to various redox reactions including chemical and biochemical redox reactions, although the formation of isocyanate may slightly limit practical application.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.

Figures of IR spectra, TG/DTA curves, photographs, GPC curves, ^1H NMR spectra and identifications, and stress-strain curves (PDF).

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Notes

The authors declare no competing financial interest.

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- (48) Note: Lap-shear adhesion strength of Cemedine High Super 30 was 5.24 ± 0.40 MPa.

For Table of Content