

# Facile Synthesis of Main-Chain Degradable Block Copolymers for Performance Enhanced Dismantlable Adhesion

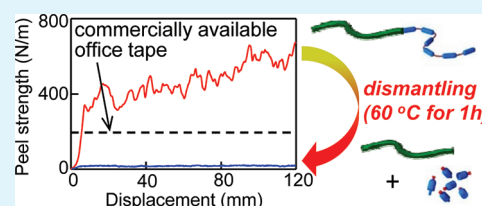
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## Supporting Information

**ABSTRACT:** Block copolymers consisting of readily degradable polyperoxides and non-degradable vinyl polymers as the block segments were successfully synthesized by reversible chain transfer catalyzed polymerization, which is one of living radical polymerization techniques. The block copolymers showed characteristic morphology and wettability being different from the polymer blends. When block copolymers containing polyperoxide and polymethacrylate blocks were heated below 150 °C, the polyperoxide blocks were completely degraded and the polymethacrylate blocks were recovered without degradation. Block copolymers containing a poly(2-ethylhexyl methacrylate) block were then investigated as a dismantlable adhesion material, which requires adequate bonding strength during use and easy debonding on demand. Among the several block copolymers, the one consisting of poly(2-ethylhexyl methacrylate) and polyperoxide from methyl sorbate (PPMS) ( $M_n = 4900$ ) exhibited good performance as a pressure-sensitive adhesive (PSA). After heating the test specimens in a temperature range from 60 to 100 °C, PSA performance, which was evaluated by 180° peel strength and shear holding power measurements, was significantly diminished. Especially, after heating at 100 °C for 1 h, spontaneous debonding of some test specimens was observed because of the evolution of volatile acetaldehyde from PPMS.

**KEYWORDS:** block copolymer, polyperoxide, degradable polymer, pressure-sensitive adhesive (PSA), morphology, wettability



## INTRODUCTION

Block copolymers show different bulk and interfacial properties from corresponding random copolymers and polymer blends due to the specific morphology such as microphase separation. The synthesis of novel block copolymers has attracted much attentions not only from the view point of synthetic chemistry but also from a wide perspective, including the investigation of morphology, the development of novel functional and/or high performance materials, and so on.

The structure control of block copolymers and available conditions for block copolymer synthesis have greatly progressed with marked improvement in living radical polymerization techniques. Living radical polymerization is tolerant to impurities and polar substituents, and thus it is a powerful method to synthesize end-functionalized vinyl polymers including block copolymers not only on a laboratory scale but also on an industrial scale. However, the synthesis of main-chain functionalized polymers by living radical polymerization is limited to a few examples such as main-chain degradable polyesters<sup>1–3</sup> and optoelectronic polymers containing anthracene units in the main chain<sup>4</sup> by the radical ring-opening polymerization of cyclic monomers. Block copolymers containing a cleavable linkage or main-chain degradable polymer blocks are one of the most fascinating functional materials for nanoporous materials.<sup>5,6</sup> In most cases, degradation was achieved by ozonolysis, photolysis, thermolysis, and chemical etching. Polyperoxides, which contain peroxy bonds as a repeating unit in the main chain, undergo main-chain

degradation by various stimuli such as heating, photoirradiation, redox reaction with amine, and enzymatic decomposition. Polyperoxides can be categorized into a new type of and readily degradable polymer because of their characteristic degradation behavior, i.e., radical chain mechanism. For example, thermolysis of polyperoxides rapidly proceeded at around 100 °C,<sup>7</sup> where most of other organic polymeric materials are stable. Polyperoxides were prepared by the radical copolymerization of diene monomer with molecular oxygen in good yield,<sup>7,8</sup> and we reported the facile synthesis of functional polyperoxides containing network and branched structures and their application.<sup>9–12</sup> We previously reported the application of polyperoxides to dismantlable adhesion.<sup>12</sup>

Adhesion techniques enable different materials to tightly bond and have been widely used in industrial, medical, and domestic applications. In addition to the properties before and during use, i.e., handling ability, bonding strength, durability, and so on, debonding ability after use is also one of the important issues. In order to achieve easy debonding on demand with reliable bonding in use, stimuli responsive materials were incorporated in adhesive materials and/or stimuli responsible polymers were used as adhesives. When the properties of the adhesives are changed to less favorable to adhesion by the response to stimuli, easy debonding is

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achieved. Adhesives having such functions are called dismantlable adhesives and are promising materials in the fields of recycle, reuse and rework. Degradable network polymers<sup>13–16</sup> and curable pressure-sensitive adhesives (PSAs)<sup>17,18</sup> are the typical example of dismantlable adhesion. More recently, dismantlable adhesion based on a new concept has been developed, i.e., shape memory polymers,<sup>19,20</sup> polyelectrolyte brushes,<sup>21</sup> and so on. We revealed that polyperoxide from methyl sorbate (PPMS) functioned as a PSA and the values of shear holding power and peel strength were efficiently decreased by the thermal and photo degradation of PPMS.<sup>12</sup> However, stick–slip failure was observed before degradation, i.e., during use, probably due to high  $T_g$  ( $T_g = -13\text{ }^\circ\text{C}$ ) and/or high storage modulus of PPMS as a PSA material. In order to improve the PSA performance during use with maintaining dismantlability, we conceived the use of block copolymers consisting of degradable polyperoxides and polymers showing good PSA performance such as poly(meth)acrylates. Another merit to use a block copolymer is that the weight fraction of polyperoxide in the resulting material is reduced, and thus exothermic heat evolution during thermal degradation is reduced.<sup>9</sup> Dismantlable adhesion using readily degradable polyperoxides are applicable for rework process and temporary bonding.

Block copolymers containing a polyperoxide block, i.e., main chain degradable block copolymers, have been synthesized by conventional radical polymerization of vinyl monomers in the presence of vinyl polyperoxides as radical initiators.<sup>22,23</sup> However, the structural control of the resulting block copolymers cannot be expected for conventional radical polymerization. In this study, the synthesis of main chain degradable block copolymers consisting of polyperoxides and non-degradable vinyl polymers was investigated using living radical polymerization techniques. Due to the reactive and degradable nature of polyperoxides,<sup>7,24</sup> available polymerization conditions for polyperoxide synthesis are restricted, i.e., polymerizations should be carried out at low temperature such as below  $40\text{ }^\circ\text{C}$  in dark and reductants such as an amine should be excluded from the polymerization system. Furthermore, reagents used for living radical polymerization are required to tolerate dissolved oxygen, which is an essential comonomer in the synthesis of polyperoxides. In this study, considering the limitations for the reaction conditions, we chosen reversible chain transfer catalyzed polymerization (RTCP)<sup>25,26</sup> to synthesize block copolymers containing polyperoxides. The performance of the resulting block copolymers in dismantlable adhesion was investigated and will be discussed in terms of the structure of block copolymers.

## EXPERIMENTAL SECTION

**Materials.** 2-Ethylhexyl methacrylate (2EHMA), benzyl methacrylate (BzMA), styrene (S), methyl sorbate (MS), and 2,4-hexadiene (HD) were distilled under reduced pressure prior to use. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was recrystallized from methanol. *N*-Iodosuccinimide (NIS) (TCI, > 98.0%), iodine ( $I_2$ ) (Wako, > 99.8%), and osmium tetroxide crystal ( $OsO_4$ ) (TABB, > 99.9%) were used as received without further purification. Other reagents and solvents were used without further purification.

**Measurement.** The number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The  $^1H$  NMR spectra were recorded by a Bruker AV300N spectrometer. Thermogravimetric and differential thermal

analyses (TG/DTA) were performed on a Seiko TG/DTA6200 at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under  $N_2$  at a flow rate of  $200\text{ mL}/\text{min}$ . The differential scanning calorimetric (DSC) analysis was performed using a Seiko EXSTAR6200 at the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Atomic force microscope (AFM) images were observed using a NanoScope IIIa system (Digital Instruments/Veeco) in height and phase modes. Transmission electron microscope (TEM) observation was performed on a JEOL 2100 equipped with energy-dispersive X-ray spectrometer (EDS) with  $200\text{ kV}$  accelerating voltage. Static contact angles were measured using  $1\text{ }\mu\text{L}$  of deionized water at room temperature. The average value of five measurements at different positions was adopted.

The adhesion tests were performed according to "ASTM D3654, standard test methods for shear adhesion of pressure-sensitive tapes" and "ASTM D3330, standard test method for peel adhesion of pressure-sensitive tape" methods, using a Tokyo Testing Machine (TTM) universal testing machine, LSC-1/30, with a  $1\text{ kN}$  (at maximum) load cell unless otherwise described. All the adhesion tests were performed at  $25\text{ }^\circ\text{C}$ . Peel rate for  $180^\circ$  peel test was  $30\text{ mm}/\text{min}$ . For the shear holding power test, using  $198\text{ g}$  of weight, we recorded time to failure ( $T_f$ ) and creep distance after  $10\text{ min}$  ( $L_{10\text{ min}}$ ) and  $60\text{ min}$  ( $L_{60\text{ min}}$ ). The average value of three measurements was adopted. All adhesion tests were performed at room temperature without light shielding.

**Preparation of AFM Samples.** The  $2.5\text{ wt } \%$  of chloroform solutions of polymers were spin-coated ( $250\text{ rpm}$  for  $5\text{ sec}$  and subsequent  $2500\text{ rpm}$  for  $40\text{ sec}$ ) on glass. The film thickness was determined by scratching the films and measuring the step height between the glass and the film surface by AFM in height mode and confocal laser microscopy (Keyence VK-8710). Both measurements resulted in similar film thickness, i.e., ca.  $500\text{ nm}$  on average.

**Preparation of TEM Samples.** An amorphous carbon film was vacuum-deposited on mica. Polymer thin films (ca.  $50\text{ nm}$ ) were spin-coated on the amorphous carbon film on mica using the  $0.5\text{ wt } \%$  chloroform solution of polymer. The spin-coated polymer film on an amorphous carbon film was floated on water and transferred on copper grids. The samples were dried in vacuo for  $12\text{ h}$  and then stained by  $OsO_4$  for  $30\text{ min}$ .

**UV Irradiation of Polymer Films.** The spin-coated films were subjected to photoirradiation using low pressure mercury lamp with Pyrex glass filter at room temperature. The films were located at a  $10\text{ cm}$  distance from the lamp.

**Preparation of Joint for Shear Holding Power Tests.** Glass ( $26.0 \times 76.0 \times 1.0\text{ mm}^3$ ) plate was cleaned by ultrasonication in acetone for  $15\text{ min}$  and in 2-propanol for  $15\text{ min}$ . Typically, block copolymer ( $100\text{ mg}$ ) was dissolved in chloroform ( $0.2\text{--}0.3\text{ mL}$ ), and then applied on the specimen. The specimen was dried in vacuo for  $3\text{ h}$  in the dark, and the mating surfaces were pressed together. The specimen was clamped and kept at room temperature for  $3\text{ h}$  in the dark. The adhered area was fixed at  $325\text{ mm}^2$  ( $12.5 \times 26.0\text{ mm}^2$ ).

**Preparation of Joint for  $180^\circ$  Peel Tests.** SUS430 ( $150 \times 50 \times 0.5\text{ mm}^3$ ) plate was cleaned by ultrasonication in acetone for  $15\text{ min}$  and in 2-propanol for  $15\text{ min}$ . Typically,  $30\text{ wt } \%$  acetone solution of block copolymer was applied on a PET film ( $50\text{ }\mu\text{m}$  thickness) by Baker type film applicator ( $100\text{ }\mu\text{m}$  gap). The film was dried in vacuo for  $12\text{ h}$  in the dark, and was cut to  $20\text{ mm}$  wide. The film was pressure bonded on SUS plate using  $2\text{ kg}$  of hand roller.

**Thermal Treatment of Test Joint.** For the thermal treatment, the test joint was placed in a preheated oven. After a predetermined time, the joint was removed from the oven and was naturally cooled to room temperature.

**Synthesis of Block Copolymer.** A typical polymerization procedure was as follows. In a Pyrex glass tube, the mixture of 2EHMA ( $4.96\text{ g}$ ,  $25\text{ mmol}$ ), AMVN ( $308\text{ mg}$ ,  $1.0\text{ mmol}$ ), NIS ( $11\text{ mg}$ ,  $0.05\text{ mmol}$ ), and  $I_2$  ( $127\text{ mg}$ ,  $0.50\text{ mmol}$ ) was placed and sealed under vacuum after three times freeze-thaw cycles. The polymerization carried out at  $40\text{ }^\circ\text{C}$  in dark and quenched by cooling to  $-78\text{ }^\circ\text{C}$ . The reaction mixture was dissolved in toluene and was purified by three times reprecipitation in methanol. The resulting polymer, iodine-terminated poly(2HEMA) (P2EHMA-I), was dried under vacuum for  $24\text{ h}$  at room temperature. In a Schlenk flask, the mixture of P2EHMA-

**Table 1. Results of RTCP of 1,3-Diene Monomer (DM) with Oxygen in the Presence of Iodine-Terminated Vinyl Polymer (P-I) at 30 °C for 6 h<sup>a</sup>**

block copolymer	P-I ( $M_n$ , $M_w/M_n$ )	DM	Conv. (%)	$M_n$	$M_w/M_n$	$M_{n,th}$	PP content(NMR) <sup>b</sup> (wt%)	PP content(TG) <sup>c</sup> (wt%)
PBzMA- <i>b</i> -PPMS-5k	PBzMA-I (5000, 1.24)	MS	19.2	5900	1.28	11 000	23.3	21.3
P2EHMA- <i>b</i> -PPMS-5k	P2EHMA-I (3700, 1.15)	MS	19.2	4900	1.42	9800	30.4	23.9
P2EHMA- <i>b</i> -PPHD-5k	P2EHMA-I (3900, 1.21)	HD	71.5	5100	1.19	20 200	14.5	15.6
P2EHMA- <i>b</i> -PPMS-10k	P2EHMA-I (9000, 1.16)	MS	24.2	9900	1.23	16 700	18.8	16.3
P2EHMA- <i>b</i> -PPHD-10k	P2EHMA-I (9000, 1.16)	HD	63.8	10 700	1.19	23 600	<sup>d</sup>	22.3
PS- <i>b</i> -PPMS-5k	PS-I (4500, 1.20)	MS	12.9	5000	1.23	5300	<sup>d</sup>	<sup>d</sup>

<sup>a</sup> $[P-I]/[AMVN]/[NIS]/[DM] = 1.0/0.13/0.13/200$  in dichloroethane, dichloroethane/DM = 1/1 in weight. <sup>b</sup>Polyperoxide content determined by <sup>1</sup>H NMR. <sup>c</sup>Polyperoxide content determined by TG as shown in Figure 6. <sup>d</sup>Not determined.

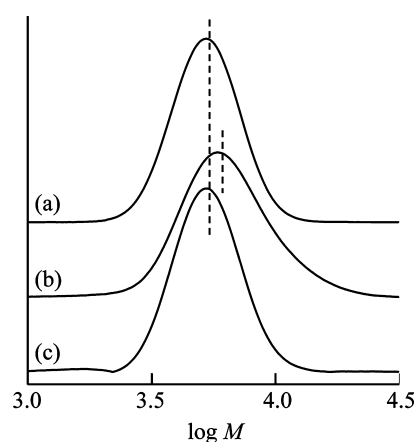
I (1.42 g), MS (12.01 g, 76.9 mmol), AMVN (15 mg, 0.05 mmol), NIS (11 mg, 0.05 mmol), and dichloroethane (12 g) was placed and dissolved air was displaced by oxygen. The polymerization carried out at 30 °C for 6 h in dark and quenched by cooling to -78 °C. The reaction mixture was purified by three times reprecipitation in methanol. The precipitate was dried under vacuum for 12 h at room temperature. The theoretical number average molecular weight ( $M_{n,th}$ ) of the block copolymer was calculated using eq 1

$$M_{n,th} = M_n(P-I) + \{[DM]_0/[P-I]_0\} \{([DM]_0 - [DM]_t) / [DM]_0\} MW_{DM+O_2} \quad (1)$$

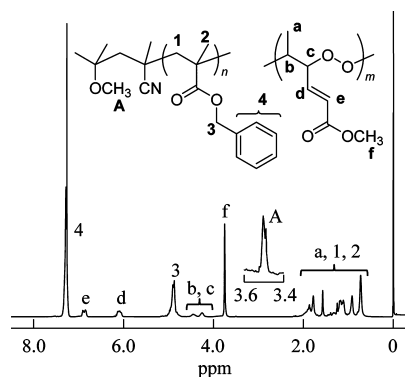
Where  $M_n(P-I)$ ,  $[P-I]_0$ ,  $[DM]_0$ ,  $[DM]_t$ , and  $MW_{DM+O_2}$  denote the  $M_n$  of iodine-terminated polymer, the initial concentration of P-I, the initial concentration of diene monomer (DM), the concentration of DM after 6 h, and the total molecular weight of DM and oxygen.

## RESULTS AND DISCUSSION

**Synthesis of Block Copolymers Containing a Polyperoxide Block.** RTCP of 1,3-diene monomers with oxygen was carried out in the presence of iodine-terminated vinyl polymers as a polymeric dormant species (Table 1). The iodine-terminated vinyl polymers were prepared by RTCP of the corresponding monomers. GPC curves obtained before and after the chain extension of iodine-terminated poly(benzyl methacrylate) (PBzMA-I) are shown in curves a and b in Figure 1. After the polymerization, the shift of GPC curve to higher molecular weight was observed suggesting the successful chain extension from PBzMA-I. The resulting polymer had much smaller  $M_n$  (= 5900) than the  $M_{n,th}$  (= 11000) because of the formation of free PPMS as described later. Although the  $M_n$  value may include some errors because of the polystyrene calibration curve, the currently observed difference between the values of  $M_n$  and  $M_{n,th}$  seems to be too large to be explained by the difference in Mark-Houwink-Sakurada parameters. In the <sup>1</sup>H NMR spectrum of the resulting polymer, characteristic resonance peaks due to an  $\alpha$ -end group, PBzMA, and PPMS were observed (Figure 2). On the basis of the relative peak intensities of -OCH<sub>3</sub> in  $\alpha$ -end (A), benzylic proton in PBzMA (3), and -OCH<sub>3</sub> in PPMS (f), the molecular weight of each block was calculated to be  $M_n(NMR) = 5900$  and 2200 for the PBzMA and PPMS blocks, respectively. The  $M_n(NMR)$  value of PPMS block (= 2200) was higher than that calculated by an increase in  $M_n$  from GPC, (= 900) and lower than that calculated by the conversion of MS (= 6100). These results



**Figure 1.** GPC curves of (a) PBzMA-I ( $M_n = 5000$ ,  $M_w/M_n = 1.24$ ), (b) PBzMA-*b*-PPMS-5k ( $M_n = 5900$ ,  $M_w/M_n = 1.28$ ), and (c) PBzMA-*b*-PPMS-5k after heating at 110 °C for 5 h ( $M_n = 5100$ ,  $M_w/M_n = 1.10$ ). Dashed lines indicate peak top.

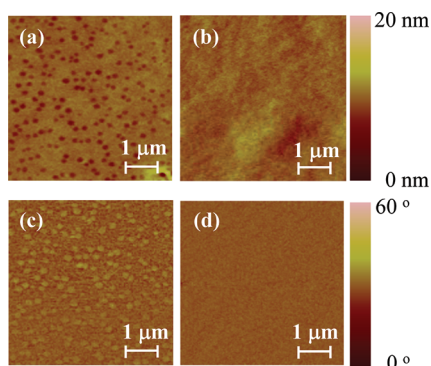


**Figure 2.** <sup>1</sup>H NMR spectrum of PBzMA-*b*-PPMS-5k in CDCl<sub>3</sub>.

suggest that the chain transfer of peroxy propagating radical and the subsequent re-initiation formed free PPMS and the free PPMS was partly removed by precipitation using methanol which is a good solvent for PPMS. Precise control of the RTCP of MS with oxygen seems to be very challenging because of the high reactivity of oxygen centered propagating radical. The contents of polyperoxide calculated by the <sup>1</sup>H NMR analysis agreed with those determined by TG because both measure-

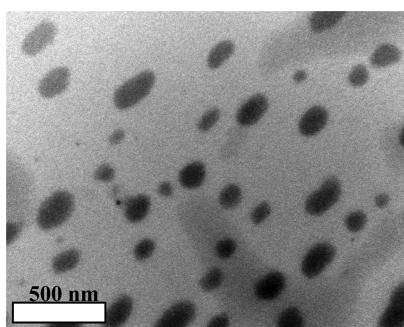
ments do not distinguish free PPMS from PPMS in block copolymers (Table 1).

The resulting polymer clearly showed distinct morphology and surface wettability attributable to block copolymers consisting of PBzMA and PPMS blocks. In the AFM height and phase images, the resulting block copolymer, PBzMA-*b*-PPMS-5k, showed spherical domains, whereas such morphology was not detected in the case of the polymer blend of PBzMA ( $M_n = 5000$ ) and PPMS ( $M_n = 4000$ ), weight ratio of which was as same as that in PBzMA-*b*-PPMS-5k (Figure 3). A



**Figure 3.** AFM images of spin-coated polymer films recorded on (a, b) height, and (c, d) phase modes; (a, c) PBzMA-*b*-PPMS-5k, and (b, d) the polymer blend of PBzMA ( $M_n = 5000$ ) and PPMS ( $M_n = 4000$ ), the weight ratio of which was as same as that of PBzMA-*b*-PPMS-5k.

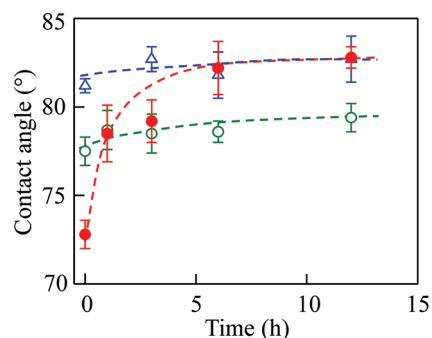
similar spherical morphology was also observed in the TEM image of PBzMA-*b*-PPMS-5k, where the spherical domains were stained by OsO<sub>4</sub> (Figure 4 and the Supporting



**Figure 4.** TEM image of spin-coated PBzMA-*b*-PPMS-5k stained by OsO<sub>4</sub>.

Information, Figure S-1). It is known that OsO<sub>4</sub> is highly reactive toward non-aromatic double bonds such as the one in polyisoprene (PI) and less reactive toward aromatic rings such as the one in polystyrene. PPMS has a non-aromatic double bond in the side chain and thus the stained spherical domains are attributed to a PPMS block. The size of PPMS domains was not uniform because the microscopic studies were performed using the as spin-coated film, i.e., without annealing, to avoid degradation of PPMS. The domain size and inter-domain distance are in the order of 10 - 10<sup>2</sup> nm, which appear to be larger than those expected from the molecular weight of PBzMA-*b*-PPMS-5k ( $M_n = 5900$ ). As mentioned above, PBzMA-*b*-PPMS-5k contains free PPMS, molecular weight and the content of which are not clear. The morphology of the binary and/or ternary mixture of block copolymers and

homopolymers have been experimentally<sup>27–30</sup> and theoretically<sup>31</sup> studied. The addition of homopolymer tended to increase the size of microphase separation,<sup>29</sup> and the addition of polystyrene (PS) ( $M_n = 16\,700$ ) to the block copolymer of PS and PI ( $M_n = 31\,600$ , PS/PI = 48/52 in wt%) resulted in twice inter-domain distance.<sup>27</sup> Furthermore, in the presence of a homopolymer, the appearance of two phases, such as spheres and disordered phases, was predicted by theoretical calculation,<sup>31</sup> and ill-defined microdomains and macrophase separation were experimentally observed with an increase in homopolymer content.<sup>29</sup> Taking into account these reports, it is obvious that the morphology of PBzMA-*b*-PPMS-5k is affected by the existence of homopolymers. However, conclusive discussion about phase, such as enlarged ordered microphase separation, disordered microphase separation, or macrophase separation, is difficult at current stage. The surface wettability of PBzMA-*b*-PPMS-5k was evaluated by the CA of water. The CA value of PBzMA-*b*-PPMS-5k was  $72.8 \pm 0.8^\circ$ , which was larger than that of PPMS ( $= 47.3^\circ$ ) and was smaller than that of PBzMA ( $= 81.2 \pm 0.4^\circ$ ). The CA value of PBzMA-*b*-PPMS-5k is explained by the surface morphology that PPMS spherical domains are spreading over a PBzMA matrix. After the decomposition of PPMS domains by UV irradiation, CA values increased with increasing irradiation time and reached as high as that of PBzMA (Figure 5). In the case of the polymer



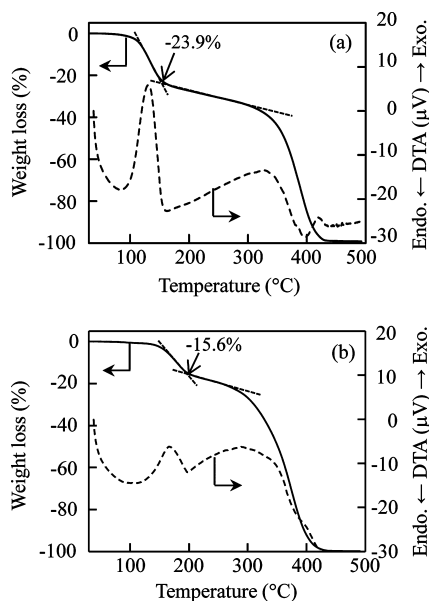
**Figure 5.** Static contact angles of deionized water versus photo-irradiation time: on PBzMA-*b*-PPMS-5k (red solid circles), PBzMA (blue triangles), and the polymer blend of PBzMA ( $M_n = 5000$ ) and PPMS ( $M_n = 4000$ ), the weight ratio of which was as same as that of PBzMA-*b*-PPMS-5k (green circles). The dashed lines are shown as a visual guide.

blend, no marked increase in CA values was observed after UV irradiation suggesting that the surface is mainly covered by UV inactive PBzMA, which has lower surface free energy than PPMS. It is reported that a polymer having lower surface free energy is enriched at the surface of both miscible polymer blends and the thick film of immiscible polymer blends.<sup>32,33</sup> The existence of small amount of PPMS and/or the difference in the molecular weight, i.e., the number of end groups, explain the slightly smaller CA for the polymer blend (CA =  $77.5 \pm 0.8^\circ$ ) than PBzMA.

Various types of block copolymers were synthesized by the a similar method and the results are shown in Table 1. All the block copolymers consist of a non-degradable block such as polymethacrylates and PS and a main chain degradable block such as PPMS and the polyperoxide from HD (PPHD).

**Degradation Behavior of Block Copolymers.** The degradation behavior of the obtained block copolymers was investigated by TG/TDA, GPC, and <sup>1</sup>H NMR analysis. The

TG/TDA curves of P2EHMA-*b*-PPMS-5k and P2EHMA-*b*-PPHD-5k are shown in Figure 6. Both polymers showed two-



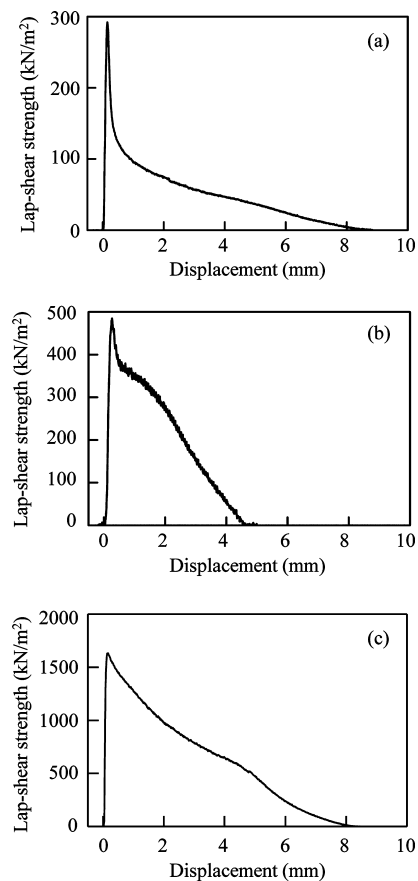
**Figure 6.** TG (—) and DTA (---) curves for the P2EHMA-*b*-PPMS-5k (a) and P2EHMA-*b*-PPHD-5k (b) under nitrogen flow at a heating rate of 10 °C/min. The inserted numbers indicate the weight ratio of polyperoxide in the block copolymers.

step weight-loss and the first step was accompanied by the evolution of heat, which was typically observed for the thermal degradation of polyperoxide.<sup>7</sup> As inserted in Figure 6, the weight loss in the first degradation step of P2EHMA-*b*-PPMS-5k (23.9 wt %) and P2EHMA-*b*-PPHD-5k (15.6 wt %) roughly agreed with the content of polyperoxide determined by <sup>1</sup>H NMR analysis (30.4 and 14.5 wt % for P2EHMA-*b*-PPMS-5k and P2EHMA-*b*-PPHD-5k, respectively). In order to analyze the residual after the first degradation step, P2EHMA-*b*-PPMS-5k was isothermally heated for 5 h at 110 °C, which is higher than the initial decomposition temperatures of PPMS ( $T_{\text{init}} = 107.9$  °C).<sup>7</sup> The residual was identified as P2EHMA by <sup>1</sup>H NMR and resulted in the identical GPC curve to P2EHMA-I (Figure 1c). These results showed that the degradation of a PPMS block completely proceeded at 110 °C and did not induce the degradation of a P2EHMA block. By contrast, although the initial decomposition temperature of PPHD ( $T_{\text{init}} = 95.1$  °C) is lower than that of PPMS,<sup>7</sup> P2EHMA-*b*-PPHD-5k was required to be heated at 150 °C for 5h in order to completely degrade a PPHD block. In our previous work, it was reported that the radical chain degradation of PPHD was suppressed by the existence of 1,4-diene structure, whereas PPMS predominantly consisted of 5,4-diene structure and was smoothly degraded.<sup>7</sup> The difference in the degradation mechanism of PPMS and PPHD is also true for the case of block copolymers.

Large heat evolution during the degradation of polyperoxides may be a drawback for the practical application of polyperoxides as a material. We previously reported that the heat of decomposition of network polymers consisting of non-degradable polymers and polyperoxy units as the cross-linking points was smaller than that of network polymers consisting only of polyperoxy units by a factor of ten to hundred.<sup>9</sup> The heat of decomposition, i.e.,  $\Delta H$ , is approximately proportional

to the area of a DTA peak. The peak area of the first degradation step of P2EHMS-*b*-PPMS-5k was approximately 27% of that of free PPMS and the ratio corresponds to the content of PPMS block in the block copolymer (30.4 wt % by <sup>1</sup>H NMR and 23.9 wt % by TG). The heat of the degradation of block copolymers is efficiently suppressed due to a reduction in polyperoxide content.

**Application to Dismantlable Adhesion.** The PSA performance of the block copolymers consisting of a polyperoxide and P2EHMA was examined by lap-shear strength, 180° peel strength, and shear holding power measurements. The lap-shear strength-displacement curves of glass specimens bonded by the block copolymers are shown in Figure 7. The block copolymers containing a PPMS, i.e.,



**Figure 7.** Representative lap-shear strength-displacement curves for the glass joint bonded by (a) P2EHMA-*b*-PPMS-5k, (b) P2EHMA-*b*-PPMS-10k, and (c) P2EHMA-*b*-PPHD-5k. The lap-shear strength-displacement curve of P2EHMA-*b*-PPMS-10k was measured with a 10 kN (at maximum) load cell.

P2EHMA-*b*-PPMS-5k and P2EHMA-*b*-PPMS-10k, resulted in a characteristic steep peak probably due to the stringiness of adhesives, whereas P2EHMA-*b*-PPHD-5k showed linear-like decrease in load after reaching the maximum value. In our previous work,<sup>12</sup> PPMS showed a lap-shear strength-displacement curve similar to P2EHMA-*b*-PPHD-5k, i.e., without steep peak. To see the origin of the steep peak, lap-shear strength tests of P2EHMA ( $M_n = 3500$ ) and the polymer blend of P2EHMA and PPMS ( $M_n = 3000$ ), weight ratio of which was as same as that in P2EHMA-*b*-PPMS-5k, were also carried out (see the Supporting Information, Figure S-2). Their lap-shear strength-displacement curves did not show a steep peak and

thus it is concluded that the stringiness is a particular observation in P2EHMA-*b*-PPMS-5k and P2EHMA-*b*-PPMS-10k. The values of lap-shear strengths were calculated from the maximum load and are summarized in Table 2. Compared to

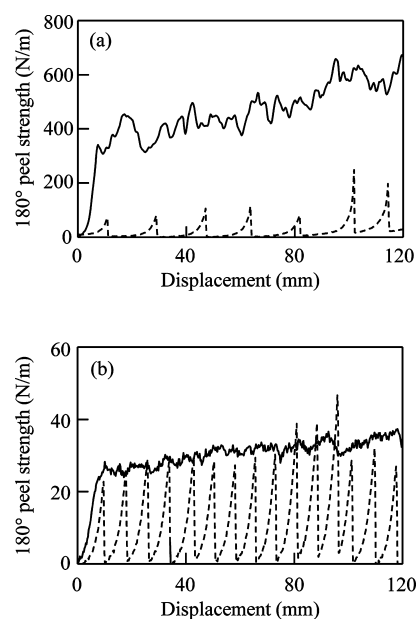
**Table 2. Results of Shear Adhesion and 180° Peel Tests of Specimens Bonded by Various Polymers**

polymer	lap-shear strength (kN/m <sup>2</sup> )	180° peel strength (N/m)	$L_{10 \text{ min}}$ (mm)
P2EHMA- <i>b</i> -PPMS-5k	292 ± 59	525 ± 278	0.1
P2EHMA- <i>b</i> -PPHD-5k	1690 ± 49	34.9 ± 8.0	~0
P2EHMA- <i>b</i> -PPMS-10k	> 3080 <sup>b</sup>	stick-slip failure	~0
P2EHMA- <i>b</i> -PPHD-10k	> 3080 <sup>b</sup>	stick-slip failure	~0
P2EHMA/PPMS <sup>b</sup>	40.6	stick-slip failure	7.5
P2EHMA ( $M_n = 3400$ )	> 3080 <sup>b</sup>	stick-slip failure	~0
PPMS ( $M_n = 3100$ ) <sup>12</sup>	13.5 ± 4.0	stick-slip failure	<sup>c,d</sup>
PPHD ( $M_n = 4400$ )	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>

<sup>a</sup>Maximum load exceeded 1kN. <sup>b</sup>The polymer blend of P2EHMA ( $M_n = 3500$ ) and PPMS ( $M_n = 3000$ ), the weight ratio of which was as same as that of P2EHMA-*b*-PPMS-5k. <sup>c</sup>Not determined because of too weak adhesion strength. <sup>d</sup>Time to failure against 100 g of weight was 530 ± 260 s.

the polyperoxides, PPMS (13.5 ± 4.0 kN/m<sup>2</sup>) and PPHD (below detection limit), the block copolymers showed larger lap-shear strength (> 292 ± 59 kN/m<sup>2</sup>) and the trend was more significant for the block copolymer having larger  $M_n$ , i.e., the one with longer P2EHMA. Although microscopic studies of P2EHMA-*b*-PPMS were not carried out, a similar morphology to PBzMA-*b*-PPMS is expected, i.e., some kinds of phase separation with the matrix of P2EHMA block and the domain of PPMS. The increased lap-shear strength can be attributed to the matrix of P2EHMA block.

The 180° peel strength and shear holding power tests were carried out and the results are shown in Table 2. Here, the shear holding power was evaluated by the creep distance of the specimen hanging 198 g of weight after 10 min ( $L_{10 \text{ min}}$ ). The 180° peel strength of P2EHMA-*b*-PPMS-5k reached to 525 ± 278 N/m without stick-slip (Figure 8a). The strength is more than twice as high as that of commercially available office tape and is strong enough for some practical application.<sup>34</sup> The shear holding power of P2EHMA-*b*-PPMS-5k ( $L_{10 \text{ min}} = 0.1$  mm) was also much improved compared to the case of PPMS, where specimens hanging 100 g of weight was completely detached in 530 ± 260 sec.<sup>12</sup> In contrast, the polymer blend of PPMS and P2EHMA resulted in stick-slip failure with low 180° peel strength (See the Supporting Information, Figure S-3b) and low shear holding power ( $L_{10 \text{ min}} = 7.5$  mm). The improved shear holding power of P2EHMA-*b*-PPMS-5k is due to P2EHMA matrix as described above. The good performance in 180° peel strength of P2EHMA-*b*-PPMS-5k is possibly due to its specific morphology and the stringiness. It is speculated that PPMS domain resulted in large 180° peel strength and P2EHMA matrix and/or stringiness reduce stick-slip failure. In the case of P2EHMA-*b*-PPMS-10k, stick-slip failure with low 180° peel strength was obtained (Figure 8a). The peel behavior is similar to that of P2EHMA (See the Supporting Information, Figure S-3a) and it is considered that the morphology and thus peel behavior of P2EHMA-*b*-PPMS-10k are mainly governed by long P2EHMA block. In spite of no adherability of PPHD, P2EHMA-*b*-PPHD-5k resulted in the constant 180° peel strength (34.9 ± 8.0 N/m) (Figure 8b), which was not as high as that for P2EHMA-*b*-PPMS-5k. The shear holding



**Figure 8.** Representative 180° peel strength-displacement curves for the test specimens bonded by (a) P2EHMA-*b*-PPMS-5k (—) and P2EHMA-*b*-PPMS-10k (---), and (b) P2EHMA-*b*-PPHD-5k (—) and P2EHMA-*b*-PPHD-10k (---).

power of P2EHMA-*b*-PPHD-5k ( $L_{10 \text{ min}} \approx 0$  mm) was superior to that of P2EHMA-*b*-PPMS-5k ( $L_{10 \text{ min}} = 0.1$  mm). In the case of P2EHMA-*b*-PPHD-10k, stick-slip failure was observed because of the major contribution of long P2EHMA block (Figure 8b).

To evaluate dismantlability, the 180° peel strength and shear holding power tests were carried out after heating the test specimens. Here, shear holding power was evaluated by time to failure ( $T_f$ ) and/or creep distance after 60 min ( $L_{60 \text{ min}}$ ) using 198 g of weight to compare widely varying strength. All the measurements were performed after the test specimens were cooled down to room temperature. The results of P2EHMA-*b*-PPMS-5k are summarized in Table 3. The 180° peel strength significantly decreased from 530 ± 280 to 72 ± 57 N/m even after heating at 50 °C, which is much lower than the initial degradation temperature of PPMS (= 107.9 °C).<sup>7</sup> In fact, the weight loss after heating up to 60 °C for 60 min was less than 3 %. A similar result was observed in our previous work using PPMS and was interpreted as the plasticizer effect of the small amount of degradation product such as acetaldehyde and fumaraldehyde monoester.<sup>12</sup> The current results are also explained in the same manner, i.e., a plasticizer effect. After heating at 100 °C for 60 min, the weight loss was 30.5 %, which is as the same as the PPMS content estimated by <sup>1</sup>H NMR analysis, and the 180° peel strength significantly decreased below detection limit, where some of test tapes spontaneously detached from a stainless steel plate (see the Supporting Information, Figure S-4). The formation of a large amount of volatile acetaldehyde resulted in not only plasticizer effect but also internal stress, and the efficient dismantling was achieved. Considering practical applications, one might worry about the formation of toxic acetaldehyde during dismantling process. As we reported, the degradation product of polyperoxides can be changed to less toxic ketones such as acetone by choosing the structure of diene monomer.<sup>24</sup> The shear holding power did not decrease after heating at 50 °C for 1 h, i.e.,  $L_{60 \text{ min}} = 1.0$  mm, and started to decrease after heating above 60 °C, where

**Table 3. Results of 180° Peel Strength and Shear Holding Power Tests of the Specimens Bonded by P2EHMA-*b*-PPMS-5k after Heating**

temp. (°C)	time (min)	weight loss (wt %)	180° peel strength (N/m)	holding power	
				$T_f$ (s)	$L_{60 \text{ min}}$ (mm)
<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	530 ± 280	> 6000	1.0
50	60	2.1	72 ± 57 (0.14) <sup>b</sup>	> 6000	1.0
60	10	0.7	150 ± 41 (0.29) <sup>b</sup>	<sup>c</sup>	<sup>c</sup>
60	30	1.8	44 ± 16 (0.08) <sup>b</sup>	<sup>c</sup>	<sup>c</sup>
60	60	2.9	27 ± 7 (0.05) <sup>b</sup>	2100 ± 360	2.6 ± 0.6
70	60	<sup>c</sup>	<sup>c</sup>	410 ± 160	<sup>c</sup>
100	60	30.5	n.d. <sup>d</sup> (~0) <sup>b</sup>	8 ± 4	<sup>c</sup>

<sup>a</sup>Before heating. <sup>b</sup>The value in the parentheses is the ratio of the 180° peel strength after heating relative to that before heating. <sup>c</sup>No data. <sup>d</sup>Not determined because of too weak strength.

$T_f = 2100 \pm 360$  s and  $L_{60 \text{ min}} = 2.6 \pm 0.6$  mm (Table 3). In the case of PPMS, significant reduction in shear holding power was already observed after heating at 50 °C.<sup>12</sup> The shear holding power of P2EHMA-*b*-PPMS-5k became less sensitive to the degradation of a PPMS block compared to the case of PPMS due to the decreased weight fraction of degradable component, i.e., PPMS block, and/or microphase separation. P2EHMA-*b*-PPHD-5k showed similar dismantlability to P2EHMA-*b*-PPMS-5k, i.e., the 180° peel strength decreased from  $35 \pm 8.0$  to  $8.3 \pm 4.0$  N/m and almost zero after heating at 60 and 100 °C, respectively, for 1 h (Table 4). However, even after

**Table 4. Results of 180° Peel Strength and Shear Holding Power Tests of the Specimens Bonded by P2EHMA-*b*-PPHD-5k after Heating for 60 min**

temp. (°C)	weight loss (wt %)	180° peel strength (N/m)	$T_f$ (s)
<sup>a</sup>	<sup>a</sup>	35 ± 8.0	> 6000
60	0.5	8.3 ± 4.0 (0.24) <sup>b</sup>	> 6000
70	2.2	<sup>c</sup>	2480 ± 840
100	4.3	n.d. <sup>d</sup> (~0) <sup>b</sup>	28 ± 14

<sup>a</sup>Before heating. <sup>b</sup>The value in the parentheses is the ratio of the 180° peel strength after heating relative to that before heating. <sup>c</sup>No data. <sup>d</sup>Not determined because of too weak strength.

heating at 100 °C for 1 h, the weight loss was only 4.3 % because of the different degradation mechanism from PPMS as described above.

## CONCLUSION

Block copolymers consisting of main chain degradable polyperoxides and non-degradable vinyl polymers were successfully synthesized by the RTCP. Polyperoxides from sorbic ester and HD and vinyl polymers such as polymethacrylates and polystyrene were available as the building blocks. The thin film of PBzMA-*b*-PPMS-5k showed characteristic morphology and wettability attributable to block copolymers. The polyperoxide block was completely degraded by heating up to 150 °C, where the degradation of vinyl polymer blocks did not occur. P2EHMA-*b*-PPMS-5k and P2EHMA-*b*-PPHD-5k showed much better PSA behavior than PPMS and PPHD, respectively, with maintaining dismantlability. Especially it is noteworthy that P2EHMA-*b*-PPMS-5k resulted in high 180° peel strength, which was twice as high as commercially available office tapes, and efficient dismantlability after heating at 100 °C for 1 h, where some test specimens showed spontaneous debonding. The good performance as a PSA is attributed to a characteristic morphology and/or stringiness of the block

copolymer. The current results suggest that block copolymers containing degradable polyperoxides are useful materials for a temporary bonding-type dismantlable PSA.

## ASSOCIATED CONTENT

### Supporting Information

EDS profile and adhesion test. This material is available free of charge via Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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