Precise Synthesis of Acrylic Block Copolymers and Application to On-demand Dismantlable Adhesion Systems in Response to Photoirradiation and Postbaking

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High-molecular-weight and functional acrylic block copolymers containing both the reactive and polar repeating units were synthesized using organotellurium-mediated living radical polymerization (TERP) technique. The block copolymers consisted of poly(tert-butyl acrylate) as the reactive segment and the random copolymer sequence containing n-butyl, 2-ethylhexyl, and 2-hydroxyethyl acrylate repeating units as the adhesive segment. The block copolymers exhibited high performance for the dismantlable adhesion responsible to dual external stimuli consisting of photoirradiation and the postbaking in the presence of a photo acid generator.

Keywords: block copolymer, controlled polymerization, dismantlable adhesion, living radical polymerization, peel strength, photo acid generator, pressure sensitive adhesion

1. Introduction

Dismantlable adhesion is a new adhesion technique satisfying both strong bonding during use and easy debonding after use, and recently attracts attention in the fields of material recycling and product-manufacturing processes using temporary bonding.[2-12] We previously reported the properties of adhesion materials using the block copolymers consisting of poly(tert-butyl acrylate) (PtBA) and poly(2-ethylhexyl acrylate) (P2EHA) as the reactive and adhesive polymer sequences, respectively, which were synthesized by atom transfer radical polymerization (ATRP) technique.[13] Based on the results of the 180º peel test of the pressure-sensitive adhesive tapes manufactured with the block copolymers as the adhesives, it was demonstrated that the adhesive strength of the tapes rapidly reduced on heating in the presence of an acidic catalyst due to the side-group degradation of PtBA. We further proposed the use of a photo acid generator (PAG) responsible to UV irradiation and postbaking for the on-demand control of the adhesive properties, and verified the effectiveness of the reactive acrylate block copolymers combined with PAG for the dismantlable adhesion systems. However, the peel strength of the adhesive materials prepared by ATRP significantly depended on their composition and molecular weight. The copolymers exhibited high strength in a narrow range of the composition of the hard and soft segments. This was because of the low cohesive force of the polymers and it was expected that an increase in the molecular weight of the polymer and the introduction of a polar group would be valid for manufacturing high-strength adhesion materials. Therefore, we carried out the synthesis of high-molecular-weight and functional acrylic block copolymers containing polar repeating units and the application to the well-designed dismantlable adhesive materials with reliable performance. We adopted the organotellurium-mediated living radical polymerization (TERP) technique, which is the most useful method for the synthesis of various polyacrylates with a functional group at the side group and chain ends as well as the good control of molecular weight and its distribution.[14,15] The
adhesive segments consisted of the random copolymers of n-butyl, 2-ethylhexyl, and 2-hydroxyethyl acrylates (nBA, 2EHA, and HEA, respectively), while the PtBA segment was reactive in response to dual external stimuli consisting of photoirradiation and postbaking. In this paper, we describe a new approach for the synthesis of well-defined block copolymers and the application of the obtained block copolymers as the dismantlable adhesion materials.

2. Experimental
The NMR spectra were recorded using a Bruker AV300 spectrometer in chloroform-d or acetone-d$_6$. The number- and weight-average molecular weights ($M_n$ and $M_w$) were determined by size exclusion chromatography (SEC) using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. Commercially available acrylates were distilled before use. Diphenyl ditelluride (DPDT) and $N$-hydroxynaphthalimide triflate (NIT) was used as received. Other organotellurium compounds were synthesized according to the method described in the literature.

The adhesion tests were performed according to the standard test method for the peel adhesion of pressure-sensitive tape (ASTM D3330) using a Tokyo Testing Machine universal testing machine, LSC-1/30, with a 1 kN load cell at maximum. The adhesive polymers (30 wt%) in toluene or acetone were coated on a PET film, and dried overnight under reduced pressure at room temperature. A strip of the PET film coated with the adhesive polymers was placed to a stainless steel plate, and then pressed using a hand roller. The UV irradiation, heating, and 180° peel test were carried out after the specimen was left to stand over 30 min at room temperature. For the UV irradiation, the test piece was placed at a distance of 10 cm from the UV source (Toshiba SHL-100UVQ-2) at room temperature. For the thermal treatment, the test piece was placed in a preheated oven for a determined time. All the adhesion tests were performed at 23 °C. The average value of three measurements was typically recorded.

3. Results and Discussion
The living radical polymerization of the acrylates using various organotellurium compounds as the chain transfer agent was carried out in order to synthesize block copolymers with well-defined chain structures containing a polar repeating unit (Scheme 1). An initiating system using organo-

monotellurium compounds effectively controlled the living radical polymerization of non-polar and polar acrylate monomers, but the monotellurides were sensitive toward oxygen. Yamago et al. previously reported the polymerization system using in-situ generated initiators from ditellurides and an azo initiator as the practical protocols for TERP. In this study, therefore, we used organoditellurium compounds, which are stable rather than organomonotellurides, in the presence of binary azo initiators with different decomposition rates, i.e., 2,2’-azobisisobutyronitrile (AIBN) and 2,2’-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) with half lifes ($t_{1/2}$) of 20 h and 12 min at 60 °C, respectively (Scheme 2).

The polymerization of tBA was carried out using DPDT in the presence of AIBN and AMVN. The results of the polymerization are shown in Table 1. Only a trace amount of polymer was produced during the polymerization in the presence of AIBN at 60 °C due to the low decomposition rate of AIBN and the polymerization retardation by the existence of a large amount of DPDT. The polymerization at 95 °C resulted in an increase in the polymer yield, but the $M_w/M_n$ value was high as 1.62, as a result of the less control of the radical polymerization by the deactivation of the telluride chain-end and the occurrence of bimolecular termination producing dead polymer chains. The charged AIBN was rapidly consumed ($t_{1/2}$ = 12 min at 95 °C). Similar results were obtained during the polymerization at 60 °C using AMVN, of which the
The use of a larger amount of AMVN and a prolonged polymerization time led to the increases in both the $M_n$ and $M_w/M_n$ values.

In order to control the polymerization reaction at a high conversion, we concurrently used both AMVN and AIBN as the radical sources (Table 1 and Fig. 1). We expected that the organomono-telluride species would be effectively produced from DPDT by the fast decomposition of AMVN, and the polymerization would be persistently promoted by the slow and continuous supply of radical species from AIBN; the $t_{1/2}$ value for AIBN is ca. 20 h at 60 ºC. The addition of AIBN actually accelerated the polymerization keeping the controlled propagation and we consequently succeeded in the simultaneous achievement of the high conversion and the high $M_n$ values with a narrow molecular weight distribution.

The high-molecular-weight block copolymers with well-defined chain structures were similarly synthesized using the organomono- and organoditellurium compounds. After the homopolymerization of tBA at a high conversion (over 75% conversion), either 2EHA or nBA as the second monomer with a small amount of HEA was added to the polymerization system, according to the reactions in Scheme 1. The random copolymerization occurred during the second stage reaction. The typical SEC traces of the precursor PtBA and the obtained block copolymer are shown in Fig. 2. The $M_w/M_n$ values tended to be greater for the polymerization systems in the presence of HEA. This suggests the possibility of significant chain transfers to the monomer or polymer during the polymerization of the polar and functional acrylate monomer. The composition and structures of the obtained polymers were enough to be used as the adhesive polymer materials for dismantlable pressure-sensitive adhesion in this study.

### Table 1. Synthesis of PtBA by TERP Using DPDT in the Presence of AMVN and AIBN

<table>
<thead>
<tr>
<th>[AMVN]/[AIBN]</th>
<th>temp (ºC)</th>
<th>time (h)</th>
<th>conv. (%)</th>
<th>$M_n /10^4$</th>
<th>$M_w/M_n$</th>
</tr>
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<tbody>
<tr>
<td>0/1.5</td>
<td>60</td>
<td>5</td>
<td>trace</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>5</td>
<td>75.9</td>
<td>4.42</td>
<td>1.62</td>
</tr>
<tr>
<td>1.2/0</td>
<td>60</td>
<td>5</td>
<td>19.0</td>
<td>1.61</td>
<td>1.18</td>
</tr>
<tr>
<td>1.3/0</td>
<td>60</td>
<td>5</td>
<td>74.1</td>
<td>6.42</td>
<td>1.43</td>
</tr>
<tr>
<td>1.4/0</td>
<td>60</td>
<td>5</td>
<td>88.5</td>
<td>7.61</td>
<td>1.46</td>
</tr>
<tr>
<td>1.2/1.0</td>
<td>60</td>
<td>1</td>
<td>4.5</td>
<td>0.97</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3</td>
<td>19.2</td>
<td>2.89</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5</td>
<td>84.1</td>
<td>8.82</td>
<td>1.31</td>
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</tbody>
</table>

$t_{1/2}$ value was also 12 min. The use of a larger amount of AMVN and a prolonged polymerization time led to the increases in both the $M_n$ and $M_w/M_n$ values.

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The high-molecular-weight block copolymers with well-defined chain structures were similarly synthesized using the organomono- and organoditellurium compounds. After the homopolymerization of tBA at a high conversion (over 75% conversion), either 2EHA or nBA as the second monomer with a small amount of HEA was added to the polymerization system, according to the reactions in Scheme 1. The random copolymerization occurred during the second stage reaction. The typical SEC traces of the precursor PtBA and the obtained block copolymer are shown in Fig. 2. The $M_w/M_n$ values tended to be greater for the polymerization systems in the presence of HEA. This suggests the possibility of significant chain transfers to the monomer or polymer during the polymerization of the polar and functional acrylate monomer. The composition and structures of the obtained polymers were enough to be used as the adhesive polymer materials for dismantlable pressure-sensitive adhesion in this study.
The 180° peel test was carried out using the block copolymers including the HEA repeating units in the presence of NIT as the PAG. NIT produces trifluorosulfonic acid as the strong acid under UV irradiation. A small amount of water or any other proton donor contained in the adhesion systems participates in the reactions for an acid generation (see Scheme 3). The 180° peel strength was investigated using a strip of the PET film coated with the adhesive polymers and a stainless steel plate as the substrate for adhesion. The results of the peel test are summarized in Table 2. The strengths of the adhesion tapes using the HEA-containing block copolymers prepared by the TERP method were 300–450 N/m, being higher than those reported for the previous results using the PtBA- \( b \)-P2EHA synthesized by ATRP [13] and also for PtBA \( 39.4 \)-\( b \)-P(tBA \( 3.6 \)-co-2EHA \( 57.0 \)) without the HEA units. The high strength values were obtained by the use of the HEA-containing block copolymers, in contrast to the adhesives using non-polar polyacrylates with a low cohesive force leading to the occurrence of cohesive failure at a low peeling strength. The observed peeling strengths were higher than that for a commercially available pressure-sensitive adhesion tape under similar peel conditions. The peel strength and failure mode were determined by the ratio of hard and soft segments, the glass transition temperature \( (T_g) \) of the soft segment, and the content of the polar HEA units in the soft segment. For the block copolymers including the polar HEA units, interfacial failure at the steel plate side was observed.

The heating treatment resulted in an increase in the adhesion strength for the most cases, due to the closer contact between the adhesive layer including a polar hydroxyl group and a steel plate surface. Simultaneously, failure mode was changed from the interfacial failure between the steel plate and the adhesives to the cohesive one due to enhanced dipolar interaction at the metal-adhesive interface after heating. The peel strengths at the cohesive failure correspond to the cohesive force of the polymer materials, i.e., 350 N/m and 920 N/m for the block copolymers containing the 2EHA and nBA units, respectively. A difference in the \( T_g \) values of the soft segments (–70 and –52 °C for the P2EHA and PnBA segments, respectively) is significantly related to a difference in the cohesive forces at room temperature. No drastic change in the strength and the failure mode was observed under UV irradiation without any heating. Being largely different from the results after single stimulus either heating or UV irradiation, the postbaking after UV irradiation resulted in the great change in the adhesive property, as expected (Table 2 and Fig. 3(a)). Only small magnitude of adhesion strength (4–18 N/m) remained after dual stimuli and the adhesion tapes were spontaneously

<table>
<thead>
<tr>
<th>polymer</th>
<th>stimuli</th>
<th>peel strength (N/m)</th>
<th>relative value</th>
<th>failure mode</th>
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</thead>
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<tr>
<td>PtBA(<em>{37.8})-( b )-P(tBA(</em>{5.4})-co-2EHA(<em>{52.5})-co-HEA(</em>{4.3})) ((M_n = 2.85 \times 10^5, M_w/M_n = 1.49))</td>
<td>none</td>
<td>302 ± 18</td>
<td>1</td>
<td>SUS-interfacial</td>
</tr>
<tr>
<td>PtBA(<em>{24.1})-( b )-P(tBA(</em>{3.7})-co-nBA(<em>{67.0})-co-HEA(</em>{3.8})) ((M_n = 2.39 \times 10^5, M_w/M_n = 1.48))</td>
<td>none</td>
<td>448 ± 45</td>
<td>1</td>
<td>SUS-interfacial</td>
</tr>
<tr>
<td>PtBA(<em>{39.4})-( b )-P(tBA(</em>{3.6})-co-2EHA(_{57.0})) ((M_n = 2.11 \times 10^5, M_w/M_n = 1.43))</td>
<td>none</td>
<td>63.3</td>
<td>1</td>
<td>cohesive</td>
</tr>
<tr>
<td>P(tBA(<em>{35.5})-co-nBA(</em>{60.8})-co-HEA(_{3.7})) ((M_n = 2.42 \times 10^5, M_w/M_n = 1.67))</td>
<td>none</td>
<td>347 ± 36</td>
<td>1</td>
<td>SUS-interfacial</td>
</tr>
</tbody>
</table>

\(^a\) NIT 0.4 mol% toward tBA units. Peel rate, 30 mm/min.
peeled off with a help of the evolution of an isobutene gas. The failure mode became complex because of the foamed adhesives by the gas evolution. The interfacial failure at the PET-film side of the adhesive was observed in some cases, and the complicated cohesive failure occurred in the other cases. The failure behavior changes depending on the cohesive force of the adhesives and the amount of evolved gas at the interfaces. The use of the block copolymers was superior to the random copolymer system at similar molecular weight and composition because the random copolymer resulted in stick-slip failure for dismantling by applied dual stimuli, as shown in Table 2.

No change was observed in the IR and NMR spectra and the DSC traces of the adhesive polymers after photoirradiation, but a small part of the polymers became insoluble. This suggests the occurrence of cross-linked polymers by the partial intermolecular reaction between the side chains. The almost polymers were insoluble after the photoirradiation and the postbaking. Therefore, we analyzed the GPC elution curves of a model reaction system in order to clarify a reaction mechanism for gelation (cross-linking) during the UV irradiation and the subsequent heating in the presence of NIT (Fig. 4). When the same mass of high-molecular-weight PnBA ($M_n = 1.47 \times 10^5$, $M_w/M_n = 1.19$) and low-molecular-weight P(nBA-co-HEA) ($M_n = 8.9 \times 10^3$, $M_w/M_n = 1.07$) were irradiated for 1 h in bulk in the presence of 1 wt% of NIT, an additional peak was observed at the elution time that corresponding to the twice of the original P(nBA-co-HEA). Further heating induced the increment in the intensity and the broadening of the new peak and a decrease in the peak intensity of the original P(nBA-co-HEA). The formation of an additional shoulder peak was also observed for the higher-molecular-weight P(nBA) (curve D). The 40-min heating resulted in the cross-linking of the whole polymers. The P(nBA-co-HEA) chains underwent intermolecular transesterification between the hydroxyl group and the $n$-butyl ester

![Fig. 3](image-url)

Fig. 3. (a) Peel strength-displacement curves for peel test of PtBA$_{37.8}$-b-P(tBA$_{5.4}$-co-2EHA$_{52.5}$-co-HEA$_{4.3}$) in the presence of 0.4 mol% of NIT. Original (blue), after heating at 100 °C for 1 h (orange), after UV irradiation for 1 h (purple), after UV irradiation for 1 h and the subsequent heating at 100 °C for 1 h (red). (b) Comparison of the dismantlable adhesion property of the block and random copolymers for the quick response to external stimuli; UV irradiation for 1–10 min and subsequent heating at 150 °C for 5 min.

![Fig. 4](image-url)

Fig. 4. RI and UV responses for GPC elution curves of the mixture of PnBA and P(nBA-co-HEA) in the presence 1 wt% of NIT before UV irradiation and heating (A, blue), after UV irradiation for 1 h (B, purple), after UV irradiation for 1 h and the subsequent heating at 100 °C for 10 min (C, green), and after UV irradiation for 1 h and the subsequent heating at 100 °C for 20 min (D, red).
group in the presence of an acidic catalyst to produce twice molecular-weight P(nBA-co-HEA) at the initial stage of the reaction (curve C). The reaction between the hydroxyl group of P(nBA-co-HEA) and the \( n \)-butyl ester group of \( \text{PnBA} \) is also possible, but an increment of the molecular weight was small to be detected as a change in the GPC elution curve. The transesterification were frequently repeated between various polymers and led to the broad peak appearance at the higher-molecular-weight regions of the original \( \text{PnBA} \) and P(nBA-co-HEA).

In the GPC elution curves monitored by the UV detector, the peak intensity increased even after photoirradiation without postbaking, suggesting the corporation of the NIT and its decomposition products into any reaction with the polymer chains. The intensity further increased during the postbaking. The possible reaction mechanism is as follows. The naphthalimide cations formed by the photodecomposition of NIT can directly react with the hydroxyl group and with the ester groups after transformation to \( \text{N-hydroxynaphthalimide} \) in the presence of a strong trifluoromethanesulfonic acid, as shown in Scheme 3. These reactions accompany the introduction of thenaphthalimide moiety into the polymer side chain, leading to the unusual increment of the peak intensity of the UV-detected GPC elution curves.

**Conclusion**

We successfully synthesized high-molecular-weight and functional acrylic block copolymers containing both the reactive and polar repeating units using the modified TERP technique in the presence of binary azo initiators with different decomposition rates and confirmed the high performance of the obtained block copolymers as the dismantlable adhesion materials responsible to dual external stimuli consisting of photoirradiation and the postbaking in the presence of a photo acid generator.

**References**

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