



Acetal-protected acrylic copolymers for dismantlable adhesives with spontaneous and complete removability



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ABSTRACT

Acetal-protected acrylic copolymers consisting of 1-isobutoxyethyl acrylate (iBEA), 2-ethylhexyl acrylate (2EHA), and 2-hydroxyethyl acrylate (HEA) repeating units were applied to the pressure-sensitive adhesive (PSA) types of dismantlable adhesives. The random and block copolymers with a relatively high HEA content showed good PSA properties before dismantling treatment. The deprotection of the acetal-protected group of the iBEA unit took place in response to individual external stimuli, soaking in boiling water and UV irradiation in the presence of a photoacid generator. The random copolymers containing an HEA unit of more than 10 mol% and an iBEA unit of more than 70 mol% achieved spontaneous debonding with interfacial failures at both the stainless steel and polyethylene terephthalate support film sides by soaking in boiling water within 10 min, whereas the corresponding block copolymer did not achieve interfacial failure even after a 20-min soaking. Photoirradiation of the random copolymers containing *N*-hydroxynaphthalimide triflate as a photoacid generator resulted in interfacial failures at both sides with a sufficiently reduced peel strength, where cross-linking arose due to the transesterification and transesterification of a hydroxy group in the HEA unit along with deprotection.

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1. Introduction

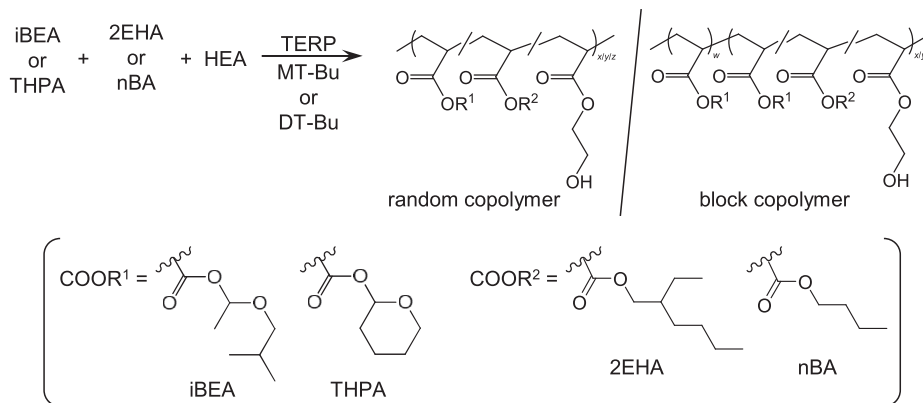
Dismantlable adhesives are a new class of functional adhesives which possess a sufficient bonding strength during use and effective reduction in bonding strength in response to external stimuli on demand. Various types of dismantlable adhesives using physical and/or chemical property changes were reported, for instance, for degradable network polymers [1,2], photo curable polymers [3,4], reversible cross-linkable polymers [5,6], ion-conducting polymers [7–9], shape memory polymers [10], polyelectrolyte brushes [11,12], and thermally expansive microcapsules [13]. Dismantlable adhesion techniques are expected to be useful in various fields including building materials for housing, rubber materials, electronics, medical and dental applications, and manufacturing processing. Many applications require debonding without an adhesive deposit on the materials, i.e., interfacial failures, in addition to

effective reduction in the bonding strength. However, a strong interfacial interaction among adhesive polymers and substrates is preferred in order to avoid accidental debonding during use. The requirement of opposite properties for the same adhesive materials is a challenging issue when designing dismantlable adhesives.

We have previously reported the design of dismantlable adhesives using degradable polyperoxides [14,15] and reactive acrylic polymers [16–20]. Main-chain degradable polyperoxides and their derivatives, such as cross-linked polymers and block copolymers, acted as curable adhesives and pressure sensitive adhesives (PSAs), and their bonding strength decreased by the photo- and thermal-induced degradations of the polyperoxides [14,15]. However, the main-chain degradation of the polyperoxides accompanying the formation of non-volatile low molecular weight degradation products tended to bring about a reduction in the cohesive force, and subsequently, it resulted in cohesive failure during the dismantling process. In the system using reactive acrylic polymers for PSAs, the transformation of a *t*-butyl acrylate (tBA) unit to an acrylic acid (AA) unit with the elimination of isobutene gas and the transesterification of a 2-hydroxyethyl acrylate (HEA) unit providing cross-linking were utilized to reduce the adhesive

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Scheme 1.

strength [17–20]. Forming by isobutene elimination decreased an effective adhered area and cross-linking increased the modulus of the adhesive polymers exceeding the appropriate range for PSAs [3,4,6]. These side-chain reactions synergistically reduced the adhesive strength and optimization of the molecular weight, copolymer composition, and monomer sequence led to dismantling with adhesive failure, i.e., interfacial failure between an adhesive polymer and a polyethylene terephthalate (PET) support film [17–20]. However, interfacial failure between stainless steel (SUS) and an adhesive polymer was not achieved because of an increased hydrophilicity of the used adhesive polymers during the transformation of the tBA to the AA unit.

Acetal-protected vinyl polymers, such as poly(tetrahydropyranyl acrylate) (PTHPA), poly(1-isobutoxyethyl methacrylate), and poly(4-(1-(1-isobutoxy)ethoxy)styrene), were reported as acid-labile vinyl polymers and have been applied to deep UV resists [21], phototackification [22], positive working electrostatic imaging [23], and three-dimensional microfluidic channels [24]. We focused on the simple synthesis and workup of acetal-protected acrylate monomers by the reaction of AA with vinyl ethers, an expected good copolymerizability of them with other conventional acrylates, and the easy deprotection of the protected group under simple conditions, for example, hydrolysis without an acidic catalyst and acidolysis using a photoacid generator at room temperature without baking [23]. In this study, the dismantlable PSA behavior of the acetal-protected acrylic copolymers consisting of 1-isobutoxyethyl acrylate (iBEA) or 2-tetrahydropyranyl acrylate (THPA), 2-ethylhexyl acrylate (2EHA), and HEA repeating units was investigated in order to achieve the complete removal of an adhesive layer from both substrates, SUS and PET, during dismantling. To induce the deprotection, two individual stimuli, i.e., soaking in boiling water and UV irradiation in the presence of a photoacid generator (PAG), were applied. The effects of the copolymer composition and sequence structure on the dismantlability including the adhesion strength and failure modes were examined in detail.

2. Experimental

2.1. Materials

2EHA, HEA, and *n*-butyl acrylate (nBA) were purchased from Tokyo Chemical Industry Co., Ltd., and distilled under reduced pressure prior to use. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Wako Pure Chemicals Co., Ltd., and recrystallized from methanol. Other reagents and solvents were used without further purification. *N*-Hydroxynaphthalimide triflate

(NIT, 99%, Sigma–Aldrich Co.), isobutyl vinyl ether (containing KOH, 99.0%, Tokyo Chemical Industry Co., Ltd.), 3,4-dihydro-2*H*-pyran (96.0%, Tokyo Chemical Industry Co., Ltd.), and *p*-toluenesulfonic acid monohydrate (99.0%, Wako Pure Chemicals Co., Ltd.) were used as received. iBEA and THPA were synthesized according to the method described in the literature [24]. Ethyl 2-(*n*-butyltellanyl)-2-methylpropionate (MT-Bu) [25] and di-*n*-butyl ditelluride (DT-Bu) [26] were synthesized according to the methods described in the literature. The homopolymers of iBEA and THPA (PiBEA and PTHPA) were synthesized by free radical polymerization using AIBN as a radical initiator. The M_n and M_w/M_n values and glass transition temperatures (T_g) of the resulting polymers were as follows: 7.79×10^4 , 3.66, and -10 °C for PiBEA and 5.80×10^4 , 2.54, and 27 °C for PTHPA, respectively. All copolymers were synthesized by organotellurium mediated radical polymerization (TERP) using DT-Bu combined with binary azoinitiators or MT-Bu [27]. The former catalyst system was previously reported as a conventional method to synthesize acrylic polymers with a well-controlled structure and high molecular weight [17]. The representative structures and characteristics of the acetal-protected acrylic copolymers are shown in Scheme 1 and Table 1.

2.2. Synthesis of iBEA

Pyridine (0.32 mL, 0.004 mol), *p*-toluenesulfonic acid monohydrate (0.76 g, 0.004 mol), and AA (6.74 g, 0.093 mol) were dissolved in 80 mL of dichloromethane. To the solution, isobutyl vinyl ether (16.22 g, 0.162 mol) was added dropwise under an argon atmosphere with stirring. After the addition, stirring of reaction mixture was maintained at room temperature for 40 h. The reaction mixture was passed through a silica gel column chromatography

Table 1
Sequence structure and characteristics of acetal-protected acrylic copolymers.

Polymer	Sequence structure ^a	$M_n/10^4$	M_w/M_n	T_g ^b (°C)
R1	P(iBEA _{79.5} -co-nBA _{20.5})	9.12	1.42	-19
R2	P(iBEA _{75.6} -co-2EHA _{20.2} -co-HEA _{4.2})	10.5	1.30	-19
R3	P(iBEA _{77.4} -co-2EHA _{14.3} -co-HEA _{8.3})	10.5	1.76	-20
R4	P(iBEA _{74.0} -co-2EHA _{15.2} -co-HEA _{10.8})	11.5	1.72	-20
R5	P(iBEA _{77.1} -co-2EHA _{11.1} -co-HEA _{11.8})	9.95	1.44	-15
R6	P(iBEA _{72.5} -co-2EHA _{13.5} -co-HEA _{14.0})	10.9	1.61	-19
R7	P(iBEA _{50.6} -co-2EHA _{35.7} -co-HEA _{13.7})	11.4	1.55	-32
R8	P(iBEA _{88.2} -co-HEA _{11.8})	10.4	1.44	-14
R9	P(THPA _{44.3} -co-2EHA _{34.6} -co-HEA _{21.1})	7.71	1.71	-11
R10	P(THPA _{58.6} -co-2EHA _{26.1} -co-HEA _{15.3})	6.48	1.44	-4
B1	PiBEA _{59.3} - <i>b</i> -P (iBEA _{13.0} -co-2EHA _{12.5} -co-HEA _{15.2})	8.75	1.45	-23, -12

^a The subscripts denote the molar fraction of each monomer unit.

^b Determined by DSC.

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