Supporting Information

In Situ Formation of Core–Shell Nanoparticles in Epoxy Resin via Reversible Addition–Fragmentation Chain Transfer Dispersion Polymerization

Eun Ho Lee,[‡a] Kyoungho Kim,[‡a] Gyeongdong Yeom,[a] Bongkuk Seo,[b] Wonjoo Lee,[b] Youngchang Yu,[*b] Aruna Kumar Mohanty[*a] and Hyun-jong Paik[*a]

[a]Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Korea.

[b]Center for Advanced Specialty Chemicals, Korea Research Institute of Chemical Technology, Ulsan, 44412, Republic of Korea

Experimental

Materials

2-Cyano-2-propyl dodecyl trithiocarbonate (CPDTC, 97%) was purchased from Aldrich and used as received. 2-Hydroxypropyl methacrylate (HPMA, Alfa Aesar >97%), methyl methacrylate (MMA, DAEJUNG, 99%), glycidyl methacrylate (GMA, Aldrich, 97%), hexyl acrylate (HA, TCI, >96.0%), 2-ethylhexyl methacrylate (EHMA, TCI, >99%) was passed through an alumina column to remove inhibitor. *N,N*-Dimethylformamide (DMF, DAEJUNG, 99.5%), ethyl alcohol, anhydrous (DAEJUNG, 99.9%) used as received. Azobisisobutyronitrile (AIBN, Junsei, 98%) was recrystallized from methanol. Diglycidyl ether of bisphenol A (DGEBA) (YD-128, Kukdo chemical., EEW 184-190 g/eq) was used as received. Deionized water was used throughout this work. Triethylenetetramine (TETA, Aldrich >97%) or dicyandiamide (DICY, Dyhard 100S, Alzchem) was used as an amine hardener. 3,3'-(4-Methyl-1,3-phenylene)bis(1,1-dimethylurea) was used as a curing accelerator (Dyhard UR 500, Alzchem).

Preparation of macro-RAFT RAFT agent

For the preparation of poly(methyl methacrylate-*co*-glycidyl methacryalte) (P(MMA-*co*-GMA)), macro-RAFT agents, 8.10 ml of MMA (0.076 mol), 3.4 ml of GMA (0.025 mol), 0.35 g of CPDTC (1 mmol), 0.017 g of AIBN (0.1 mmol), and 51.92 ml of DMF were added to a 100 ml round bottom flask and the mixture was deoxygenated by bubbling with N_2 for at 30 min. After bubbling, the flask was placed in a preheated oil bath at 70 °C for 12 h. The resulting polymer (monomer conversion = 95%; M_n = 11.5 kg mol^{-1}, $Đ$ = 1.13) was purified by precipitation into excess cold methanol followed by drying in a vacuum oven at 30 °C overnight. A similar protocol was utilized for [HPMA]$_0$/[CPDTC]$_0$ ratio of 50 (M_n = 11.3 kg mol^{-1}, $Đ$ = 1.14) to synthesize poly(2-hydroxypropyl methacrylate) (PHPMA), the macro-RAFT RAFT agents.

Preparation of diblock copolymer particles via RAFT dispersion polymerization in epoxy resin/ethanol/water mixture

All RAFT dispersion polymerizations were conducted at 10% (w/w) solids. In a typical experiment, 7.73 g of DGEBA, 14.67 ml of ethanol, 3.86 g of distilled water, 0.4 g of P(MMA-*co*-GMA), macro-RAFT agents (0.035 mmol), and 3.12 ml of EHMA (0.014 mol) were added to a 30-mL round bottom flask. The reaction vessel was placed in a pre-heated oil bath at 65 °C and stirred for 20 min to make a homogeneous mixture followed by bubbling with N_2 for at least 30 min. AIBN (0.0017 g, 0.010 mmol) was separately dissolved in 10 ml of ethanol to make a stock solution and deoxygenated by N_2 for at least 30 min. Then 1 ml of AIBN stock solution was added to the flask and the reaction mixture was stirred for 24 h at 65 °C under nitrogen. Samples were taken at a regular time to analyze the conversion and molecular weight. The monomer conversion was determined by ^{1}H NMR analysis in CDCl$_3$ and DMSO mixture (ratio of CDCl$_3$ to DMSO was 7/3 (v/v)). The molecular weight was determined by THF SEC. A similar protocol was utilized for [HA]$_0$/[PHPMA]$_0$ ratio of 400, and [HA]$_0$/[P(MMA-*co*-GMA)]$_0$ ratio of 400 to synthesize the diblock copolymers.

Preparation of diblock copolymer particles dispersed epoxy resin

After the RAFT dispersion polymerization for 24 h, water and ethanol were removed by evaporation at 65 °C under reduced pressure. Then, the diblock copolymer particles dispersed in epoxy resin was placed in a vacuum oven at 50 °C overnight to remove the remaining solvents.

Preparation of testing specimens for measuring mechanical properties

For the preparation of the specimen, the curing agent DICY and the curing accelerator UR 500 were used. The amine curing agent was formulated in accordance with the amine hydrogen equivalent weight (AHEW), and the molar ratio of the curing agent, curing accelerator, and epoxy was $[DICY]_0 : [UR\ 500]_0 : [Epoxy]_0 = 1 : 0.02 : 6.5$. The mixture of curing agent, curing accelerator, and epoxy resin was cured for 1 hour at each temperature of 120, 150, and 180 °C. The mechanical properties of the neat and block copolymer particles dispersed cured epoxy resins in the metal mold were tested by processing the plastics to prepare a $165 \times 20 \times 3$ mm test specimen for tensile strength tests by the ASTM D638 standard using UTM and of $60 \times 12 \times 3$ mm for the impact strength test by the ASTM D256 method using Izod impact tester.

Characterization

The number average molecular weights (M_n) and dispersity ($Đ = M_w/M_n$) were determined using SEC; the instrument was calibrated with poly(methyl methacrylate) standards and equipped with an Agilent 1100 pump, a RID detector, and PSS SDV (5 μm, 105, 103, and 102 Å, 8.0×300.0 mm) columns. The macro-RAFT agents, (P(MMA-*co*-GMA) and PHPMA), and block copolymer, (P(MMA-*co*-GMA)-*b*-PHA, P(MMA-*co*-GMA)-*b*-PEHMA and PHPMA-*b*-PHA), were characterized by ^{1}H NMR spectroscopy on a Varian Unity Inova-500 spectrometer using CDCl$_3$ and DMSO-d6 as the solvent. DLS data were acquired on a NanoBrook 90Plus Nanoparticle Size Analyzer (Brookhaven Instruments Corporation). FE-SEM images were acquired with a Carl Zeiss Supra 25 FE-SEM operated at 20 kV. TEM images were acquired on triamine cured epoxy samples using a HITACHI H-7600. The glass-transition temperature (T_g) of the epoxy blends were measured by DSC on a TA Instruments Q 100 DSC instrument under a nitrogen atmosphere. The polymers were sealed in an aluminum sample crucible under nitrogen protection. Then, the DSC curve was recorded following heating program (first heating at 10 °C/min from -20 to 220 °C, followed by cooling from 220 to -20 °C at 10 °C/min and then heating from -20 to 220 °C at 10 °C/min) under nitrogen environment. The second heating cycle was recorded for T_g. Tensile strength tests were conducted using a universal testing machine (UTM 5982, Instron, MA, USA). The impact strength was measured with an Izod impact tester (JJHBT-6501, JJ-test, Chengde, China) by the ASTM D256 method.
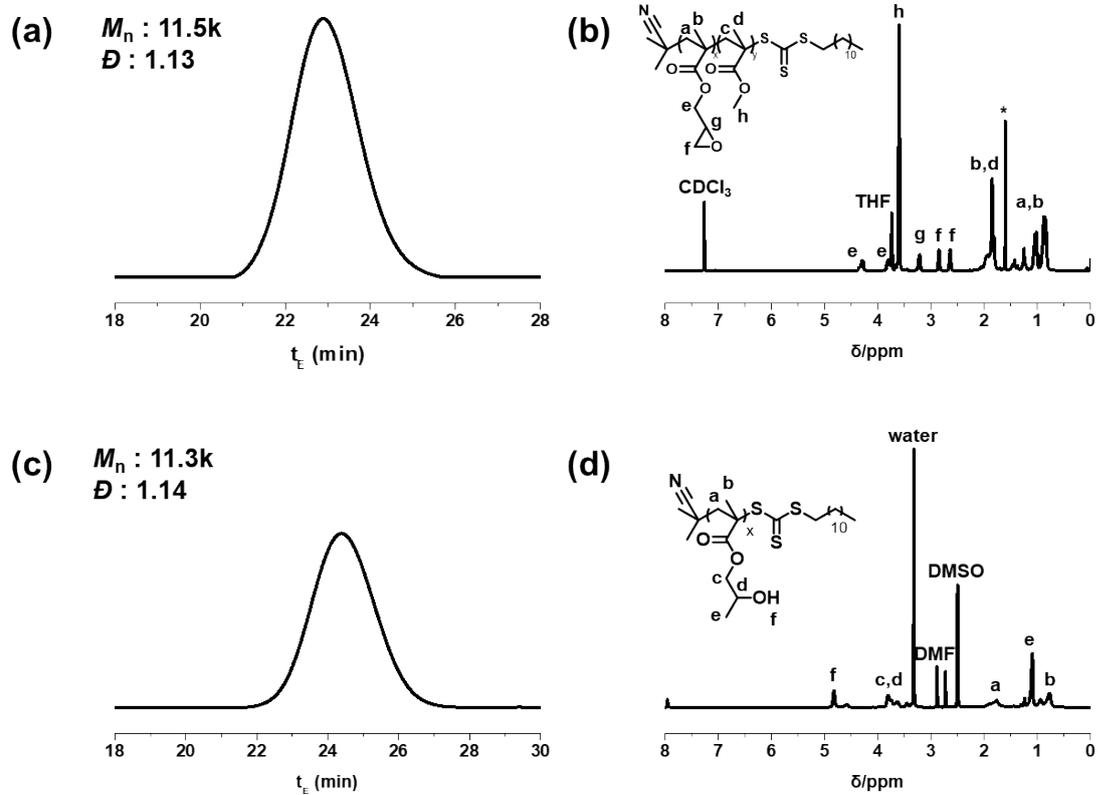
Figure S1. (a) The SEC traces of the P(MMA-*co*-GMA) macro-RAFT agents, (b) The ^{1}H NMR spectrum of P(MMA-*co*-GMA) macro-RAFT agents, (c) The SEC trace of the PHPMA macro-RAFT agents, (d) The ^{1}H NMR spectrum of PHPMA macro-RAFT agents.

The theoretical number fraction of living chains is given by equation.

$$L = \frac{[\text{RAFT}]0}{[\text{RAFT}]0 \ + \ 2f[\text{I}]0(1 - e^{-kdt})(1 - (f\text{c}/2))}$$

$[\text{RAFT}]_0$ and $[\text{I}]_0$ are the initial concentrations of RAFT agent and initiator, respectively and f is the initiation efficiency. The term $1-(f_c/2)$ represents the number of chains obtained radical termination with f_c (coupling factor) which means that termination occurs by 100% disproportionation ($f_c = 0$) as assumed in this work and 100% combination reaction ($f_c = 1$). Dissociation kinetic constant of initiator is kd and t is reaction time (seconds). The parameters are summarized in **Table S1**.

Table S1. The initial concentrations of RAFT agent ($[\text{RAFT}]_0$) and initiator ($[\text{I}]_0$). Initiation efficiency (*f*), decomposition kinetic constants of initiator (k_d), reaction time (t) and coupling factor (f_c)

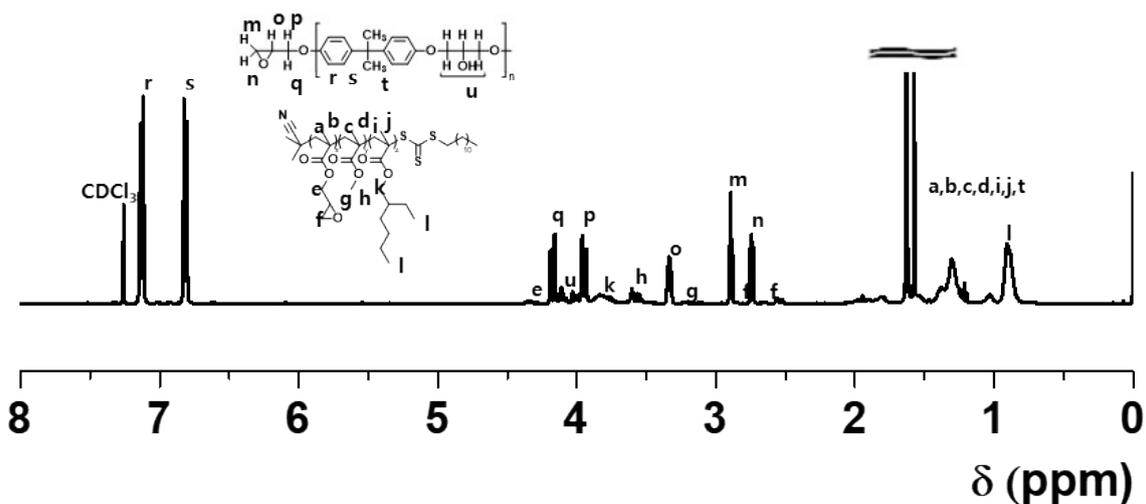|	
$[\text{RAFT}]_0$	0.0146 M
$[\text{I}]_0$	0.0146 M
f	0.5
k_d	3.65 x 10^{-5} s^{-1}
t	43200 s
f_c	0

Figure S2. ^{1}H NMR spectrum of epoxy resin and P(MMA-*co*-GMA)-*b*-PEHMA after removing EtOH and water.
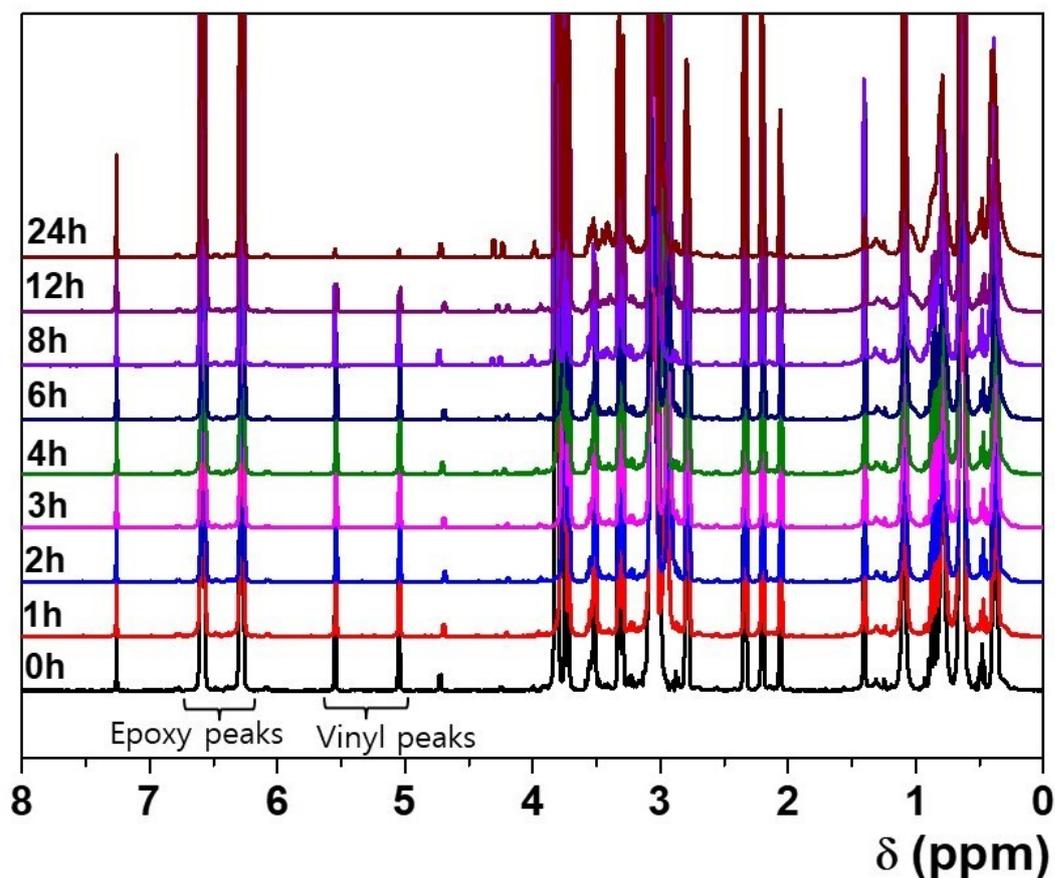

Figure S3. Evolution of ^{1}H NMR spectrum during the synthesis of P(MMA-*co*-GMA)-*b*-PEHMA.

The monomer conversion during the RAFT dispersion polymerization is determined using ^{1}H NMR spectroscopy. During the reaction, the samples were prepared periodically by mixing a certain amount of reaction mixture with the NMR solvent such as CDCl$_3$ (or DMSO-d6). In the ^{1}H NMR spectrum (Figure S3), the monomer conversion was calculated by comparing the vinyl proton peaks (5 ~ 5.5 ppm) of monomers in the reaction mixture with the normalized benzene proton peaks (6.6 ppm) of epoxy resin.
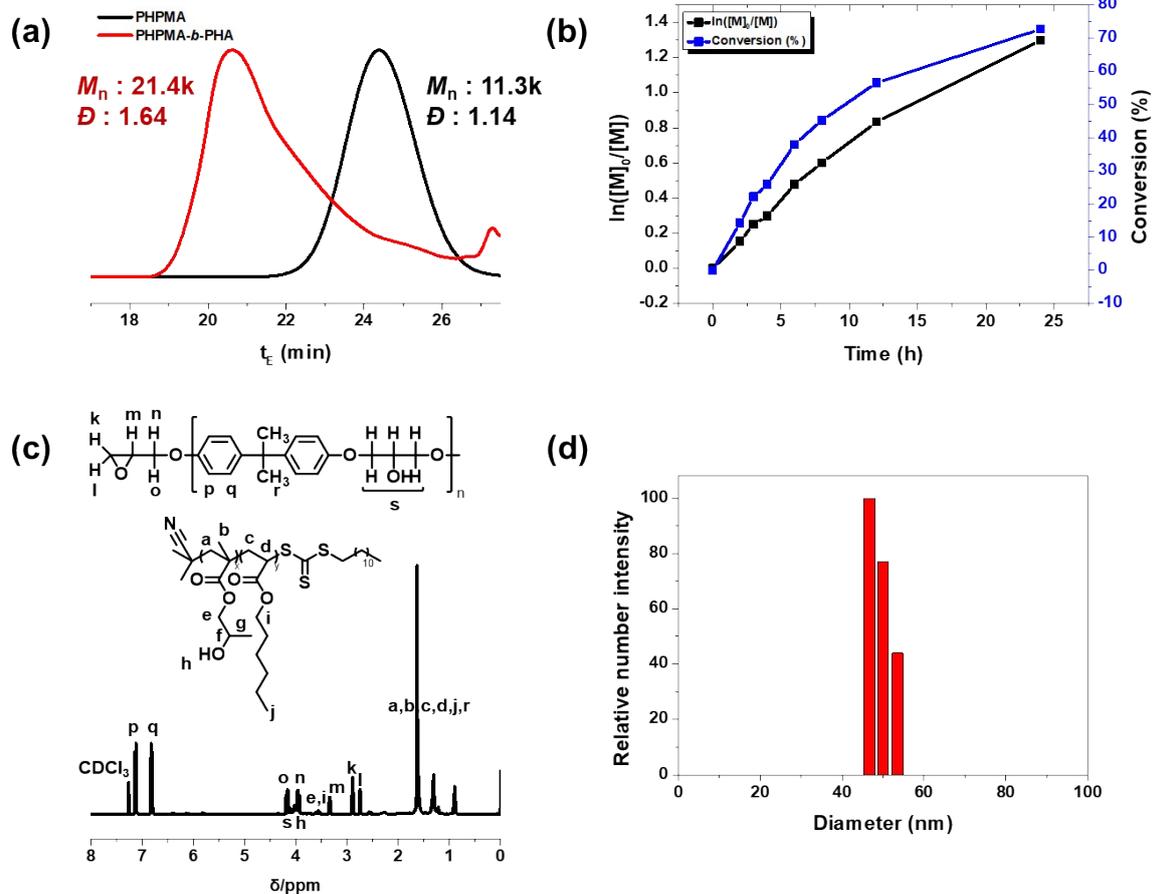
Figure S4 (a) The SEC traces of the PHPMA macro-RAFT agents (black line) and PHPMA-*b*-PHA (red line), (b) The ln([M]/[M]$_0$) and monomer conversion versus time plot for RAFT dispersion polymerization of HA in the presence of PHPMA macro-RAFT agents, (c) The ^{1}H NMR spectrum of epoxy resin and PHPMA-*b*-PHA after removing EtOH and water, (d) DLS number-based size distribution obtained for PHPMA-*b*-PHA diblcok copolymer particle prepared by RAFT dispersion polymerization.
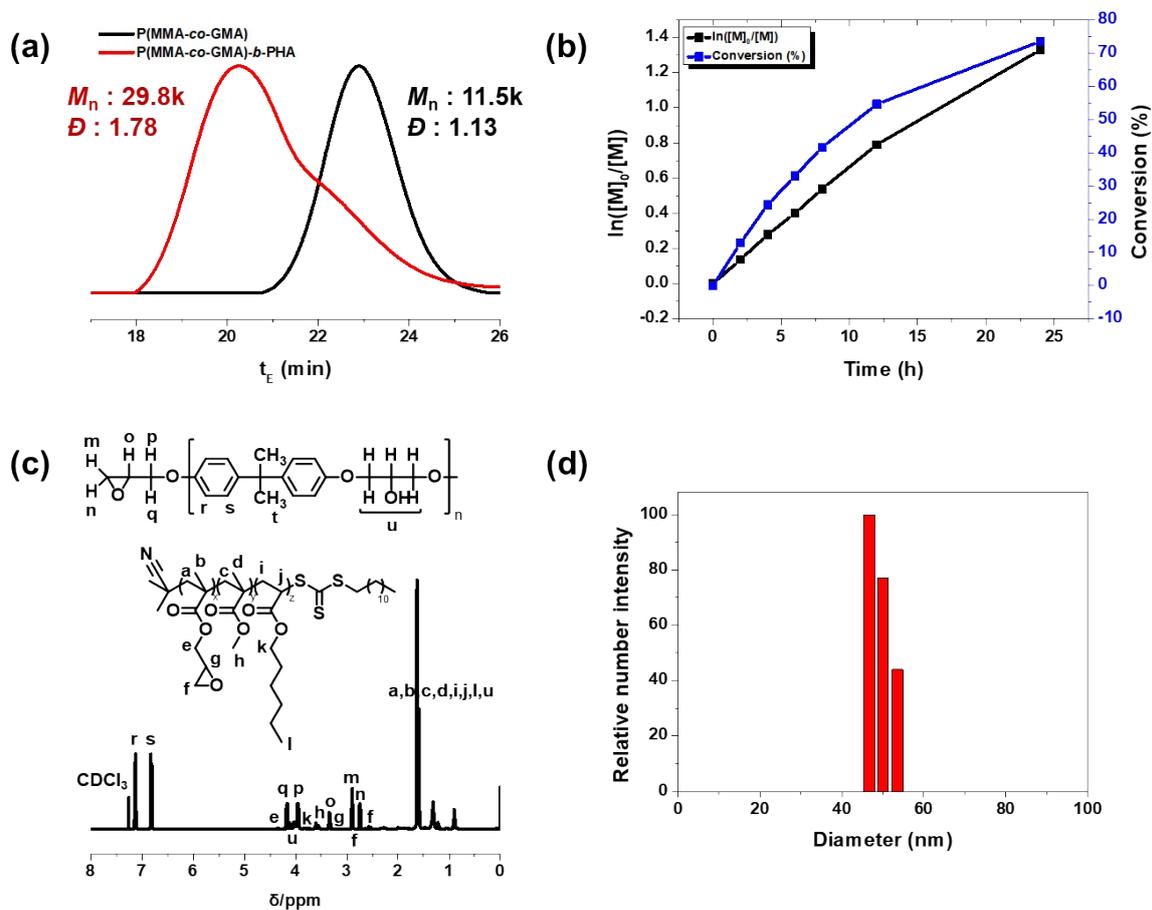
Figure S5. (a) The SEC traces of the P(MMA-*co*-GMA) macro-RAFT agents (black line) and P(MMA-*co*-GMA)-*b*-PHA (red line), (b) The ln([M]/[M]$_0$) and monomer conversion versus time plot for RAFT dispersion polymerization of HA in the presence of P(MMA-*co*-GMA) macro-RAFT agents, (c) The ^{1}H NMR spectrum of epoxy resin and P(MMA-*co*-GMA)-*b*-PHA after removing EtOH and water, (d) DLS number-based size distribution obtained for P(MMA-*co*-GMA)-*b*-PHA diblcok copolymer particle prepared by RAFT dispersion polymerization.
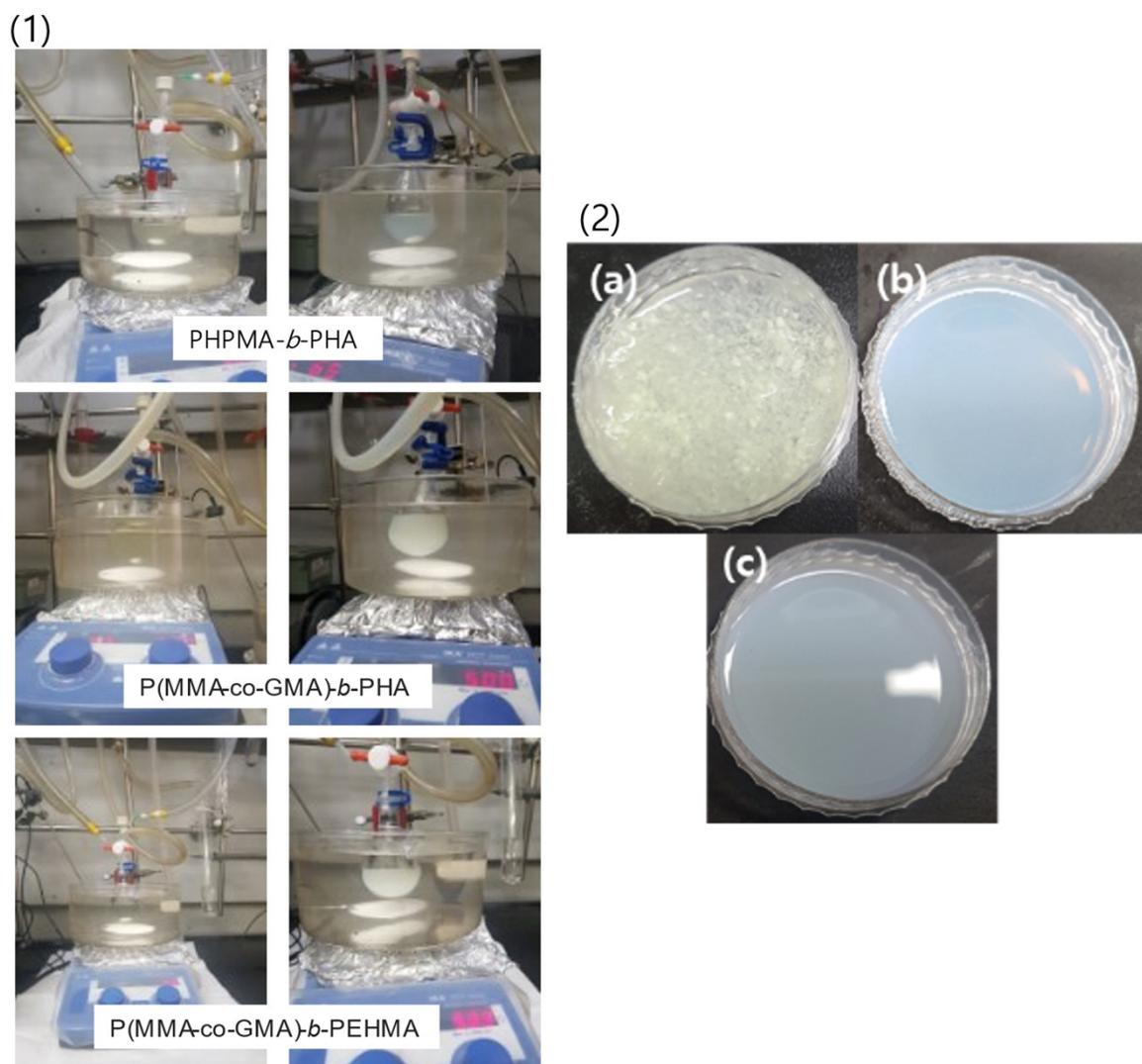
Figure S6. Digital photographs of (1) phase transformation during block copolymer synthesis and (2) block copolymer particles dispersed epoxy resin after removal of ethanol and water: (a) PHPMA-*b*-PHA, (b) P(MMA-*co*-GMA)-*b*-PHA, (c) P(MMA-*co*-GMA)-*b*-PEHMA.