Unentangled Star-Shape Poly(ε-caprolactone)s as Phthalate-Free PVC Plasticizers Designed for Non-Toxicity and Improved Migration Resistance

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Supporting Information

1. INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most prolifically produced thermoplastic material because of its low cost, low combustibility, low flammability, good flame retardation, and resistance properties, low heat release profile, good electrical insulation properties, and good chemical resistance.1,2 In particular, flexible PVC is widely used in contact with the human body, for example, in medical devices, electronic devices, construction materials, infant care products, toys, and food packaging.3−5 Flexible PVC contains large amounts of low molecular weight liquid plasticizers that tailor its physical properties to such applications.6−8 The most common liquid plasticizers are phthalates, which account for more than 80% of the entire plasticizer industry. Di(2-ethylhexyl) phthalate (DEHP) comprises at least 60% of the phthalate plasticizers because it is low in price and performs well.9,10 The phthalate plasticizers, including DEHP, have been known to display a degree of toxicity since the 1940s.11,12 In particular, many studies have found that a significant fraction of the phthalate plasticizers migrates from the PVC matrix into other media in contact with the matrix. The migrated phthalate plasticizers can then act as endocrine disruptors and poison the liver, heart, kidneys, lungs, testicles, and other organs.12,13 In addition to serious health hazards, phthalate migration out of the PVC matrix leads to a loss of flexibility relative to the original flexible PVC product.5 Recent studies report that phthalate plasticizers have already accumulated in the soil, marine ecosystems, indoor air systems, foods, and the human body.12,14,15 The European Union, the United States, Canada, and other countries have passed laws to regulate the use of phthalate plasticizers in medical devices, childcare articles, and toys.9,16 Accordingly, the development of a nontoxic, phthalate-free alternative plasticizer is urgently needed for human health and enormous PVC applications.

Poly(ε-caprolactone) (PCL) is an attractive alternative to phthalate plasticizers because it is nontoxic, biocompatible, and miscible with other polymers, including PVC.17,18 The low glass transition temperature of PCL provides good flexibility to the PVC chains.19,20 We reported previously that hyperbranched poly(ε-caprolactone) (HPCL) plasticizers are highly resistant to migration and offer a high plasticizing efficiency.19 Despite their good properties, the production of HPCL plasticizers has been hampered by the need for complicated synthetic procedures, such as the synthesis of macromonomers through
protection−polymerization−deprotection steps and condensation reactions between macromonomers. Shi et al. reported the development of a “green” plasticizer using a commercially available star-shape poly(ε-caprolactone) (SPCL). Unfortunately, this “green” plasticizer underwent significant migration out of the PVC blend, reaching migration levels near those found in DEHP, because the commercially available SPCL with short branched segments contained many impurities, such as unreacted ε-caprolactone (CL) monomers and cyclic PCL molecules (see Figure S1 in the Supporting Information). These results indicated that the molecular architecture of the commercial SPCL was not as well-controlled as thought because of the backbiting transesterification side reactions from the terminal hydroxyl groups of the SPCL segments. Nevertheless, SPCL bearing short branched segments remains an attractive alternative PVC plasticizer because of its high biocompatibility, low melting point, high free volume, and good miscibility with PVC. Furthermore, the degree of entanglement and the relaxation time for SPCL are smaller than for a linear analogue with the same molecular weight. Thus, it is positively necessary to solve the chronic problems that arise during the synthesis of SPCL, such as backbiting transesterification side reactions, to use an SPCL with short branched segments as an alternative plasticizer.

Here, we developed an unentangled star-shape PCL (UESPCL) with extremely short branched segments capable of providing excellent flexibility to PVC and improving the migration resistance from PVC using a facile pilot-scale pseudo-one-pot process. At room temperature, UESPCLs were transparent viscous liquids and exhibited Newtonian behaviors. UESPCLs were biologically safe without producing an acute toxicity response, and they displayed good processability and high miscibility with PVC. The flexible PVCs prepared using UESPCLs exhibited good flexibility and transparency properties that were comparable to those obtained from DEHP. Most of all, the migration of UESPCLs from the flexible PVCs was negligible, whereas considerable quantities of DEHP migrated out of the flexible PVCs. Thus, we anticipate that UESPCLs can be used as a nontoxic alternative plasticizer for the preparation of phthalate-free flexible PVCs, which are tremendously attractive for applications in medical devices, food packaging, and infant care products.
2. EXPERIMENTAL SECTION

2.1. Materials. ε-Caprolactone (CL) and trimethylolpropane (TMP) were purchased from Alfa Aesar Co., Ltd., U.S.A., and Tokyo Chemical Industry Co., Ltd., Japan, respectively. Dipentaerythritol (DPTOL), ethylene glycol (EG), tin(II) 2-ethylhexanoate (Sn(Oct)2), and acetic anhydride (Ac2O) were purchased from Sigma-Aldrich Ltd., Korea. Di-(2-ethyl-hexyl) phthalate (DEHP) was obtained from Junsei Chemical Co., Ltd., Japan. The suspension-grade poly(vinyl chloride) (PVC) resin (η0 ≈ 300,000 cP at 220 °C) was kindly provided by Hanwha Chemical Co., Ltd., Korea. The secondary plasticizer E-700 (epoxidized soybean oil) was supplied by Songwon Co., Ltd., Korea. The thermal stabilizer ADK STAB RUP-110 was obtained from Adeka Korea Co., Ltd., Korea. All chemicals were used without further purification.

2.2. Synthesis and Characterization of UESPCLs. UESPCLs were prepared using a facile 1 L pilot-scale pseudo-one-pot process via an end-capping reaction and a vacuum purification process without the use of organic solvents or additional processes, such as precipitation, washing, or filtering. Four UESPCLs were prepared, denoted UESPCLm-n, with variations in the number of branched segments (m) and the degree of polymerization of the individual branched segments (n): UESPCL3-3, UESPCL3-5, UESPCL6-3, and UESPCL6-5. The chemical architectures of UESPCLs are illustrated schematically in Scheme 1. The number of branched segments was controlled according to the hydroxyl functionalities of the core materials, 3 (TMP) or 6 (DPTOL). The degree of polymerization of the individual branched segments, referred to as the length of branched segments, was controlled by the molar ratio of CL to the hydroxyl groups on the core material ([CL]/[core−OH]). Briefly, the calculated quantity of the initiator TMP or DPTOL was dissolved in CL (570.70 g, 5.0 mol). The homogeneous mixture was heated to a reaction temperature of 110 °C, and a catalytic amount of Sn(Oct)2 was added. The specific amounts of the chemicals used are listed in Supporting Information Table S1. The polymerization reaction proceeded for 3 h and was terminated by capping the terminal hydroxyl groups of the as-polymerized UESPCLs using an excess quantity of end-capping agent Ac2O. UESPCLs were purified to remove unreacted CL monomers and excess Ac2O using a vacuum purification process with heating at 110 °C for 24 h, where the ultimate pressure of the vacuum system was 6.7 Pa. Finally, we obtained a transparent viscous liquid (or soft waxy) UESPCLs. All reactions were carried out under a nitrogen atmosphere, with the exception of the vacuum purification process. The synthesis of UESPCLs was adjusted to yield a 95−97% monomer conversion efficiency because the PCL segment cyclization was rapid at monomer conversions of nearly 100%. The monomer conversion efficiency was determined based on the 1H nuclear magnetic resonance (NMR) spectra (prior to the purification process) and was calculated from the relative intensities of the methylene proton peaks for the unreacted CL monomer and for PCL in the branched segments of UESPCLs. As a control sample, we also synthesized EG-cored linear PCL (LPCL, \( M_n \approx 2430 \text{ g/mol} \)) with acetate end groups, and the structural properties of this sample were compared with those of UESPCLs.

The end-capping and vacuum purification process, introduced here, played a key role in the isolation of UESPCLs with extremely short branched segments. In fact, the precipitation and filtering methods typically used in PCL production were not adequate for producing purified UESPCLs because UESPCLs had extremely short branched segments and their solubilities were very similar to those of the CL monomers. It should be noted that the undesired cyclization of the branched segment occurred in the uncapped UESPCL by attributing to the backbiting transesterification side reactions from the terminal hydroxyl groups during the vacuum purification and collection processes (Figure 1). The terminal hydroxyl groups of the as-polymerized UESPCLs were, therefore, capped with an acetate group. We next applied a vacuum treatment to...
remove the unreacted CL monomers and excess Ac₂O from the as-polymerized UESPCLs and to collect the purified UESPCLs. The end-capped UESPCLs did not display the undesired cyclization of the PCL segments after the vacuum purification process (Figure 1). As a result, we successfully obtained the purified UESPCLs with extremely short branched segments through an end-capping and vacuum purification process. The chemical architectures of UESPCLs were analyzed by 1H NMR spectroscopy using a Bruker Avance spectrometer 600, with chloroform- d (CDCl₃-d) as the solvent. The number and average length of branched segments (Nnumber and Nlength) in UESPCLs were determined from the integral ratio of 1H NMR peaks between the core moiety peak and the end-capping moiety peaks and between the end-capping moiety peak and the methylene proton peak of the CL repeating unit in the branched segment, respectively. The number-average molecular weights of UESPCLs were calculated using Nnumber and Nlength denoted MnumberNMR (see Table 1 footnote). The molecular weights of UESPCLs were also measured using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), denoted MnMALDI using an Applied Biosystems Voyager-DE STR spectrometer with a nitrogen laser (337 nm, 3 ns pulse width) operated in the linear mode. The matrix solution was prepared using dihydrobenzoic acid (DHB) dissolved in a tetrahydrofuran (THF) matrix, and the samples were mixed with the matrix solution in volumetric ratios of 1:1. The glass transition temperature, Tg, and melting temperature, Tm, of UESPCLs were measured by differential scanning calorimetry (DSC) using a Netzsch DSC 200 F3 with a heating rate of 20 °C/min over the temperature range of −100 to 100 °C under a nitrogen atmosphere. The complex viscosities of UESPCLs were measured by dynamic mechanical spectroscopy using a stress-controlled rheometer TA Instruments AR2000. The AR2000 was operated in a cone-and-plate geometry with a 1° angle and a 60 mm diameter cone, and the gap between the cone and the plate was 80 μm in all measurements. Dynamic frequency sweeps were performed over the angular frequency range 0.5–100 rad s⁻¹ and the temperature range 30–90 °C, measured in 10 °C intervals. The strain values were determined, using a dynamic strain sweep, to lie within the linear viscoelastic region. The thermal resistance of UESPCLs was observed using thermogravimetric analysis (TGA) measurements collected on a TA Instruments Q500 with a heating rate of 10 °C/min over the temperature range 25–600 °C under a nitrogen flow.

2.3. Acute Toxicity Test of UESPCLs. The biological safety profiles of UESPCLs were evaluated by performing acute toxicity tests, based on the OECD 423 guidelines, at the Korea Institute of Toxicology (KIT), Korea. Briefly, the experimental rats (Crl: CD (SD)) were divided into four groups, each of which contained five males and five females. A single dose of 500, 1000, and 2000 mg UESPCLs/kg body weight was given to three experimental groups, and the remaining group served as a control group. The three experimental and one control groups were observed 1, 2, and 4 h after dosing, and once daily thereafter, for a total of 15 days. All rats were sacrificed at the end of the observation period and subjected to a necropsy analysis.

2.4. Processing Properties of UESPCLs. The absorption and fusion properties were measured by mixing PVC with UESPCLs using conventional manufacturing methods for fabricating flexible PVC sheet products. The formulations of the flexible PVCs were 100 parts per hundred (phr) PVC resin (65 wt %), 50 phr UESPCL plasticizer (32 wt %), 2 phr E-700 as a secondary plasticizer (1 wt %), and 3 phr ADK STAB RUP-110 as a thermal stabilizer (2 wt %). The absorption properties of UESPCLs into the PVC resin were observed by measuring the dry time based on the American Standard Testing Methods (ASTM) D2396–94 using a C.W. Brabender planetary mixer heated at 80 °C and operated at 30 rpm. The fusion properties of PVC/UESPCLs were investigated by measuring the fusion time according to the ASTM D2538-02 procedure using a C.W. Brabender mixer heated at 90 °C and operated at 30 rpm. Prior to the fusion time measurements, the PVC/UESPCL compounds were produced using a Henschel mixer, heated to 120 °C and operated at 2,000 rpm, in order to completely absorb UESPCLs into the PVC resin. Given the measured absorption and fusion properties, flexible PVC sheets were prepared with dimensions of 250 × 250 × 2 mm³ using a hot press operated at 180 °C for 10 min. Next PVC, PVC/DEHP, and PVC/LPCL sheets were prepared according to the same procedure, and their properties were compared to those of PVC/UESPCLs. The miscibility properties of PVC and UESPCLs were measured using solid-state 1H NMR spectroscopy methods performed on a Bruker minispec mq 20 spectrometer operated at 40 °C, with a proton resonance frequency of 19.95 MHz.

2.5. Characterization of the Flexible PVCs. The plasticizing efficiency of UESPCLs was evaluated based on the lowering of the Tg of PVC/UESPCLs relative to the corresponding values of PVC/DEHP and PVC/LPCL. The Tg values were measured by DSC using a heating rate of 10 °C/min over the temperature range −100 to 100 °C under a nitrogen atmosphere. The flexibility properties of PVC/UESPCLs were investigated by measuring their Shore A and D hardness values according to the ASTM D2240 procedures. The mechanical properties of PVC/UESPCLs were determined by measuring the tensile strength, elongation at break, and tear strength according to the ASTM D638 and ASTM D624 procedures. The measurements were conducted using an Instron 4204 universal testing machine at a crosshead speed of 500 mm/min. The optical properties of PVC/UESPCLs were investigated by measuring the transmittance and haze values using a BYK Gardner Haze-Gard Plus hazemeter.
2.6. Migration Resistance Test of the Flexible PVCs.

The migration resistance values of UESPCLs were evaluated by immersing flexible PVC sheet samples in n-hexane at 50 °C for 2 h, according to the Food and Drug Administration (FDA) procedure 21 CFR 177.1520, performed in the Société Générale de Surveillance (SGS) Korea Co., Ltd. The degree of plasticizer migration was measured under harsher conditions: the quantities of UESPCLs that migrated out of the PVC/UESPCL samples and into the liquid, solid, and gas phases were measured and compared to the corresponding values measured for PVC/DEHP. Flexible PVC sheet samples were prepared with dimensions of 20 × 20 × 2 mm³. The extractability properties of UESPCLs were tested according to the ASTM D2199-82 procedure, in which the samples were immersed in 1 L n-hexane (liquid phase) and stirred at 50 °C for 7 days. The exudability of UESPCLs was tested according to the ASTM D5227-95 procedure, in which the samples were placed between two unplasticized poly(methyl-methacrylate) (PMMA) sheets (solid phase) and then pressed under 10 tons with heating at 50 °C for 7 days. The volatility of UESPCLs was tested according to the ASTM D2199-82 procedure, in which the samples were positioned at the center of activated carbons (granular, 4–14 mesh) in a glass Petri dish. The assembly was then placed in an oven, and air was circulated (gas phase) at 80 °C for 7 days.

3. RESULTS AND DISCUSSION

3.1. Synthesis of UESPCLs.

UESPCLs formed a transparent viscous liquid (or a soft waxy) with a high-yield mass production exceeding 93% (Supporting Information Figure S2). As shown in Scheme 1, UESPCLs were designed to have three (TMP) or six (DPTOL) branched segments, N_number and to have three or five individual branched segment lengths, N_length. The successful syntheses and purification of UESPCLs and their molecular architectures were confirmed using 1H NMR spectroscopy and MALDI-TOF-MS. The 1H NMR spectra of UESPCLs displayed peaks corresponding to the branched segment moieties (4.06, 2.31, 1.64, and 1.38 ppm), the core moiety (0.89 ppm for TMP or 3.39 ppm for DPTOL), and the end-capping acetate moiety (2.04 ppm). The CL and the end-capping acetate moiety (2.04 ppm). The CL monomer peaks (4.22, 2.63, 1.86, and 1.76 ppm) were superposed and were independent of the angular frequency, indicative of a Newtonian fluid. This result suggested that UESPCLs did not display chain entanglement, even at room temperature, because of the presence of short branched segments. The lack of chain entanglement can lead to fast molecular motions and provide PVC chains with a high flexibility.

The temperatures that corresponded to the onset weight loss, T_do, in each of UESPCLs were measured using TGA and are listed in Table 1. UESPCL3-3 and UESPCL6-3 (with small values of N_length) showed lower T_do values than UESPCL3-5 and UESPCL6-5 (longer N_length). This result indicated that the thermal stabilities of UESPCLs also depended on their end group concentration. The decomposition of conventional PCLs was influenced by a syn Ei mechanism and an unzipping mechanism. The unzipping reactions proceeded from the end groups after water had been generated through the syn Ei reactions. Thus, UESPCLs with smaller N_length values had higher end group concentrations and resulted in lower T_do values relative to UESPCLs prepared with larger N_length values. Meanwhile, the T_do values of UESPCLs were 313–323 °C, whereas that of DEHP was 242 °C. This result indicated that the weight loss of UESPCLs was negligible during heating up to 300 °C, whereas the weight loss of DEHP began at 242 °C (Supporting Information Figure S4). This result suggested that UESPCLs should display better thermal resistance properties than DEHP in the context of conventional flexible PVC manufacturing processes, which are generally conducted at 200 °C.

3.2. Biological Safety of UESPCLs.

The acute toxicities of UESPCLs were tested using a predictive model for biological concentration (see Table 1).²⁷,²⁸ Thus, UESPCL3-3 and UESPCL6-3, which featured relatively high end group concentrations, formed transparent viscous liquids, even at room temperature, with significantly low T_do values.

The rheological properties of UESPCLs were observed by measuring the complex viscosities, \( \eta'' \), at various temperatures as a function of the angular frequency. Figure 2 shows the master curves of the complex viscosities for UESPCLs as a function of the reduced angular frequency, at 60 °C.
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The results provided by KIT revealed that none of the treated (experimental) rats died during the 15 day observational period after a single dose of UESPCLs. No significant weight changes were observed in any of the treated rats. Additionally, no pathological changes were observed on the skin, fur, or eyes, and the rats’ behaviors remained unchanged except for the experimental group that received a single dose of 2000 mg kg$^{-1}$ UESPCL3-5. In this group of five males and five females, two males and two females displayed a prone position and moderately irregular respiration at 4 h after dosing, but they returned to baseline thereafter. These behavioral changes may have resulted from the relatively high value of $T_{\text{m}}$ for UESPCL3-5, which was assumed a soft waxy phase at room temperature. After conducting observations over 15 days, all animals, including those in the control group, were sacrifice and dissected to collect blood from the heart and remove internal organs for gross and histopathologic observations. The three experimental groups displayed no histopathological changes in the liver, kidney, heart, spleen, ovaries, testes, or intestines relative to the control group. The acute oral toxicity tests revealed that UESPCLs yielded toxic doses of over 2000 mg kg$^{-1}$, whereas UESPCL3-5 yielded a toxic dose of 1000 mg kg$^{-1}$. These doses suggested that UESPCLs are biologically safe and nontoxic.

3.3. Processing Properties of PVC/UESPCLs. The absorption and fusion properties of materials are important for preparing powdered mixtures of polymer resins and liquid additives, such as plasticizers. We prepared a series of phthalate-free flexible PVC samples using UESPCLs as alternative plasticizers. The absorption and fusion properties of these samples were investigated by determining the dry time and fusion time, respectively. The absorption and fusion properties of the flexible PVC prepared using DEHP were also measured for comparison to the properties of the phthalate-free flexible PVCS prepared using UESPCLs. The dry times of PVC/UESPCLs were measured by analyzing the torque curves during mixing of the powdered PVC resin (100 phr, 65 wt %), UESPCLs (50 phr, 32 wt %), and other additives in a planetary mixer heated at 80 °C and operated at 30 rpm, according to the ASTM D2396-94 procedure. As shown in Figure 3a, the torque curves of the mixtures increased immediately after the addition of UESPCLs and additives, indicating that UESPCLs wetted and solvated the surfaces of the PVC powders. The torque curves then gradually decreased as the mixtures flowed more freely due to the permeation of UESPCLs into the PVC powders. After UESPCLs had been completely absorbed into the PVC powders, the torque curves of the mixtures stopped falling and slowly began to rise again. The minimum value of the torque curves is called the dry point. We determined the dry times of PVC/UESPCLs by measuring the time between the addition of UESPCLs and achievement of the dry point in the sample. As listed in Table 2, the dry times of PVC/UESPCLs were ordered as follows: PVC/UESPCL3-3 < PVC/UESPCL3-5 < PVC/UESPCL6-3 < PVC/UESPCL6-5. Typically, the viscosity of a plasticizer will affect the dry time of the flexible PVC. Thus, we measured the viscosities of UESPCLs using a Brookfield DV-II+ viscometer heated at the mixing temperature (80 °C). The resulting viscosities were ordered as follows: UESPCL3-3 (65 (cP)) < UESPCL3-5 (112 (cP)) < UESPCL6-3 (127 (cP)) < UESPCL6-5 (210 (cP)), which corresponded to the ordering of the PVC/UESPCLs dry times. These results clearly indicated that the low viscosities of UESPCLs facilitated absorption into the PVC powders and resulted in a shorter dry time for PVC/UESPCLs. We noted that the viscosities of UESPCLs followed the total molecular weights of UESPCLs (Table 1) rather than their molecular architecture parameters, $N_{\text{number}}$ and $N_{\text{length}}$. Thus, the dry times of PVC/UESPCLs appeared to depend on the total molecular weights of UESPCLs, regardless of their architectures. Meanwhile, the dry times and torque loads of PVC/UESPCLs were higher than the corresponding values obtained from PVC/DEHP because the viscosities of PVC/UESPCLs were much higher than the viscosity of DEHP (7 (cP) at 80 °C).

The fusion time measurements were conducted by preparing the PVC/UESPCL compounds in which UESPCLs were completely preadsorbed. We then analyzed the torque curves of the PVC/UESPCL compounds at 90 °C, 30 rpm according to the ASTM D2538-02 procedure (Figure 3b). The fusion times of PVC/UESPCLs were determined by measuring the time between the addition of the PVC/UESPCL compounds and achievement of the maximum value of the torque curve (the fusion point). The fusion properties of the PVC/DEHP compound were also observed. As listed in Table 2, the fusion times of PVC/UESPCLs were ordered as follows: PVC/UESPCL3-3 < PVC/UESPCL3-5 < PVC/UESPCL6-3 < PVC/UESPCL6-5. Paul et al. reported that the fusion time of PVC tended to shorten as the plasticizer viscosity decreased. PVC/UESPCLs followed this general relationship between the fusion time and the viscosity; UESPCLs with a low viscosity yielded a short PVC/UESPCLs fusion time. All of PVC/UESPCLs, however, displayed fast fusion times compared to PVC/DEHP, although DEHP displayed a much lower viscosity than UESPCLs. Presumably, these results were attributed to an increase in the miscibility of UESPCLs with PVC because of the relatively large number of carbonyl groups in UESPCLs.
As shown in Supporting Information Figure S5, the interaction radius between PVC and UESPCLs on length scales of less than 10 nm, respectively, and these values increased with increasing τ. PVC/UESPCLs exhibited single lattice relaxation times of the protons in the PVC/UESPCL blends. PVC/UESPCLs displayed excellent miscibility with PVC. Thus, all UESPCLs apparently provided molecular-level miscibility with an average domain size of less than 8 nm in the PVC/UESPCLs blends, indicating that UESPCLs displayed excellent miscibility with PVC.

The actual miscibility between PVC and UESPCLs was measured experimentally to investigate the influence of UESPCL architectures on the miscibility of PVC/UESPCLs. We characterized the spin–lattice relaxation times of neat PVC, UESPCLs, and PVC/UESPCLs to evaluate the miscibility between PVC and UESPCLs on length scales of less than 10 nm. As shown in Supporting Information Figure S5, the values of \( \ln(\Delta T_1) \), where \( \Delta T_1 \) is the spin-diffusion coefficient, were measured to determine the upper limit on the average domain size for the UESPCLs and PVC blends increased with increasing \( N_{\text{length}} \) and \( N_{\text{number}} \) for UESPCLs. Thus, all UESPCLs apparently provided

### Table 3. Glass Transition Temperatures and Percentage Plasticizing Efficiencies

<table>
<thead>
<tr>
<th></th>
<th>PVC</th>
<th>PVC/UESPCL3-3</th>
<th>PVC/UESPCL3-5</th>
<th>PVC/UESPCL6-3</th>
<th>PVC/UESPCL6-5</th>
<th>PVC/DEHP</th>
<th>PVC/LPCL</th>
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<tbody>
<tr>
<td>( T_g ) (°C)</td>
<td>84.8</td>
<td>82.5</td>
<td>82.0</td>
<td>81.9</td>
<td>81.7</td>
<td>81.5</td>
<td>81.3</td>
</tr>
<tr>
<td>( E_{\Delta T_1} ) (%)</td>
<td>0</td>
<td>92.9</td>
<td>92.1</td>
<td>87.4</td>
<td>87.3</td>
<td>100.0</td>
<td>82.1</td>
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The solubility parameters of UESPCLs were used to evaluate the theoretical miscibility between PVC and UESPCLs based on the chemical architectures of UESPCLs. The solubility parameter was calculated with consideration for the contributions of the dispersion forces, permanent dipoles, and hydrogen bonds, called the Hansen solubility parameter (see Supporting Information Table S2). Then, the interaction radius between PVC and UESPCLs was 8.13–8.26 ((J/cm³)¹/²), and that between PVC and DEHP was 7.20 ((J/cm³)¹/²), indicating that UESPCLs and DEHP were miscible with PVC.

The actual miscibility between PVC and UESPCLs was determined by measuring the spin–lattice relaxation times of neat PVC, UESPCLs, and PVC/UESPCLs to evaluate the miscibility between PVC and UESPCLs on length scales of less than 10 nm. As shown in Supporting Information Figure S5, the values of \( \ln(\Delta T_1) \), where \( \Delta T_1 \) is the spin-diffusion coefficient, were measured to determine the upper limit on the average domain size for the UESPCLs and PVC blends increased with increasing \( N_{\text{length}} \) and \( N_{\text{number}} \) for UESPCLs. Thus, all UESPCLs apparently provided molecular-level miscibility with an average domain size of less than 8 nm in the PVC/UESPCLs blends, indicating that UESPCLs displayed excellent miscibility with PVC.

### Table 2. Dry Times and Fusion Times

<table>
<thead>
<tr>
<th></th>
<th>PVC/UESPCL3-3</th>
<th>PVC/UESPCL3-5</th>
<th>PVC/UESPCL6-3</th>
<th>PVC/UESPCL6-5</th>
<th>PVC/DEHP</th>
<th>PVC/LPCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry time (s)</td>
<td>308</td>
<td>348</td>
<td>520</td>
<td>566</td>
<td>222</td>
<td></td>
</tr>
<tr>
<td>fusion time (s)</td>
<td>66</td>
<td>72</td>
<td>76</td>
<td>80</td>
<td>110</td>
<td></td>
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</table>

The glass transition behaviors of neat PVC, PVC/UESPCLs, PVC/DEHP, and PVC/LPCL as shown in Supporting Information Figure S6, single glass transitions were observed for each PVC/UESPCL DSC thermogram. These transitions occurred between the transitions of the corresponding neat components, and the glass transitions of the neat components themselves were absent from the blend curves, indicating that PVC and UESPCLs were miscible. The single \( T_g \) values for PVC/UESPCLs were determined by the inflection points of the glass transition curves and are listed in Table 3. As shown in Table 3, the \( T_g \) values of PVC/UESPCLs fell below 2 °C, indicating that the samples were sufficiently flexible at room temperature. The plasticizing efficiencies of UESPCLs were calculated using the equation,

\[
E_{\Delta T_g} = \frac{\Delta T_g}{\Delta T_g^{\text{DEHP}}} \times 100
\]

where \( E_{\Delta T_g} \) is the plasticizing efficiency of the plasticizer and \( \Delta T_g \) represents the reduction in \( T_g \) from neat PVC to flexible PVC. All UESPCLs exhibited \( E_{\Delta T_g} \) values that exceeded 87.3% of the value of DEHP. In particular, UESPCL3-3 yielded a value of 92.9% (Table 3). These results showed that UESPCLs were as good as DEHP in providing excellent flexibility to the PVC. The ordering of the UESPCL \( E_{\Delta T_g} \) values corresponded to the inverse ordering of the \( T_g \) values, as shown in Tables 1 and 3. It should be noted that the \( T_g \) values of UESPCLs were proportional to their respective total molecular weights, irrespective of the molecular architecture. Thus, the \( E_{\Delta T_g} \) values, that is, the degree of flexibility in UESPCLs, were found to be inversely proportional to the total molecular weight rather than to the molecular architecture parameters. On the other hand, LCPL exhibited relatively high \( T_g \) and low \( E_{\Delta T_g} \) values compared to PVC/UESPCL6-3, which had a similar total molecular weight (Table 3), indicating that the branched architecture of UESPCL6-3 improved the plasticizing efficiency.

The Shore hardness offers a direct measurement of the flexibility of a material. The Shore hardness values of the samples prepared here were measured using two types of indenters: type A and type D Durometers. As shown in Figure 4a, PVC/UESPCL3-3 and PVC/UESPCL3-5 yielded Shore A and D hardness values that were similar to those of PVC/DEHP, although PVC/UESPCL6-3 and PVC/UESPCL6-5 yielded slightly higher Shore A and D hardness values.
compared to the values of PVC/DEHP. These results revealed that PVC/UESPCLs had excellent flexibilities that were similar to the flexibility properties of PVC/DEHP. Taken together and considering the flexibility properties, UESPCL3-3, which showed the highest $E_{\Delta T}$ value and the lowest Shore hardness value, was thought to be the most suitable plasticizer for preparing phthalate-free flexible PVC products.

The mechanical properties of PVC/UESPCLs were investigated based on the stress–strain behaviors and the tear strength. As shown in Supporting Information Figure S7, all PVC/UESPCLs exhibited typical ductile stress–strain behaviors with shapes that resembled the curve obtained from PVC/DEHP. All of PVC/UESPCLs, however, displayed a higher tensile strength and a larger elongation at break value compared to PVC/DEHP. PVC/UESPCL6-5 displayed an elongation at break value that was 23% greater than the value obtained from PVC/DEHP. The elongation at break values of PVC/UESPCLs increased as the total molecular weight increased, whereas PVC/UESPCLs displayed comparable tensile strength values across the series (see Table 4). These results indicated that UESPCLs conveyed a larger degree of stretchability to the PVC than did DEHP. The tear strength values of PVC/UESPCLs increased in the order PVC/UESPCL3-3 < PVC/UESPCL3-5 < PVC/UESPCL6-3 < PVC/UESPCL6-5 (Figure 4b), indicating that the toughness values of UESPCLs increased with increasing $N_{\text{length}}$ and $N_{\text{number}}$. Furthermore, PVC/UESPCL6-5 exhibited a 30% greater toughness compared to PVC/DEHP. Thus, an increase in the stretchability of PVC/UESPCLs was attributed to an improved toughness due to the introduction of UESPCLs with a total molecular weight exceeding that of DEHP. These properties allow UESPCLs to provide excellent stretchability and fracture toughness to the PVCs, to much greater effect than DEHP. PVC/LPCL displayed a ductile stress–strain curve, higher tensile strength, and larger elongation at break compared to PVC/DEHP (Supporting Information Figure S7); however, the stretchability and fracture toughness of LPCL was lower than the values obtained from UESPCL6-3 for similar total molecular weights. As a result, we found that star-shaped polymers have a better overall plasticizing performance than linear polymers because of their branching architecture.

Figure 4c shows images of flexible PVC sheets prepared using either UESPCLs or DEHP. As shown in Figure 4c, the PVC/UESPCL and PVC/DEHP samples were transparent and did not differ in appearance, suggesting that all samples displayed similar optical properties. The optical properties were evaluated quantitatively by measuring the transmittance and haze values of the PVC/UESPCLs and PVC/DEHP samples. As shown in Figure 4d, the transmittance values of PVC/UESPCLs were similar to the values obtained from PVC/DEHP. The haze values of PVC/UESPCLs were also similar to the value obtained from PVC/DEHP, although PVC/UESPCL3-5 had a slightly higher haze value and PVC/UESPCL6-3 had a slightly lower haze value. The similarities between the optical properties of PVC/UESPCLs and PVC/DEHP proposed that UESPCLs can be useful in transparent flexible PVC products.

3.5. Migration Resistance of UESPCLs. The migration resistance of UESPCLs was tested according to FDA procedures for simulating plasticizer migration from food packaging products into oily foods. n-Hexane was used as an extraction medium because the solubility profile of n-hexane is similar to that of cooking oil. The weight loss attributed to the loss of the plasticizer from a PVC product heated in n-hexane at
50 °C for 2 h must not exceed 5.5% if it is to be used in contact with foods, for example, in plastic food wrap, food bags, or food storage containers. As shown in Figure 5a, the weight losses of PVC/UESPCLs were negligible during the test period, whereas PVC/DEHP showed a weight loss of nearly 10%. These results indicated that UESPCLs can be useful for manufacturing flexible PVC products for use in the food packaging industry, whereas DEHP is prohibited from use in products that come in contact with food. The degree of plasticizer migration was calculated by measuring the specimen weight loss during the test period:

\[
\text{degree of plasticizer migration (\%) = } \frac{W_f - W_i}{W_i \times x} \times 100
\]

where \(W_f\) and \(W_i\) represent the specimen weights before and after the tests, respectively, and \(x\) is the weight fraction of plasticizer in the specimens. Here, we assumed that the weight losses of the specimens were due only to UESPCLs or DEHP (32 wt%), although the secondary plasticizer (1 wt%) and the thermal stabilizer (2 wt%) also migrated during the tests. As shown in Figure 5b, a trace quantity of UESPCLs migrated out of the PVC/UESPCL specimens under all conditions examined, whereas a considerable quantity of DEHP migrated out of the PVC/DEHP specimens. Particularly, more than 80% of DEHP present in the specimen migrated into the liquid phase, 25 times the degree of migration of UESPCLs. These results indicated that the migration of UESPCLs from the flexible PVCs was markedly reduced. It should be noted that the migration of UESPCLs decreased as the total molecular weight increased. This trend was observed under other migration conditions as well (exudability and volatility) and clearly revealed that the drastically high migration resistance of UESPCLs was attributed to an increase in the total molecular weight of UESPCLs. The migration of UESPCLs was also thought to be restricted by the numerous carbonyl groups present in the branched segments, which formed attractive interactions with the PVC chains. These effects quite reduced the degree of UESPCl migration, even under harsh conditions. Consequently, our nontoxic UESPCLs can be useful for fabricating phthalate-free flexible PVC products designed for close contact with the human body, such as medical devices, infant care products, or food packaging products. Such products would avoid potential health risks and environmental concerns based on the migration properties of the phthalates currently in use.

4. CONCLUSIONS

We developed unentangled star-shape poly(ε-caprolactone)s (UESPCls) as nontoxic alternative plasticizers for use in phthalate-free flexible PVC products. UESPCLs were synthesized and purified to have a precisely controlled architecture through a facile pilot-scale pseudo-one-pot process combined with the end-capping and the vacuum treatment techniques. UESPCLs were transparent viscous liquids with unentangled Newtonian behaviors due to their extremely short branched segments. The compounds were found to be biologically safe without inducing acute toxicity. PVC/UESPCLs exhibited good processability with a fast fusion rate and a high miscibility with an average domain size of less than 8 nm. Moreover, UESPCLs provided excellent flexibility, transparency, stretchability, and fracture toughness to its PVC mixture, and the mixture properties were comparable to those conveyed by DEHP.

Table 4. Tensile Strengths and Elongations at Break

<table>
<thead>
<tr>
<th></th>
<th>PVC/UESPCL3-3</th>
<th>PVC/UESPCL3-5</th>
<th>PVC/UESPCL6-3</th>
<th>PVC/UESPCL6-5</th>
<th>PVC/DEHP</th>
<th>PVC/LPCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>tensile strength (kg/mm²)</td>
<td>1.96</td>
<td>1.96</td>
<td>2.04</td>
<td>2.00</td>
<td>1.83</td>
<td>1.95</td>
</tr>
<tr>
<td>elongation at break (%)</td>
<td>322</td>
<td>336</td>
<td>338</td>
<td>343</td>
<td>278</td>
<td>326</td>
</tr>
</tbody>
</table>
UESPCLs were nearly resistant to migration from the flexible PVCs into a liquid phase, whereas considerable quantities of DEHP migrated out of the flexible PVC under identical circumstances. UESPCLs are, therefore, tremendously attractive as nontoxic alternative plasticizers for use in phthalate-free flexible PVC products ranging from medical devices to food packaging products.

**ASSOCIATED CONTENT**

Supporting Information

Synthesis formulations of UESPCLs; Hansen solubility parameter terms and interaction radii for UESPCLs and DEHP; 1H NMR spectra of Cl, TMP, and commercially available SPCL (polycaprolactone triol, PCL-T); MALDI-TOF mass spectrum of PCL-T; images of UESPCL3-3 and UESPCL6-3 at room temperature (25 °C); 1H NMR spectra of UESPCLs prepared using two core materials (TMP or DPTOL); TGA thermograms of UESPCLs and DEHP; logarithmic plots of the relaxation intensity vs. the delay time for PVC/UESPCLs and their neat components; DSC DPTOL); TGA thermograms of UESPCLs and DEHP; tensile time for PVC/UESPCLs and their neat components; DSC

**REFERENCES**


