

Hyperbranched Poly(ϵ -caprolactone) as a Nonmigrating Alternative Plasticizer for Phthalates in Flexible PVC

JEONGSOO CHOI[†] AND
SEUNG-YEOP KWAK*

*Hyperstructured Organic Materials Research Center (HOMRC),
and School of Materials Science and Engineering, Seoul
National University, San 56-1, Shillim-dong, Gwanak-gu,
Seoul 151-744, Korea*

Hyperbranched (dendritic) poly(ϵ -caprolactone)s (HPCLs) were synthesized to have architectural variations, which are the different lengths of linear segments and different numbers of branches, and were used as plasticizers for flexible poly(vinyl chloride) (PVC). The plasticization efficiency estimated by the lowering of glass transition temperature and the enhancement in ultimate elongation indicated that the HPCLs with the shorter linear segments and the larger number of branches imparted as high flexibility as di-(ethylhexyl) phthalate (DEHP) and much higher flexibility than their linear analogue, linear poly(ϵ -caprolactone), which is one of currently used polymer plasticizers. Volatility, extractability, and exudation tests for PVC/HPCL samples showed that there was no plasticizer migration even at very harsh condition, while ca. 7–78% of additives in PVC/DEHP was migrated out of samples, indicating that the HPCL can be used as an alternative plasticizer to remove the potential health risk from migrating phthalates during end use.

Introduction

Flexible poly(vinyl chloride) (PVC) is a plasticized, rubbery polymeric material that is widely used, particularly in military, construction, biomedical, baby-care, and food packaging applications. Flexible PVC contains large amounts of liquid plasticizer(s) to tailor its physical properties to such applications (1). However, these liquid plasticizers usually migrate from flexible PVC products into the external environment sometimes directly into animal and human bodies (2). Recently, some liquid plasticizers have become suspected of or even classified as endocrine disruptors. Substantial evidence of the toxicity of liquid plasticizers has been gathered, in particular for members of the phthalate series such as di-(ethylhexyl) phthalate (DEHP or DOP), which is by far the most commonly used plasticizer in flexible PVC applications (3). Recent studies showed that these phthalates had been found in the soil, indoor air, and seawater, indicating that the phthalates endanger the environment and ecosystem (4–6). Moreover, end-use environments resulting in contact of PVC products with biological fluids are reported to

accelerate the migration of these low molecular weight additives, which raises enormous concerns about the use of low molecular weight liquid plasticizers in such PVC applications as medical devices, baby-feeding accessories or toys (3, 7–9). In reaction to the public concerns about plasticized PVC products, more and more countries have introduced regulations on the use of phthalate esters in some flexible PVC applications. For example, the European Commission issued (in 1999) and renewed (in 2003) an emergency ban on the use of six phthalate esters (DEHP, diisononyl phthalate, diisodecyl phthalate, dibutyl phthalate, benzyl butyl phthalate, and di-*n*-octyl phthalate) in toys and childcare articles that are intended to be placed in the mouths of children under the age of three (9). Other countries such as the United States and Canada have introduced similar types of regulations on the use of these phthalates in toys that are likely to be intended for oral use by children.

To solve these problems, researchers have tested several approaches, but they seem incomplete. For example, other low molecular weight (MW) plasticizers with toxicities that are still controversial can impart flexibility as good as that provided by DEHP, but still undergo plasticizer migration (1). Posttreatment approaches involving surface treatment and crosslinking have been shown to successfully inhibit plasticizer migration but result in deterioration of the physicochemical properties of the resulting PVC products (10, 11). To achieve complete inhibition of plasticizer migration and minimize property deterioration, blending PVC with suitable polymeric plasticizers seems to be one of the better approaches. Unfortunately, the many different polymeric plasticizers studied so far, including nitrile rubbers, polyesters, and copolymers, all impart insufficient flexibility to PVC (1, 12).

Unlike conventional linear polymers, hyperbranched polymers (HBPs) are known to possess unique physical and chemical properties originating from their three-dimensional globular architectures and/or many of functional endgroups. Therefore, a lot of attention is being given to their potential applications in various fields from drug delivery to coatings (13). Because of their good solubility in various solvents and excellent processability, HBPs are being applied as conjugated functional materials with superior optical, electronic, and magnetic properties (14). In addition, HBPs are receiving increasing attention in applications of both biomaterials and nanomaterials because HBPs with multifunctional terminal groups in a narrow polydispersity can be obtained at a relatively low cost by improving synthetic techniques (15, 16). Applications in coating resins or polymer additives such as tougheners, adhesive agents, and processing aids are evidence of the potential of HBP application in the conventional polymer industry (17–20). There have been few studies that employed polymeric plasticizers with branched architectures. In their pioneering work, Huber et al. reported the use of branched polymeric plasticizers prepared by esterifying a reaction mixture incorporating a dibasic acid, a monocarboxylic acid, a trihydric alcohol, and a glycol (21). More recently, Lindström and Hakkarainen have advanced this idea with the aim of evaluating how a low degree of branching effects the plasticizing efficiency and the properties of PVC/polyester blends (22). They blended PVC with poly-(butylenes adipates)s with a low degree of branching, synthesized by using 0.5–3.0 mol% of a branching agent, trimethylol propane, during polycondensation of 1,4-butanediol and adipic acid or its dimethyl ester, and concluded that the branching increased the plasticizing efficiency of the polyester plasticizer (22).

* Corresponding author phone: +82-2-880-8365; fax: +82-2-885-1748; e-mail: sykwak@snu.ac.kr.

[†] Current address: Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, 77 Massachusetts Ave. Rm NE47–421, Cambridge, MA 02139.

TABLE 1. General Characteristics of the Hyperbranched Poly(ϵ -caprolactone)s and Their Linear Counterpart

sample	$\langle N_{\epsilon\text{-CL}} \rangle^a$	$\langle N_{AB_2} \rangle^a$	$M_n(\text{g/mol})^b$	PDI ^b	$T_{d10}^{50}(\text{°C})^c$
HPCL-5	5.7	8.1	11,800	1.8	354
HPCL-10	10.3	5.1	12,600	1.6	348
HPCL-20	20.1	3.3	15,700	1.5	342
LPCL	N/A	N/A	10,000 ^d	1.4 ^c	331

^a Calculated with end-group analysis from ¹H NMR spectra (ref 34).

^b Measured with size exclusion chromatography using multi-angle laser light scattering (SEC-MALLS). ^c Temperature of 10% weight loss by thermal degradation. ^d As specified by the supplier, Aldrich Chemicals.

As far as we know, the concept of altering the degree of polymeric plasticizer–PVC interaction by using new plasticizer architectures, such as three-dimensional hyperbranched structures where quite long linear polyester chains are incorporated in the branching backbone units, was first reported by us in the preceding patent and preprint (23, 24). To further explore this idea, we have thoroughly investigated the structure–properties relations of our hyperbranched polymeric plasticizers and their blends with PVC that helped our understanding of how the unique molecular architecture effects the plasticization (25–29). To complete this concept, here we report the approach of using a new type of plasticizer consisting of hyperbranched poly(ϵ -caprolactone) (HPCL) for producing flexible PVC free from plasticizer migration. The distinguishing features of our approach are the optimization of the blend compatibility and the degree of plasticization accomplished by tailoring the HPCL molecular architecture with control of the length of the linear segments and of the degree of branching. The other novel aspect of this substitute plasticizer is that it provides a plasticization efficiency that is comparable to that of DEHP and at the same time perfect migration stability.

Experimental Section

Materials. The HPCLs were synthesized by carrying out the self-condensation polymerization of AB₂ macromonomers prepared via the controlled ring-opening polymerization of ϵ -CL and hydrogenation. We synthesized three different HPCLs denoted HPCL-5, HPCL-10, and HPCL-20, with architectures that differ in the average number of ϵ -caprolactone (ϵ -CL) units incorporated in their branching backbones, $\langle N_{\epsilon\text{-CL}} \rangle$, and in the average number of incorporated AB₂ macromonomer units, $\langle N_{AB_2} \rangle$. General characteristics of the synthesized HPCLs are listed in Table 1. More detailed information for the syntheses and general characterizations on HPCLs are well described in our previous publication (25).

Flexible PVC Formulation. In this study, three different types of flexible PVC samples were made by using (1) synthesized HPCLs (2), DEHP, the most widely used phthalate plasticizer, and (3) linear poly(ϵ -CL) (LPCL), the linear counterpart to HPCLs with the same chemical structure and similar molecular weight. Since these plasticizers are in different phases, i.e., HPCLs and LPCL being solid phase while DEHP being liquid phase, two different methods were used for the preparation of flexible PVC samples.

First of all, The PVC/DEHP sample was prepared by conventional plastisol method (30), where the plastisol was made by mixing the purified dry PVC powder with liquid DEHP plasticizer, epoxidized soybean oil (ESBO), and thermal stabilizer. Liquid plasticizer was added dropwise to PVC powder with manual stirring with a stainless steel spatula. The manual stirring continued until all plasticizer was added and the mixture became a viscous fluid. A mechanical stirrer with a double blade propeller was used for further mixing of

TABLE 2. Flexible PVC Formulations

function	PVC/HPCL (phr) ^a	PVC/DEHP (phr)	PVC/LPCL (phr)
matrix	PVC (100)	PVC (100)	PVC (100)
plasticizer	HPCL (65)	DEHP (60)	LPCL (65)
		ESBO ^b (5)	
thermal stabilizer	DOTM ^c (2)	DOTM (2)	DOTM (2)

^a Parts per hundred resin of PVC (weight ratios PVC:plasticizer: stabilizer = 100:65:2). ^b Epoxidized soybean oil used as a secondary plasticizer. ^c Di-*n*-octyltin mercaptide.

plastisol. After the air bubbles in the plastisol were removed by slow evacuation, plastisol was aged for more than two weeks. Then, it was placed in an oven and heated at 120 °C for 15 min.

In contrast, PVC/HPCL and PVC/LPCL samples were prepared by using common solution blending with tetrahydrofuran (THF) as a solvent (31). The commercial grade of PVC and HPCL or LPCL were separately dissolved in THF and then precipitated with cold methanol. This procedure was repeated three times for each polymer to remove all traces of additives and impurities and then the thermal stabilizer was added to the final mixture in THF. After all the ingredients of the blend were completely mixed and dissolved in THF, the remaining solvent was slowly removed being subject to heating in an oven at 60 °C. All the films were then dried in a vacuum oven at 60 °C for more than 1 week in order to completely remove all the residual solvent. The formulations of flexible PVC used in this study are summarized in Table 2.

Characterization. The chemical structures of synthesized materials were analyzed by ¹H NMR spectra (Bruker Avance DPX-300) which were also analyzed to determine the average number of ϵ -CL units in the linear oligo(ϵ -CL) segments, $\langle N_{\epsilon\text{-CL}} \rangle$, the average number of the AB₂ macromonomer units incorporated in final hyperbranched polymer, $\langle N_{AB_2} \rangle$, and consequently the number average molecular weights of HPCLs (25). The glass transition temperatures, T_g 's were measured by differential scanning calorimeter (TA instruments DSC 2920) at a heating rate of 10 °C/min. Solid-state ¹H NMR experiments were carried out at ambient probe temperature (22–25 °C) on a Bruker minispec mq 20 spectrometer at the resonance frequency of 19.95 MHz for proton. The spin–lattice relaxation times in the laboratory frame, T_1 's, were obtained by monitoring the decay of the resonance intensity of the proton magnetization after the inversion–recovery pulse sequence (180°- τ -90°). Elongations at break, ϵ_b 's, were measured from tensile tests performed by a LLOYD LR10K universal testing machine at a crosshead speed of 20 mm/min with a 100 N load cell. The dumbbell shaped mini tensile bars were made by cutting them from the 1 mm thick sheet prepared using a Wabash compression molding machine at 180 °C for 2 min.

Migration Stability. Migration stability was characterized by the amount of plasticizer migrated out of samples to the gaseous phase (volatility), liquid phase (extractability), and contacting solid substrates (exudation) under the harsh condition for 7 days to clearly determine the degree of plasticizer migration. The specimens were prepared in hot pressed sheets with dimension 50 × 50 × 0.4 mm³. All migration tests were carried out based on the appropriate American standard testing methods (ASTM). In volatility tests, the sheets were placed in the center of 200 cm³ of activated carbon, and the amount of plasticizer evaporated out under vacuum condition (10⁻²–10⁻³ Torr) at elevated temperature (70 °C) (ASTM D1203–94). In extraction tests, the sheets were immersed in 200 mL of *n*-hexane and stirred at 100 rpm at 50 °C (ASTM D1239–98; D5227–95; D2222–94). In exudation

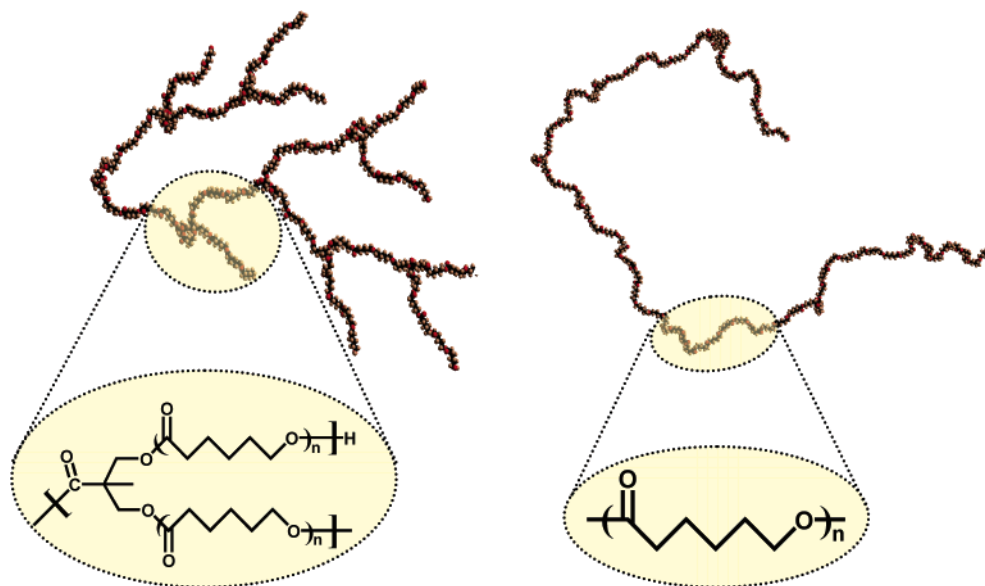


FIGURE 1. The molecular architectures of a typical HPCL and LPCL.

tests, the sheets were placed between two sheets of unplasticized polyethylene terephthalate (PET) ($70 \times 70 \times 1 \text{ mm}^3$) and pressed by 10 psi at room temperature (ASTM D2199–82).

Results and Discussion

From the values of $\langle N_{\epsilon\text{-CL}} \rangle$ and $\langle N_{\text{AB2}} \rangle$ listed in Table 1, it can be seen that the length of the linear segments increases in the order HPCL-5 < HPCL-10 < HPCL-20, and that the number of branches decreases in the order HPCL-5 > HPCL-10 > HPCL-20. A typical HPCL molecular architecture is shown in Figure 1 along with that of its linear counterpart, linear poly(ϵ -CL) (LPCL), which has a long chain without branches. Note that LPCL is considered to be one of the best substitutes for DEHP in the production of PVC in that it is safe for medical applications (32), although its plasticizing effects are not as effective as those of low MW phthalates due to its polymeric nature. As listed in Table 1, thermal degradation temperatures of HPCLs and LPCL are raging from 331 to 354 °C. These values are higher than the initial thermal degradation temperatures (200–300 °C) of plasticized PVC products prepared with the thermal stabilizer as reported elsewhere (33), implying that the thermal stability of flexible PVC samples prepared in this study was not deteriorated by using HPCLs as plasticizers.

The miscibility of the blend samples is ascertained through the measurement of glass transition temperatures, T_g 's, by differential scanning calorimetry (DSC), which is one of the most widely used techniques for evaluating blend miscibility on a scale of 10–30 nm, in terms of cooperative motion of polymer segments (34). Figure 2 shows the thermograms of neat PVC and the flexible PVC formulations prepared using the HPCLs, DEHP, and LPCL as plasticizers, which were recorded during the second heating step. As shown in Figure 2, single T_g 's are observed for all the flexible PVC formulations without T_g 's of the neat components, indicating complete miscibility.

Solid-state ^1H NMR spectroscopy was used to study the scale of miscibility. Figure 3 shows the decays of the resonance intensity of the proton magnetization, $M(\tau)$ for (a) neat polymers, PVC and HPCL-5, and (b) PVC/HPCL-5 blend, respectively. It is noteworthy that the $M(\tau)$ decays in concert

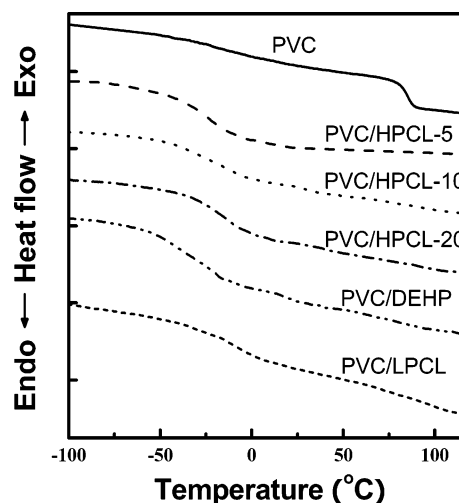


FIGURE 2. DSC thermograms of neat PVC and the flexible PVC samples plasticized with various plasticizers.

with the time constant(s) of the spin–lattice relaxation time in the laboratory frame, T_1 , as follows:

$$M(\tau) = \sum_i M_{0,i} [1 - 2 \exp(-\tau/T_{1,i})] \quad (1)$$

where M_0 is the magnetization intensity of the signal at $\tau > 5T_1$ (or initial magnetization intensity) and the subscript i represents the number of motional phase domains present in the sample. By rearranging and taking natural logarithm on both sides of the above equation, the T_1 relaxation times are determined from the curve fitting of the respective slopes of the plots as shown in Figure 3. It can be seen that the experimental data were in a good agreement with those calculated from eq 1.

Similar to the DSC results, single T_1 's are observed for the blend samples, although only for the PVC/HPCL-5 blend sample is shown here in Figure 3, implying that the blends are dynamically homogeneous over the distance as far as the spin diffusion proceeded within a time scale of proton T_1 .

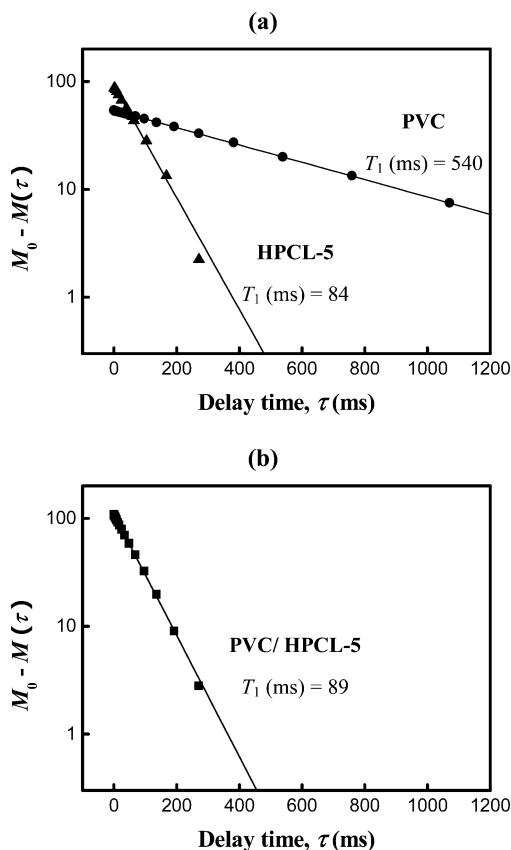


FIGURE 3. Logarithmic plots of the resonance intensity vs delay time for (a) the neat PVC and HPCL-5 and (b) their blend PVC/HPCL-5. The solid lines are fits to eq 1.

The scale of mixing can be inferred through the estimation of an average diffusive path length for effective spin diffusion (35):

$$\langle L \rangle = (6DT)^{1/2} \quad (2)$$

where $\langle L \rangle$ is the average diffusive path length, D is the spin diffusion coefficient typically known to be a value of about $100 \text{ nm}^2/\text{s}$ for a solid, and T is the characteristic time over which the spin energy diffuses. By taking the value of T_1 , the scale of homogeneous mixing of PVC/HPCL-5 blend was estimated to be ca. 6.92 nm , which indicates miscibility at a nanoscopic molecular level.

The plasticization efficiency of a plasticizer refers to its ability to bring about desired properties, in particular better processability during processing and greater flexibility in end use. Many attempts have been made to compare the plasticization efficiency of one plasticizer with that of another in terms of a single property; such results are highly dependent on the test method and the property of interest.¹ In this study, we adopted two test methods to compare the plasticization efficiencies of the plasticizers we used. One method is related to the lowering of T_g , ΔT_g , and the other to the improvement in the ultimate elongation, $\Delta \epsilon_U$.

Free volume theory is the most widely accepted theory of plasticizer action. It proposes that the addition of a plasticizer has the effect of increasing the free volume of the plasticized polymer and thus lowering T_g (1, 12). We extended this theory to provide estimates of the plasticization efficiencies of the HPCLs and LPCL relative to that of DEHP

TABLE 3. Glass Transition Temperatures, Ultimate Elongations, and Plasticization Efficiencies

data	PVC	PVC/HPCL			PVC/DEHP	PVC/LPCL
		HPCL-5	HPCL-10	HPCL-20		
T_g ($^{\circ}\text{C}$) ^a	83	-30	-24	-17	-34	-10
$E_{\Delta T_g}$ (%) ^b	0	97	91	85	100	79
ϵ_U (%) ^c	158	648	608	563	678	455
$E_{\Delta \epsilon_U}$ (%) ^d	0	94	87	78	100	57

^a Glass transition temperature. ^b Percent plasticization efficiency estimated from the lowering of glass transition temperatures. ^c Ultimate elongation. ^d Percent plasticization efficiency estimated from the improving of ultimate elongation.

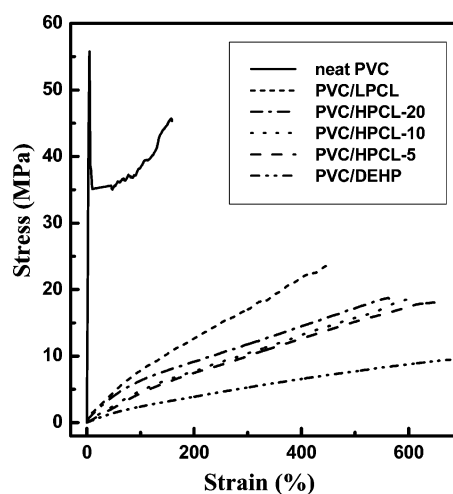


FIGURE 4. Typical strain-stress curves for neat PVC and the flexible PVC samples plasticized with various plasticizers.

by comparing the ΔT_g due to these plasticizers with that of DEHP as follows:

$$E_{\Delta T_g} (\%) = \frac{\Delta T_{g, \text{plasticizer}}}{\Delta T_{g, \text{DEHP}}} \times 100 \quad (3)$$

The calculated values of $E_{\Delta T_g}$ are summarized in Table 3 together with the T_g 's of the flexible PVC samples. As can be seen in Table 3, the $E_{\Delta T_g}$ values of the PVC/HPCLs are higher than that of PVC/LPCL. Among flexible PVC formulations plasticized by HPCLs, the $E_{\Delta T_g}$ values are in the order of PVC/HPCL-5 > PVC/HPCL-10 > PVC/HPCL-20. Moreover, the plasticization efficiency of HPCL-5 is found to be quite comparable to that of DEHP with the $E_{\Delta T_g}$ value of PVC/HPCL-5 reaching up to 97%.

The tensile properties of neat PVC and the flexible PVC formulations prepared using the HPCLs, DEHP, and LPCL were measured with a universal testing machine (UTM) and typical stress-strain curves obtained from the tests are shown in Figure 4. As shown in Figure 4, the tensile strengths of the PVC/HPCL samples (18.1–18.6 MPa) and their tensile moduli (4.4–7.1 MPa) are similar to or a little higher than those of the PVC/DEHP sample (9.5 MPa and 2.8 MPa respectively), indicating that these tensile properties did not deteriorate as a result of the use of the HPCLs as substitutes for DEHP.

Considering that the primary role of a plasticizer is to impart flexibility to unmodified PVC, the plasticization efficiencies, $E_{\Delta \epsilon_U}$, were also estimated by comparing the $\Delta \epsilon_U$ due to the HPCLs with that of DEHP:

$$E_{\Delta \epsilon_U} (\%) = \frac{\Delta \epsilon_{U, \text{plasticizer}}}{\Delta \epsilon_{U, \text{DEHP}}} \times 100 \quad (4)$$

The ϵ_U values of the flexible PVC samples and the calculated $E_{\Delta\epsilon_U}$ values are also listed in Table 3, and exhibit the same trend as the $E_{\Delta T_g}$ data with only very small deviation. As can be seen in Table 3, both the $E_{\Delta T_g}$ and the $E_{\Delta\epsilon_U}$ values of the PVC/HPCLs are distinctly higher than those of PVC/LPCL, implying that the branching molecular architecture of HPCLs might affect the overall plasticization performance. Among the PVC/HPCL samples, the plasticization efficiencies were found to increase with the use of shorter linear segments and a larger number of branches, i.e., PVC/HPCL-5 > PVC/HPCL-10 > PVC/HPCL-20. This is as expected since the molecular mobilities of the HPCLs have been found to increase with the presence of shorter linear segments and a larger number of branches, in other words with the higher relative degree of branch, as demonstrated with photon correlation spectroscopy and dynamic viscoelastic relaxation measurements, where the effects of architectural differences on the cooperative chain mobility and the dynamic viscoelastic relaxation behavior of HPCLs and LPCL were thoroughly investigated, respectively (27, 28). Moreover, the plasticization efficiency of HPCL-5 was found to be the highest and very close to that of DEHP, indicating that HPCL-5 can be used as a substitute for DEHP in flexible PVC applications. To further investigate the applicability of the HPCL in this study as more environment-friendly substitute for DEHP, characterization of the migration behavior of the PVC/HPCL-5 sample was performed and compared to that from the PVC/DEHP sample.

Migration behavior was characterized by measuring the weight loss of the specimens under three different test conditions designed to simulate the environments where flexible PVC products are used. The test methods were designed to simulate each representative environment for plasticizer migration into different contacting media. For example, the volatility test simulates the migration of plasticizer from the flexible PVC product to the atmosphere; for example, to represent plasticizer migration from flexible PVC flooring to air in a closed room at elevated temperature. The extraction test simulates the variety of environments where migration may occur to a contacting liquid media, of which examples range from food wraps to food packages to bottles to medical blood bags. In contrast, the exudation test simulates the migration which occurs with contacting the other solid substrates and often under the pressure. An example of this could be plasticizer migration from a soft PVC leather car seat to passenger cloths or that from the baby nipple to the mouth when it is bitten.

It is also noted that the test methods were modified to accelerate the migration so that the weight loss during the tests would be large enough to contrast the migration in flexible PVC plasticized by conventional DEHP with that in the PVC plasticized by HPCLs of this study. In the volatility test, the evaporation of volatile additives was accelerated by putting the specimen sheets into excess amounts of activated carbon and by drying in a vacuum chamber at elevated temperatures. In the extraction tests, the excess amount of *n*-hexane with a relatively vigorous mechanical stirring accelerated the migration of extractable parts in the blend specimens. (36, 37) Among many other solvents, *n*-hexane was selected for the extraction tests of this study since it has been widely used in extraction tests for phthalates in plasticized PVC samples and for the evaluation of migration stability for the substitute plasticizer or the posttreated PVC samples. In the exudation tests, high-pressure posed onto the sample sheets facilitated the migration of exudable parts to the contacting solid substrates. The weight losses of volatile, extractable, and exudable components were determined by

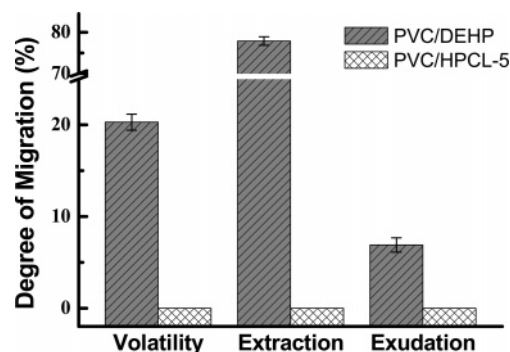


FIGURE 5. Degrees of migration for the PVC/HPCL-5 and PVC/DEHP samples determined from volatility, extractability, and exudation tests. Average weight losses of additive for the PVC/HPCL-5 and PVC/DEHP samples determined from volatility, extractability, and exudation tests. Vertical error bars represent the 95% confidence intervals.

measuring the weights of the samples before and after 7 days under the abovementioned conditions as follows:

$$\text{weight loss of additives (\%)} = \frac{W_1 - W_2}{W_1} \times 100 = \frac{W_{\text{before}} - W_{\text{after}}}{W_{\text{before}} \times \frac{67}{167}} \times 100 \quad (5)$$

where W_1 and W_2 are the weights of the additives in the specimens before and after the tests, and W_{before} and W_{after} are the weights of the sample specimens before and after the tests, respectively. Since the composition between PVC matrix and the other additives used (plasticizer plus thermal stabilizer) remained constant at 100:67, W_1 can be determined by the weight of the sample before the test (W_{before}) multiplied by the composition of additives in the specimen (67/167). In addition, since the PVC matrix can be reasonably considered as stable under the test conditions due to its well-known mechanical, chemical, and thermal resistances, the weight losses during the tests are anticipated to be come from the weight losses of the additives (eq 5).

The results are shown in Figure 5, in which 20.32 ± 0.87 , 77.88 ± 1.04 , and $6.88 \pm 0.78\%$ of the additives in the PVC/DEHP sample were found to have migrated out during the volatility, extraction, and exudation tests, respectively. These results were the averages of the values for at least five specimens of the same composition, and the confidence intervals were determined with the confidence level of 95%. In contrast, there were no weight losses of the additives in the PVC/HPCL-5, in which the average values of weight losses were determined to be less than 0.01 and the confidence intervals were negligible with being less than 0.0027 with the confidence level of 95%. The superior migration stability of the PVC/HPCL-5 is anticipated to the much higher molecular weights of HPCL-5 being over 11,800 g/mol compared to that of DEHP being 391 g/mol. The same applies to the other PVC/HPCLs samples as well as PVC/LPCL sample where the high molecular weight plasticizers used and they showed no weight losses under the same migration test conditions though not shown here.

Recognizing that DEHP makes up the bulk of the additives in the PVC/DEHP sample, it is expected that DEHP contributes most to the migrated additives, which supports previously reported ecological and environmental concerns. However, the PVC/HPCL samples were found to exhibit no migration even under rather harsh conditions, indicating their remarkable potential to remove the health risk and environmental concerns from migrating phthalates from the

various flexible PVC products during their end use. In this study, flexible PVC formulations plasticized with hyperbranched poly(ϵ -caprolactone)s with shorter linear segments in their branching backbones and a larger number of branches were found to result in much better plasticization effects than LPCL and as good as those of DEHP, with excellent migration stability. We anticipate that our design for a hyperbranched polymeric plasticizer will ultimately enable the production of ecologically safe flexible PVC formulations.

Acknowledgments

We are grateful to the Ministry for the Environment of the Republic of Korea for their support of this study through the Eco-Technopia 21 project.

Literature Cited

- Krauskopf, L. G. Plasticizers: Types, Properties, and Performance. In *Encyclopedia of PVC*, 2nd ed.; Nass, L. I., Heiberger, C. A., Eds.; Marcel Dekker: New York, 1988; Vol. 2.
- Latini, G. Potential hazards of exposure to di-(2-ethylhexyl)-phthalate in babies. *Biol. Neonate* **2000**, *78*, 269–276.
- Latini, G.; De Felice, C.; Verrotti, A. Plasticizers, infant nutrition and reproductive health. *Reprod. Toxicol.* **2004**, *19*, 27–33.
- Di Gennaro, P.; Collina, E.; Franzetti, A.; Lasagni, M.; Luridiana, A.; Pitea, D.; Bestetti, G. Bioremediation of diethylhexyl phthalate contaminated soil: A feasibility study in slurry- and solid-phase reactors. *Environ. Sci. Technol.* **2005**, *39*, 325–330.
- Clausen, P. A.; Hansen, V.; Gunnarsen, L.; Afshari, A.; Wolkoff, P. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. *Environ. Sci. Technol.* **2004**, *38*, 2531–2537.
- Mackintosh, C. E.; Maldonado, J. A.; Ikonomou, M. G.; Gobas, F. Sorption of phthalate esters and PCBs in a marine ecosystem. *Environ. Sci. Technol.* **2006**, *40*, 3481–3488.
- Tickner, J. A.; Schettler, T.; Guidotti, T.; McCally, M.; Rossi, M. Health risks posed by use of di-2-ethylhexyl phthalate (DEHP) in PVC medical devices: A critical review. *Am. J. Ind. Med.* **2001**, *39*, 100–111.
- Latini, G.; De Felice, C.; Presta, G.; Del Vecchio, A.; Paris, I.; Ruggieri, F.; Mazzeo, P. In utero exposure to di-(2-ethylhexyl)-phthalate and duration of human pregnancy. *Environ. Health Perspect.* **2003**, *111*, 1783–1785.
- Opinion on Medical Devices Containing DEHP Plasticized PVC; Neonates and Other Groups Possibly at Risk from DEHP Toxicity*; European Commission Health & Consumer Protection Directorate-General: Brussels, 2002.
- Jayakrishnan, K.; Lakshmi, S. Immobile plasticizer in flexible PVC. *Nature* **1998**, *396*, 638–638.
- Babukutty, Y.; Prat, R.; Endo, K.; Kogoma, M.; Okazaki, S.; Kodama, M. Poly(vinyl chloride) surface modification using tetrafluoroethylene in atmospheric pressure glow discharge. *Langmuir* **1999**, *15*, 7055–7062.
- Pena, J. R.; Hidalgo, M.; Mijangos, C. Plastification of poly(vinyl chloride) by polymer blending. *J. Appl. Polym. Sci.* **2000**, *75*, 1303–1312.
- Gao, C.; Yan, D. Hyperbranched polymers: from synthesis to applications. *Prog. Polym. Sci.* **2004**, *29*, 183–275.
- Hawker, C. J.; Chu, F. K.; Pomery, P. J.; Hill, D. J. T. Hyperbranched poly(ethylene glycol)s: A new class of ion-conducting materials. *Macromolecules* **1996**, *29*, 3831–3838.
- Stiriba, S. E.; Frey, H.; Haag, R. Dendritic polymers in biomedical applications: From potential to clinical use in diagnostics and therapy. *Angew. Chem., Int. Ed.* **2002**, *41*, 1329–1334.
- Sunder, A.; Kramer, M.; Hanselmann, R.; Mulhaupt, R.; Frey, H. Molecular nanocapsules based on amphiphilic hyperbranched polyglycerols. *Angew. Chem., Int. Ed.* **1999**, *38*, 3552–3555.
- Emrick, T.; Chang, H. T.; Frechet, J. M. J.; Woods, J.; Baccei, L. Hyperbranched aromatic epoxies in the design of adhesive materials. *Polym. Bull.* **2000**, *45*, 1–7.
- Gopala, A.; Wu, H.; Xu, J.; Heiden, P. Investigation of readily processable thermoplastic-toughened thermosets: IV. BMIs toughened with hyperbranched polyester. *J. Appl. Polym. Sci.* **1999**, *71*, 1809–1817.
- Kwak, S. Y.; Ahn, D. U. Processability of hyperbranched poly(ether ketone)s with different degrees of branching from viewpoints of molecular mobility and comparison with their linear analogue. *Macromolecules* **2000**, *33*, 7557–7563.
- van Benthem, R. Novel hyperbranched resins for coating applications. *Prog. Org. Coat.* **2000**, *40*, 203–214.
- Huber, C. F.; Foulks, H. C.; Aylesworth, R. D. Polyesters from Dibasic Acids, Monobasic Acids, Glycols, and Trihydric Alcohols As Plasticizers for Vinyl Resins. United States Patent No. 3,331,802, 1967.
- Lindstrom, A.; Hakkarainen, M. Environmentally friendly plasticizers for poly(vinyl chloride)—Improved mechanical properties and compatibility by using branched poly(butylene adipate) as a polymeric plasticizer. *J. Appl. Polym. Sci.* **2006**, *100*, 2180–2188.
- Kwak, S.-Y.; Choi, J. Aliphatic Polyester Compounds Having Highly Branched Structure as a Plasticizer of Poly(vinyl chloride) and Flexible Poly(vinyl chloride) Containing the Same. United States Patent No. 6,747,092 B2, 2004.
- Choi, J.; Kwak, S.-Y. Hyperbranched polymeric plasticizers for flexible poly(vinyl chloride)s free from endocrine disruptors migration. *Abstr. Pap. Am. Chem. Soc.* **2004**, *227*, U531–U531.
- Choi, J.; Kwak, S.-Y. Synthesis and characterization of hyperbranched poly(epsilon-caprolactone)s having different lengths of homologous backbone segments. *Macromolecules* **2003**, *36*, 8630–8637.
- Choi, J.; Kwak, S.-Y. Architectural effects of poly(epsilon-caprolactone)s on the crystallization kinetics. *Macromolecules* **2004**, *37*, 3745–3754.
- Choi, J.; Kwak, S.-Y. Concentration fluctuation and cooperative chain mobility of hyperbranched poly(epsilon-caprolactone)s investigated by photon correlation spectroscopy. *Polymer* **2004**, *45*, 7173–7183.
- Kwak, S.-Y.; Choi, J.; Song, H. J. Viscoelastic relaxation and molecular mobility of hyperbranched Poly(epsilon-caprolactone)s in their melt state. *Chem. Mater.* **2005**, *17*, 1148–1156.
- Choi, J.; Chun, S.-W.; Kwak, S.-Y. Influence of Hyperbranched Against Linear Architecture on Crystallization Behavior of Poly(epsilon-caprolactone)s in Binary Blends with Poly(vinyl chloride). *J. Polym. Sci.: Part B: Polym. Phys.* **2007**, *45*, 577–589.
- Kwak, S.-Y. In-Situ, Quantitative Characterization of Gelation and Fusion Mechanism in Poly(Vinyl Chloride) Plastisols by Small-Angle Light-Scattering (SALS). *Polym. Eng. Sci.* **1995**, *35*, 1106–1112.
- Chiu, F. C.; Min, K. S. Miscibility, morphology and tensile properties of vinyl chloride polymer and poly(epsilon-caprolactone) blends. *Polym. Int.* **2000**, *49*, 223–234.
- Rusu, M.; Ursu, M.; Rusu, D. Poly(vinyl chloride) and poly(epsilon-caprolactone) blends for medical use. *J. Thermoplast. Compos. Mater.* **2006**, *19*, 173–190.
- McNeill, I. C.; Mohammed, M. H.; Cole, W. J. A detailed analysis of the pyrolysis products from dioctyltin maleate and its mixture with PVC. *Polym. Degrad. Stab.* **1998**, *61*, 95–108.
- Ultrack, L. A. *Polymer Alloy and Blends*. Hanser Publishers: Munich, 1989.
- McBrierty, V. J. NMR of solid polymers—review. *Polymer* **1974**, *15*, 503–520.
- Lakshmi, S.; Jayakrishnan, A. Properties and performance of sulfide-substituted plasticized poly(vinyl chloride) as a bio-material. *J. Biomed. Mater. Res., Part B Appl. Biomater.* **2003**, *65B*, 204–210.
- Jayakrishnan, A.; Sunny, M. C. Phase transfer catalysed surface modification of plasticized poly(vinyl chloride) in aqueous media to retard plasticizer migration. *Polymer* **1996**, *37*, 5213–5218.

Received for review November 13, 2006. Revised manuscript received February 22, 2007. Accepted March 19, 2007.

ES062715T