INTRODUCTION

Thermoplastic elastomer (TPE) can be defined as a class of polymer materials that combines the service properties of elastomers with the processing properties of thermoplastics. Thermoplastic elastomer consists of two units: a soft segment that has a low glass transition temperature ($T_g$) with flexibility and a hard segment that has a high $T_g$ and acts as a physical cross-linker of soft segments [1]. Unlike vulcanized rubber, thermoplastic elastomer can be recycled; therefore it has garnered much interest as an eco-friendly material. Many studies to make novel thermoplastic elastomer have been conducted as the interest has increased in the development of eco-friendly materials [2-5]. Commercially available thermoplastic elastomers such as polystyrene-$b$-polybutadiene-$b$-polystyrene (SBS) and polystyrene-$b$-polyisoprene-$b$-polystyrene (SIS) are prepared by living radical polymerization or anionic polymerization from the initiating site on the polymer backbone. Jiang et al. [7] synthesized cellulose-$g$-(butylacrylate-co-methylmethacrylate) by living radical polymerization. Uhrig et al. [8] prepared polyisoprene-$g$-polystyrene by anionic polymerization of polysioprene.

Metallocene polymerization began with the determination of the structure of ferrocene by Wilkins and Fischer [9]. Copolymers prepared by metallocene catalysts are characterized by narrow molecular weight (m.w.) distribution, uniform comonomer incorporation and compositional distributions. Many studies [10-13] have been performed in this regard. However, few studies on graft copolymerization using a metallocene catalyst have been conducted. Of particular mention is a report by Chung et al. [14] on graft copolymerization using a metallocene catalyst.

In our laboratory, we had previously studied the copolymerization of ethylene, high $\alpha$-olefins and divinylbenzene (DVB) using a metallocene catalyst and a cocatalyst system...
[15-17]. The prepared terpolymers were found to be very flexible and contain pendant reactive vinyl groups that provide the possibility to incorporate a hard segment in the soft matrix.

In this study, we report on the terpolymerization of ethylene, 1-decene and divinylbenzene with various concentrations of 1-decene and divinylbenzene. Subsequently, we grafted various poly-(styrenic monomers) such as poly(p-methylstyrene), poly(tert-butylstyrene) and poly(α-methylstyrene) onto PEDV by coordination polymerization. The prepared graft copolymers have a soft segment and a hard segment and they could potentially be novel thermoplastic elastomers.

**EXPERIMENTAL**

High-purity grade nitrogen gas (Daemyung Gas Co.) was used after passing it through a molecular sieve (4 Å)/manganese(II) oxide column. Toluene (Samchun Pure Chemical Co., 99.5 %) was purified by distillation over sodium and benzophenone. 1-Hexene (Aldrich, 97 %), 1-octene (Aldrich, 94 %), 1-decene (Aldrich, 94 %) and 1-dodecene (Aldrich, 95 %) were also distilled over sodium and benzophenone. Inhibitors of divinylbenzene (Aldrich, 80 %) were removed by washing with 200 mL of aqueous NaOH solution, followed by drying over magnesium sulfate (Samchun Pure Chemical, 98.5 %). Divinylbenzene was then distilled under reduced pressure over CaH2, following standard purification procedures. A solution of rac-Et(Ind)2ZrCl2 (Sigma Aldrich) and dimethyllinum tetrakis(pentafluorophenyl)borate (ACROS) in toluene was prepared and used for the reactions. Samples for the thermal, mechanical and wide-angle X-ray scattering (WAXS) analyses were prepared by compression molding using a hot press.

**General procedure:** All manipulations were carried out in an inert nitrogen atmosphere. A glove box was used to prevent the contamination of catalysts. Polymerization reactions were carried out in a 300 mL stainless steel autoclave equipped with a mechanical stirrer. The polymerization was carried out at a fixed pressure of ethylene gas at 50 °C. Toluene, 1-decene, divinylbenzene and triisobutylaluminum was added into autoclave. Then the polymerization reaction was initiated by injecting cocatalyst and catalyst which are solved in small amount of toluene. After 20 min, the reaction mixture was poured into a HCl/EtOH solution. The isolated polymer was washed with EtOH and dried under vacuum. The reaction mixture was poured into a HCl/EtOH solution. The isolated polymer was washed with 200 mL of aqueous NaOH solution, followed by drying over sodium and benzophenone. Inhibitors of divinylbenzene (Aldrich, 80 %) were removed by washing with 200 mL of aqueous NaOH solution, followed by drying over magnesium sulfate (Samchun Pure Chemical, 98.5 %). Divinylbenzene was then distilled under reduced pressure over CaH2, following standard purification procedures. A solution of rac- Et(Ind)2ZrCl2 (Sigma Aldrich) and dimethyllinum tetrakis(pentafluorophenyl)borate (ACROS) in toluene was prepared and used for the reactions. Samples for the thermal, mechanical and wide-angle X-ray scattering (WAXS) analyses were prepared by compression molding using a hot press.

**RESULTS AND DISCUSSION**

Scheme-I shows the synthesis of PEDV using rac-Et(Ind)2ZrCl2 and dimethyllinum tetrakis(pentafluorophenyl) borate/trisobutylaluminum as the metallocene catalyst and cocatalyst system, respectively.

Table-I summarizes the results of the terpolymerization with various concentrations of 1-decene and divinylbenzene. When we prepared PEDV using rac-Et(Ind)2ZrCl2, it is observed a very high catalytic activity of over 14,000 kg/mol h, a weight-
averaged molecular weight of over 100,000 g/mol and a molecular weight distribution of below 3. The composition of divinylbenzene incorporated in the terpolymer backbone increased as the input concentration of divinylbenzene increased in the terpolymerization system. However, the input concentration of 1-decene in the terpolymerization did not affect its composition in the terpolymer. We observed a proportional increase in the catalytic activity with increasing input concentration of 1-decene. This observation could be explained by the comonomer effect, wherein the number of 1-decene units coordinated to the active site of the metallocene catalyst can alter the charge density of the cationic metal ion active site. As a result, the active site with a higher electrophilicity leads to stronger ion pairs between the active site and the monomers, which in turn enhances the catalytic activity [15-17]. However, the weight-averaged molecular weight tends to be inversely proportional to the input concentration of 1-decene. This can be explained on the basis that 1-decene incorporated in the terpolymer backbone increased as the input concentration of divinylbenzene increased in the terpolymerization system.

Scheme-I: Synthetic procedure of poly(ethylene-ter-1-decene-ter-divinylbenzene)

### TABLE-I

| Run | Ethylene (psi) | 1-Decene (mol/L) | Divinylbenzene (mol/L) | Catalytic activitya | Mw×10^3 (g/mol) | Mn×10^3 (g/mol) | MWDc | Yield (g) | Ethylene (psi) | 1-Decene (mol/L) | Divinylbenzene (mol/L) |
|-----|---------------|-----------------|------------------------|---------------------|-----------------|-----------------|-------|--------|---------------|-----------------|----------------------|
| 1   | 4             | 0.2             | 0.2                    | 2808                | 266-            | 78              | 3.4   | 2.34   | 78.9          | 20.5            | 0.6                  |
| 2   | 4             | 0.2             | 0.2                    | 6552                | 251             | 83              | 3.0   | 5.46   | 77.9          | 21.4            | 0.7                  |
| 3   | 4             | 0.6             | 0.2                    | 9468                | 197             | 59              | 3.3   | 7.89   | 77.5          | 21.6            | 0.9                  |
| 4   | 4             | 0.8             | 0.2                    | 14100               | 161             | 52              | 3.1   | 11.75  | 78.1          | 21.1            | 0.8                  |
| 5   | 4             | 0.8             | 0.15                   | 9828                | 179             | 64              | 2.8   | 8.19   | 85.6          | 13.89           | 0.51                 |
| 6   | 4             | 0.8             | 0.1                    | 9324                | 87              | 32              | 2.9   | 7.77   | 86.48         | 13.17           | 0.35                 |
| 7   | 4             | 0.8             | 0.05                   | 10272               | 88              | 26              | 3.4   | 8.56   | 80.22         | 19.47           | 0.31                 |

{^aPolymerization conditions: 50 °C, 20 min, 500 rpm, 300 mL stainless autoclave, rac-Et(Ind)2ZrCl2= 2.5 µmol, Al/Zr = 500 and B/Zr = 1.5; ^bDetermined by GPC data.}
terpolymer promotes chain termination reactions, resulting in the formation of low weight-averaged Mw of the terpolymers [12].

Fig. 1 shows the $^1$H NMR spectrum of PEDV. The methylene (CH$_2$) protons of ethylene and 1-decene were observed between 1.00 and 1.30 ppm. The peaks below 1.00 ppm correspond to the methyl (CH$_3$) protons of 1-decene. Multiple aromatic CH protons of divinylbenzene were observed between 7.08 and 7.22 ppm. The vinyl protons of divinylbenzene appear at 5.8 ppm. The ratio of integration of the aromatic group to vinyl group calculated by $^1$H NMR was found to range from 1.01 to 1.03. This indicates that very few pendant vinyl groups in polymer are cross-linked. However, the polymer samples were completely soluble in toluene and no gelation was observed. These observations imply that after one vinyl group of divinylbenzene was incorporated into the polymer chain, the other vinyl group of divinylbenzene does not participate in the terpolymerization, resulting in no crosslinking during the terpolymerization. We speculated that the ratio close to 1 might also be due to impurities (e.g., small amounts of ethyl benzene) present in reagent-grade divinylbenzene.

After the preparation of PEDV, we synthesized a novel thermoplastic elastomer comprising soft and hard segments by incorporating rigid pendent groups such as poly(styrenic monomers) into the prepared terpolymer (PEDV) by using graft copolymerization techniques. The grafted poly(styrenic monomers) could act as physical cross-links in the matrix soft segment.

Scheme-II illustrates the synthetic procedure of PEDV-g-poly(tert-butylstyrene). To obtain this novel thermoplastic elastomer, we used a metallocene catalyst and a dimethyl antilinium tetrakis(pentafluorophenyl)borate/triisobutyl aluminum cocatalyst system. We tested various metallocene catalysts such as bis(cyclopentadienyl) zirconium(IV) dichloride (C1), bis(n-butylcyclopentadienyl)zirconium(IV) dichloride (C2), dimethylsilylene (n-butylamido) (cyclopentadienyl) titanium(IV) dichloride (C3), bis(methylcyclopentadienyl) zirconium(IV) dichloride (C4) and trimethoxy(pentamethylcyclopentadienyl)titanium(IV) (C5).

Table-2 summarizes the results of graft copolymerization of PEDV with various metallocene catalysts using tert-butylstyrene as a graft monomer. To separate unreacted PEDV, trichlorobenzene and poly(tert-butylstyrene), the reaction mixture was refluxed in a Soxhlet extractor with hexane. Graft copolymerization occurred when C3 or C5 was used. These catalysts have a half-metallocene architecture (have one side open), unlike C1, C2 and C4. Graft copolymerization of PEDV occurs only with half-metallocene C3 or C4 catalysts, because C1, C2 and C4 restrict graft copolymerization owing to their inherent steric hindrance. A comparison of C3 and C5 shows that the bridged structure of C3 makes it less active for graft copolymerization compared to unbridged C5 [18]. The experimental results also support this observation. When C3 was used for the graft copolymerization, only 3 mol % of tert-butylstyrene was incorporated in the graft copolymer, whereas 51.9 mol % was incorporated with C5.

Fig. 2 shows the $^1$H NMR spectra of PEDV (a) and PEDV-g-tert-butylstyrene (b-f). It can be observed that in the case of $^1$H NMR spectra of (d) and (f), vinyl proton peaks of divinylbenzene at 5.8 ppm disappeared and the intensity of the double-doublet peak from the aromatic protons at 6.0 and 7.0 ppm increased fairly high compared to that of PEDV. It is suggested that the poly(tert-butylstyrene) was successfully grafted from PEDV when C3 or C5 was used as the metallocene catalyst.
As shown in Scheme-III, we prepared the PEDV-g-poly(styrenic monomers) with C3 or C5, with the following styrenic monomers: styrene, p-methylstyrene, tert-butylstyrene and α-methylstyrene. Previous reports suggest that poly(tert-butylstyrene), poly(p-methylstyrene) and poly(α-methylstyrene) have higher glass temperature $T_g$ than poly(styrene) [19,20]. Using the graft obtained from the copolymerization of PEDV, we could expect the high temperature limit of the thermoplastic elastomer.
TABLE-2
GRAFT COPOLYMERIZATION OF PEDV WITH VARIOUS CATALYSTS

| Runa | Catalysts                                                                 | M_w (× 10^3 g/mol) | M_n (× 10^3 g/mol) | MWD | Yield (g) | Composition (mol %) |
|------|----------------------------------------------------------------------------|--------------------|--------------------|-----|-----------|--------------------|
| 8    | Bis(cyclopentadienyl)zirconium(IV) dichloride (C1)                         | 161                | 52                 | 3.1 | –         | 100.0              |
| 9    | Bis(butylcyclopentadienyl)zirconium dichloride (C2)                        | 161                | 52                 | 3.1 | –         | 100.0              |
| 10   | Dimethylsilene(tert-buty lamido)(cyclopentadienyl)titanium(IV) dichloride (C3) | 176                | 55                 | 3.2 | 0.11      | 100.0              |
| 11   | Bis(methylcyclopentadienyl)zirconium(IV) dichloride (C4)                   | 161                | 52                 | 3.1 | –         | 100.0              |
| 12   | Trimethoxy(pentamethylcyclopentadienyl)titanium(IV) (C5)                  | 875                | 178                | 4.9 | 0.45      | 48.1               |

Polymerization conditions: soft segment = PEDV (by Run 4) 1 g, [tert-butylstyrene]/[Zr] = 250, 60 °C, 1 h, catalyst = 2.5 µmol, Al/Zr = 500, Al/Zr = 1.5; *Determined by GPC data; †Determined by 'H NMR data.

Fig. 2. 'H NMR spectra for PEDV and PEDV-g-tert-butylstyrene: (a) Run 4, (b) Run 8, (c) Run 9, (d) Run 10, (e) Run 11 and (f) Run 12.
Scheme-III: Synthesis of PEDV-g-poly(styrenic monomers) using C3 or C5 metallocene catalyst
Fig. 3. $^1$H NMR spectra for (a) PEDV-g-poly(tert-butylstyrene) (Run 20), (b) PEDV-g-poly(p-methylstyrene) (Run 19) and (c) PEDV-g-polystyrene (Run 17)
Table 3 summarizes the results of graft copolymerization with various styrenic monomers. When C3 was employed as the metallocene catalyst for graft copolymerization, a poor graft ratio of styrenic monomer to PEDV was obtained. In contrast, C5 proved to be a better catalyst for preparing PEDV-g-poly(styrenic monomers) with a high graft ratio. In particular, PEDV-g-poly(p-methylstyrene) (Run 19) and PEDV-g-poly(tert-butylstyrene) (Run 20) prepared by using C5 resulted in a styrenic monomer composition of over 50 mol%. PEDV-g-poly(tert-butylstyrene) (Run 20) had 51.9 mol% of the styrenic monomer and PEDV-g-poly(p-methylstyrene) (Run 19) showed the highest concentration of styrenic monomer (69.2 mol%). However, PEDV-g-poly(α-methylstyrene) could not be prepared by using any of the described metallocene catalysts. It is believed that the steric hindrance caused by the methyl group of α-methylstyrene makes the copolymerization of PEDV-g-poly(α-methylstyrene) difficult [21].

Fig. 3 shows the 1H NMR spectra of various PEDV-g-poly(styrenic monomers). As shown earlier in Fig. 2, in Fig. 3(a), we observed double-doublet peaks at 6.5 and 7.0 ppm caused by the aromatic protons of tert-butylstyrene. In Fig. 3(b), the proton peak of the methyl group in poly(p-methylstyrene) was observed at 2.3 ppm (singlet) and the aromatic proton peaks (doublet) were found at 6.5 and 7.0 ppm. Aromatic proton peaks in poly(styrene) also appeared as doublet peaks of 6.5 and triplet peaks of 7.0 ppm. From these results, we confirmed that tert-butylstyrene, p-methylstyrene and styrene were successfully grafted from PEDV by using the C5 metallocene catalyst.

Fig. 4 shows the DSC heating diagrams of PEDV and graft copolymers. The prepared graft copolymers have two Tgs, which means that the prepared polymers have phase-separated structure with a soft segment and a hard segment. Of the two Tgs, we could reasonably infer that the lower one is owing to the soft segment made of PEDV and the higher one is owing to the rigid hard segment of poly(styrenic monomers). PEDV-g-poly(styrenic monomers) had a higher melting temperature than PEDV. We believe that these results were due to the crystalline structure of the poly(styrenic monomers) graft unit. Chung et al. [14] demonstrated that the poly(styrene) graft unit has a crystalline structure.

Wide angle X-ray diffraction patterns of PEDV and graft copolymers shown in Fig. 5 supported these facts. Crystallinity of the graft copolymers is higher than that of PEDV and new crystalline peaks appear in graft copolymers. These data support that the graft moiety of poly(styrenic monomers) has crystalline structure. However, little composition of poly(styrenic monomers), like Run 17, makes the structure of the graft copolymer amorphous. This was very interesting phenomenon.

### TABLE 3

RESULTS OF GRAFT COPOLYMERIZATION WITH VARIOUS STYRENIC MONOMERS USING C3 OR C5 CATALYST

| Run | Catalysts                        | Styrenic monomer             | Mw (× 10^3) g/mol | Mw (× 10^3) g/mol | MWD | Yield (g) | Composition (mol %) |
|-----|----------------------------------|------------------------------|-------------------|-------------------|-----|-----------|---------------------|
| 13  | Dimethylsiloxane                | Styrene                      | 188               | 57                | 3.3 | 0.21      | 95.5 4.5             |
| 14  | tert-pentadienyl(methyl)tiatnium(V) | p-Methylstyrene             | 165               | 53                | 3.1 | 0.17      | 98.2 1.8             |
| 15  | tert-Butylstylene               | tert-Butylstylene            | 176               | 55                | 3.2 | 0.11      | 97.0 3.0             |
| 16  | Trimethoxy(pentamethyl)cyclopentadienyl(titanium(V)) | Styrene             | 230               | 62                | 3.7 | 0.22      | 88.6 11.4            |
| 17  | Trimethoxy(pentamethyl)cyclopentadienyl(titanium(V)) | p-Methylstyrene             | 161               | 52                | 3.1 | –         | 100 0                |
| 18  | Trimethoxy(pentamethyl)cyclopentadienyl(titanium(V)) | α-Methylstyrene             | 1237              | 214               | 5.8 | 0.41      | 30.8 69.2            |
| 19  | Trimethoxy(pentamethyl)cyclopentadienyl(titanium(V)) | tert-Butylstylene         | 875               | 178               | 4.9 | 0.45      | 48.1 51.9            |

Polymerization conditions: soft segment = PEDV (Run 4) 1 g, [styrenic monomers]/[Zr] = 250, 60 °C, 1 h, catalyst = 2.5 µmol, Al/Zr = 500 and Al/Zr = 1.5; *Determined by GPC data; **Determined by ^1H NMR data.
It is presumed that very small amounts of graft moiety cannot form crystallinity structure by itself and also break the existing crystallinity structure in PEDV. Regarding this observation, we can confirm our assumption from the DSC diagram for Run 17 where there is no melting point of PEDV-g-poly(styrene).

Table-4 summarizes melting point, glass transition temperature and crystallinity of prepared graft copolymers.

**Conclusion**

The successful preparation of a soft PEDV using a metallocene catalyst and a cocatalyst system is reported. Subsequently, we synthesized PEDV-g-poly(styreneic monomers) with metallocene catalysts, C3 and C5. The structure of the terpolymers and graft copolymers was characterized by 1H NMR. With the help of the DSC thermal diagram, we confirmed that the prepared polymers had two glass transition temperatures. This means that the prepared polymers have a phase-separated structure with soft and hard segments. PEDV-g-poly(tert-butylstyrene) and PEDV-g-poly(p-methylstyrene) have a higher temperature limit than PEDV-g-poly(styrene). We also found that very small amounts of graft moiety cannot form crystallinity structure by itself and break the existing crystallinity structure in backbone chain. We expect that the prepared copolymers could be used as candidates for preparing thermoplastic elastomers with good heat resistance.

**ACKNOWLEDGEMENTS**

The present research is supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Trade, Industry & Energy and from the Industrial connected R&D Program for Korea Institute of Industrial Technology funded by Ministry of Strategy and Finance, Republic of Korea.

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