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Preparation of Novel Thermoplastic Elastomers by Graft Copolymerization using Metallocene Catalyst and Cocatalyst System

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Poly(ethylene-*ter*-1-decene-*ter*-divinylbenzene) (PEDV) is prepared using *rac*-Et(Ind)$_2$ZrCl$_2$ and dimethylanilinium *tetrakis*-(pentafluorophenyl)borate/triisobutylaluminum as a metallocene catalyst and a cocatalyst system, respectively. The characteristic changes of the terpolymerization product according to the varying concentration of comonomers such as 1-decene and divinylbenzene (DVB) were also studied. The structure of poly(ethylene-*ter*-1-decene-*ter*-divinylbenzene) was determined by ^{1}H NMR and the catalytic activity of the terpolymerization was found to be over 14000 kg/mol·h. PEDV-*g*-poly(styrenic monomers) were prepared using various styrenic monomers such as styrene, *tert*-butylstyrene, α-methylstyrene and *p*-methylstyrene. The structure of these graft copolymers was also elucidated by ^{1}H NMR. The differential scanning calorimetry confirmed that the prepared graft copolymers had two glass transition temperatures and a high melting temperature range (250-309 °C).

Keywords: Metallocene, Graft copolymerization, Styrenic monomers, Thermoplastic elastomer.

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 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 anionic polymerization. They have a microphase-separated linear ABA triblock copolymer structure, which consists of a hard segment dispersed in a soft matrix [6]. However, linear ABA triblock units require high chain extension efficiency among the blocks and stringent polymerization conditions. Therefore, some researchers have suggested the graft copolymer structure as the next-generation architecture of thermoplastic elastomers [7].

A graft copolymer is a segmented copolymer with a linear backbone and randomly distributed branches. Because of its inherent structure, preparation of thermoplastic elastomer is possible by the graft polymerization of hard segments onto a soft backbone or *vice-versa*. Typical methods for preparing graft copolymers are either 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 polyisoprene.

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 α-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 poten-tially 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 CaH_2, following standard purification procedures. A solution of *rac*-Et(Ind)$_2$ZrCl$_2$ (Sigma Aldrich) and dimethylanilinium *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 subjected to a vigorous solvent extraction process by refluxing it with hexane in a Soxhlet extractor, to separate the soluble terpolymer from the insoluble polyethylene (by-product). ^{1}H NMR (400 MHz, $CDCl_3$, 299 K): δ ppm 0.81-0.92 (t, (-CH_3), 1-decene), 1.12-1.3 (m, (-CH_2), repeat unit), 1.32-1.46 (m, (-CH), repeat unit), 5.2 (d, -C=CH, vinyl proton in divinylbenzene), 5.7 (d, -C=CH, vinyl proton in divinylbenzene), 6.7 (d, -C=CH, vinyl proton in divinylbenzene), 7.33-7.41 (m, (CH=C), benzene ring).

Poly(ethylene-*ter*-1-decene-*ter*-divinylbenzene) (1 g) was dissolved in 100 mL of toluene under N_2 in a 250 mL flask at 50 °C. Styrenic monomers, dimethylanilinium *tetrakis*(pentafluorophenyl)borate and triisobutylaluminum were added to the solution. Subsequently, the metallocene catalyst (C1-C5) was added to the solution. The solution was stirred for 1 h. The reaction was quenched by adding methanol (5 mL). The reaction mixture was poured into an excess of methanol containing a small amount of HCl. The precipitated polymer was filtered and subjected to a vigorous Soxhlet extraction process by consecutively refluxing it with hexane and 1,2,4-trichlorobenzene for 24 h to separate unreacted PEDV and poly(styrenic monomers).

PEDV-*g*-poly(styrene): ^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ ppm 0.81-0.92 (t, (-CH_3), in 1-decene), 1.12-1.3 (m, (-CH_2), repeat unit in PEDV), 1.32-1.46 (m, (-CH), repeat unit in PEDV), 1.75 (t, (-CH) repeat unit in poly(styrene)), 6.5 and 7.1 (m, (CH=C), benzene ring). PEDV-*g*-poly(*p*-methylstyrene): ^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ ppm 0.81-0.92 (t, (-CH_3), in 1-decene), 1.12-1.3 (m, (-CH_2), repeat unit in PEDV), 1.32-1.46 (m, (-CH), repeat unit in PEDV), 1.75 (t, (-CH) repeat unit in poly(*p*-methylstyrene)), 2.3 (s, (-CH_3) in *p*-methylstyrene) 6.5 and 7.1(d, (CH=C), in benzene ring). PEDV-*g*-poly(*tert*-butylstyrene): ^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ ppm 0.81-0.92 (t, (-CH_3), 1-decene) 0.8 (s, (-CH_3), in *t*-butylstyrene), 1.12-1.3 (m, (-CH_2), repeat unit in PEDV), 1.32-1.46 (m, (-CH), repeat unit in PEDV), 1.75 (t, (-CH) repeat unit in poly(*p*-methylstyrene)), 6.5 and 7.1(d, (CH=C), in benzene ring).

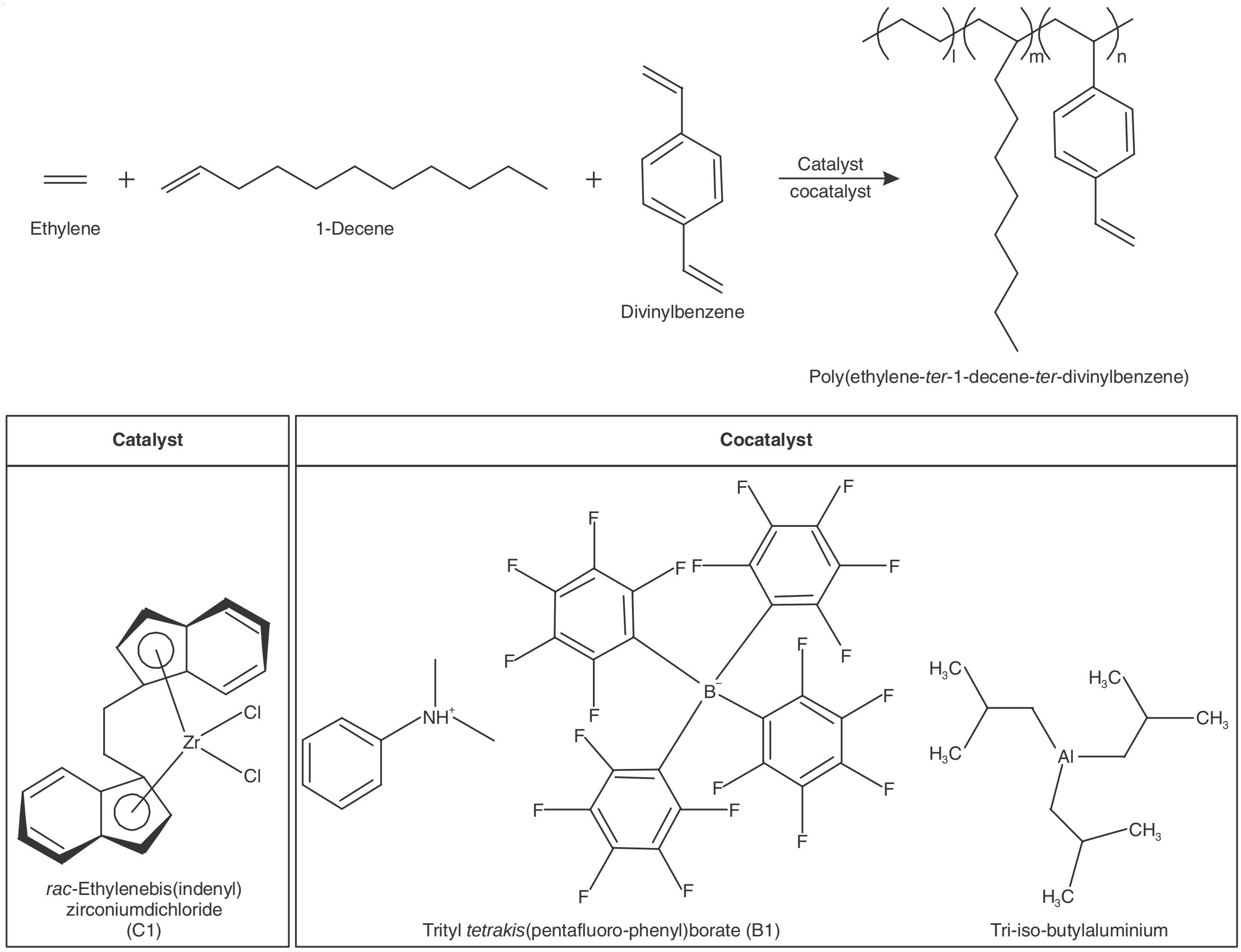
Detection method: ^{1}H NMR spectra were recorded on the AVANCE 500 MHz spectrometer (Bruker, Karlsruhe, Germany). The samples were prepared in $CDCl_3$ at 60 °C for PEDV and in 1,2,4-trichlorobenzene at 110 °C for the graft copolymer. The molecular weight and molecular weight distribution of the polymers were determined using a PL-GPC210 (Polymer Laboratories Co., Church Stretton, UK) gel permeation chromatography (GPC) instrument fitted with Styragel® (olesis guard column) HT-type columns. This test method used commercially available polystyrene standards. The analyses were performed at 140 °C and 1 mL/min with 1,2,4-trichlorobenzene as the solvent. Differential scanning calorimetry (DSC) data for the graft copolymers were recorded on the DSC7 (PERKIN ELMER Co.) calorimeter. Samples were heated from 0 to 350 °C and then cooled down at 10 °C/min to 0 °C. Following this, they were reheated at 10 °C/min to 150 °C. WAXS patterns were recorded in reflection mode at room temperature using D/MAX-2200V X-ray diffractometer (Rigaku, Tokyo, Japan) connected to a computer. The instrument used a Cu source and it performed measurements at 40 kV and 40 mA. The diffraction scans were collected over a period of 20 min, with 2θ values between 3.0° and 40.0° at a scan rate of 2 °/min.The catalytic activity of the terpolymers was calculated as following equation:

$$\text{Catalytic activity} = \frac{\text{kg of polymer}}{\text{mol} \times \text{h}}$$

RESULTS AND DISCUSSION

Scheme-I shows the synthesis of PEDV using *rac*-Et(Ind)$_2$ZrCl$_2$ and dimethylanilinium *tetrakis*(pentafluorophenyl) borate/triisobutylaluminum as the metallocene catalyst and cocatalyst system, respectively.

Table-1 summarizes the results of the terpolymerization with various concentrations of 1-decene and divinylbenzene. When we prepared PEDV using *rac*-Et(Ind)$_2$ZrCl$_2$, it is observed a very high catalytic activity of over 14,000 kg/mol h, a weight-



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

TABLE-1
TERPOLYMERIZATION OF ETHYLENE, 1-DECENE AND DIVINYLBENZENE

Run[a]	Feeding			Catalytic activity[b]	M_w[c] (× 10^3 g/mol)	M_n[c] (× 10^3 g/mol)	MWD[c]	Yield (g)	Composition (mol %)		
	Ethylene (psi)	1-Decene (mol/L)	Divinyl-benzene (mol/L)						Ethylene (psi)	1-Decene (mol/L)	Divinyl-benzene (mol/L)
1	4	0.2	0.2	2808	266-	78	3.4	2.34	78.9	20.5	0.6
2	4	0.4	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

[a]Polymerization conditions: 50 °C, 20 min, 500 rpm, 300 mL stainless autoclave, *rac*-Et(Ind)$_2$ZrCl$_2$= 2.5 μmol, Al/Zr = 500 and B/Zr = 1.5; [b]Kg of polymer/(mol of catalyst)·h; [c] Determined by GPC data.

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 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 anilinium *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 (*t*-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.

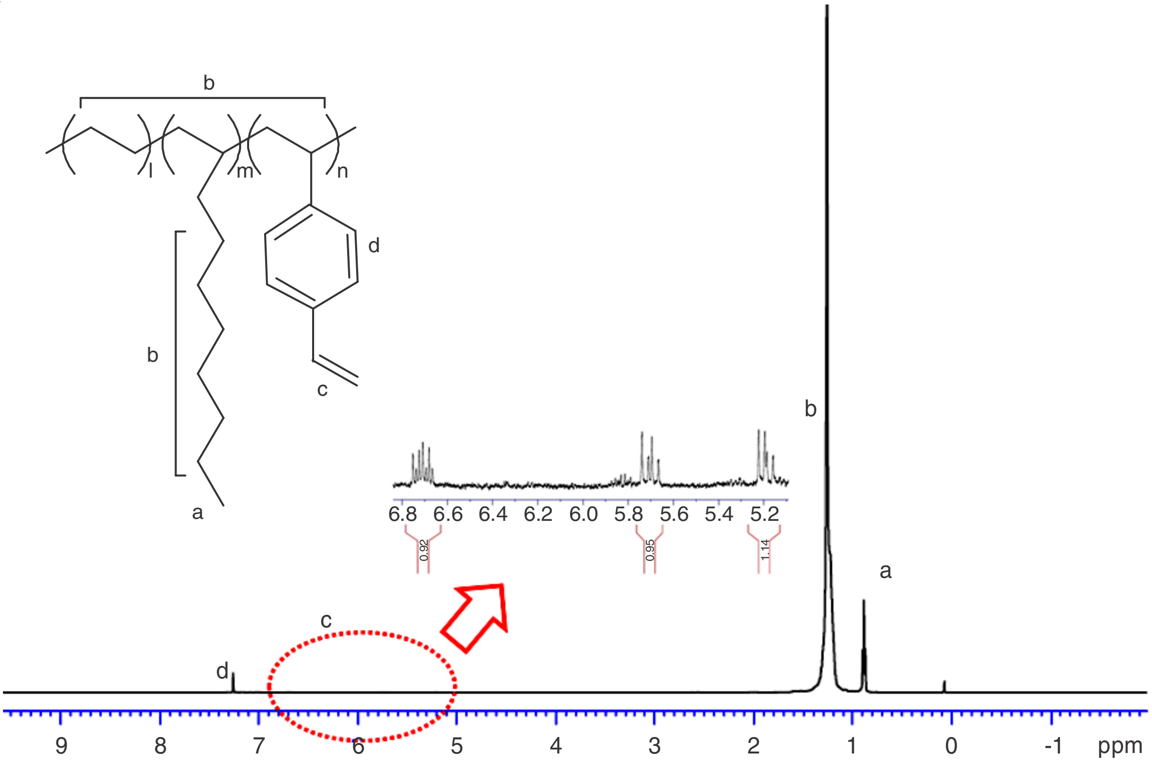
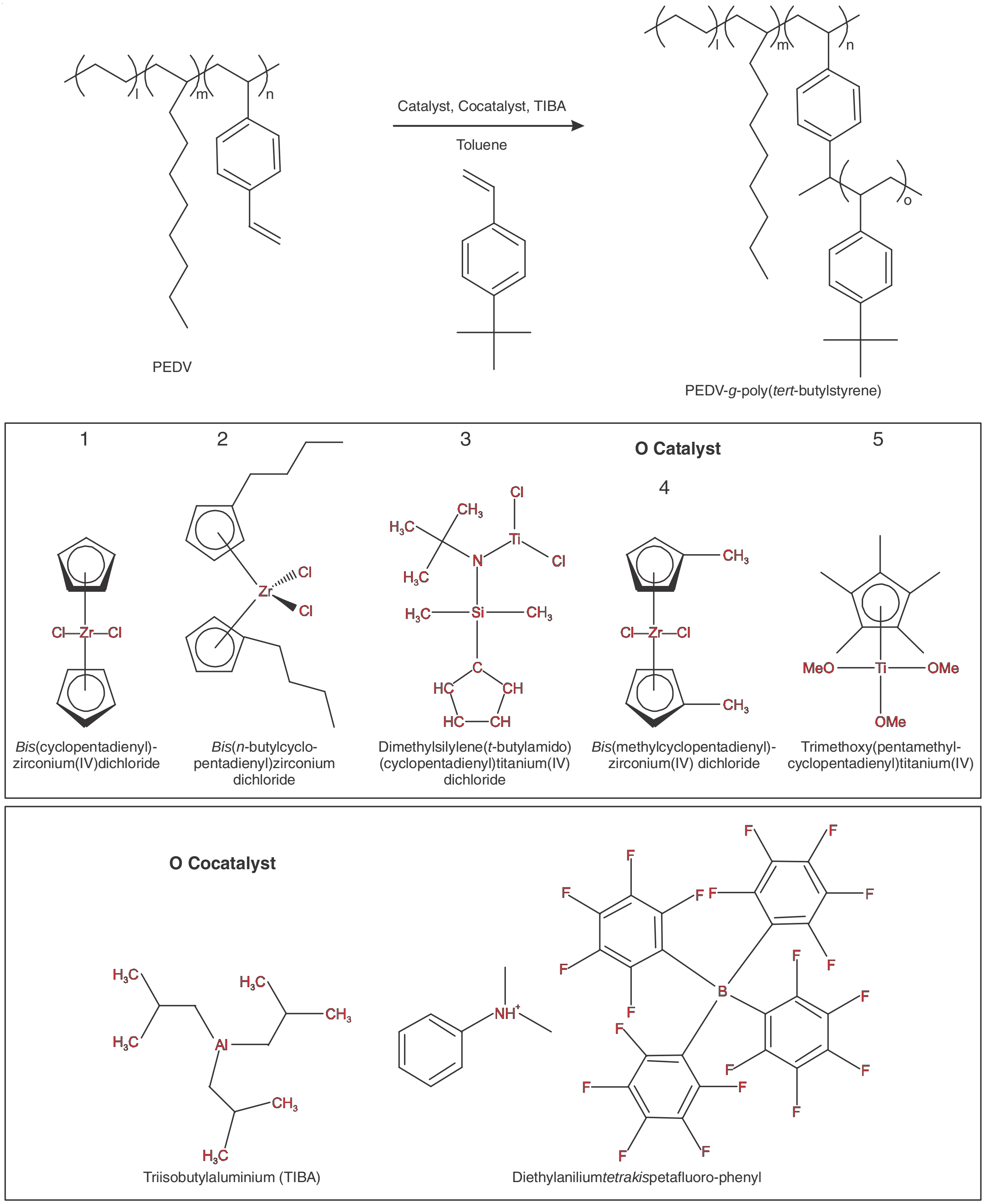


Fig. 1. ^{1}H NMR spectrum for PEDV (Run 4)



Scheme-II: Synthetic procedure of PEDV-*g*-poly(*tert*-butylstyrene)

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

Run[a]	Catalysts	M_w[b] (× 10^3 g/mol)	M_n[b] (× 10^3 g/mol)	MWD[b]	Yield (g)	Composition (mol %)[c]	
						PEDV	s-PS
8	*Bis*(cyclopentadienyl)zirconium(IV) dichloride (C1)	161	52	3.1	–	100.0	0.0
9	*Bis*(butylcyclopentadienyl)zirconium dichloride (C2)	161	52	3.1	–	100.0	0.0
10	Dimethylsilylene(*tert*-butylamido)(cyclopentadienyl)titanium(IV) dichloride (C3)	176	55	3.2	0.11	97.0	3.0
11	*Bis*(methylcyclopentadienyl)zirconium(IV) dichloride (C4)	161	52	3.1	–	100.0	0.0
12	Trimethoxy(pentamethylcyclopentadienyl)titanium(IV) (C5)	875	178	4.9	0.45	48.1	51.9

[a]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; [b]Determined by GPC data; [c]Determined by ^{1}H NMR data.

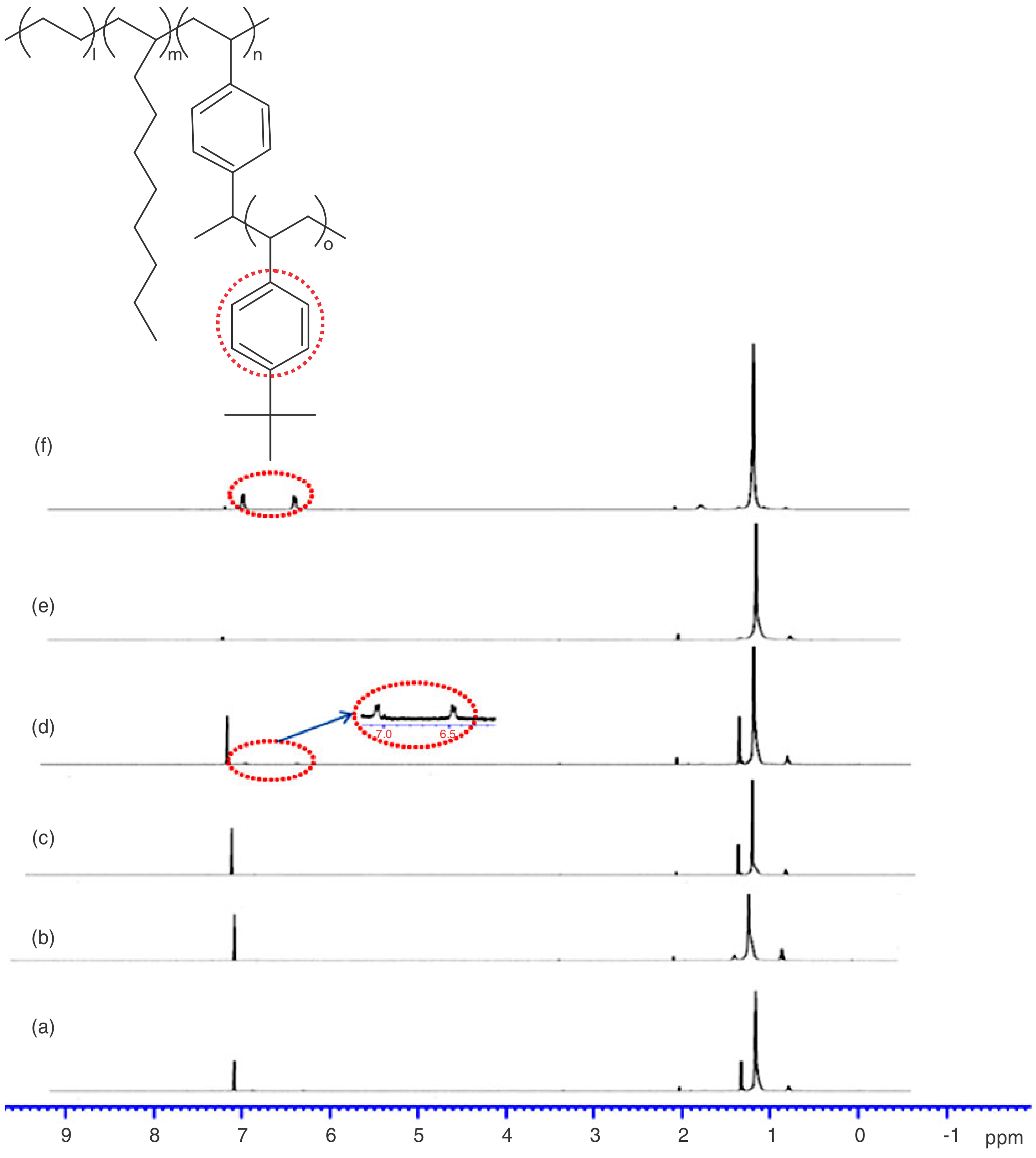
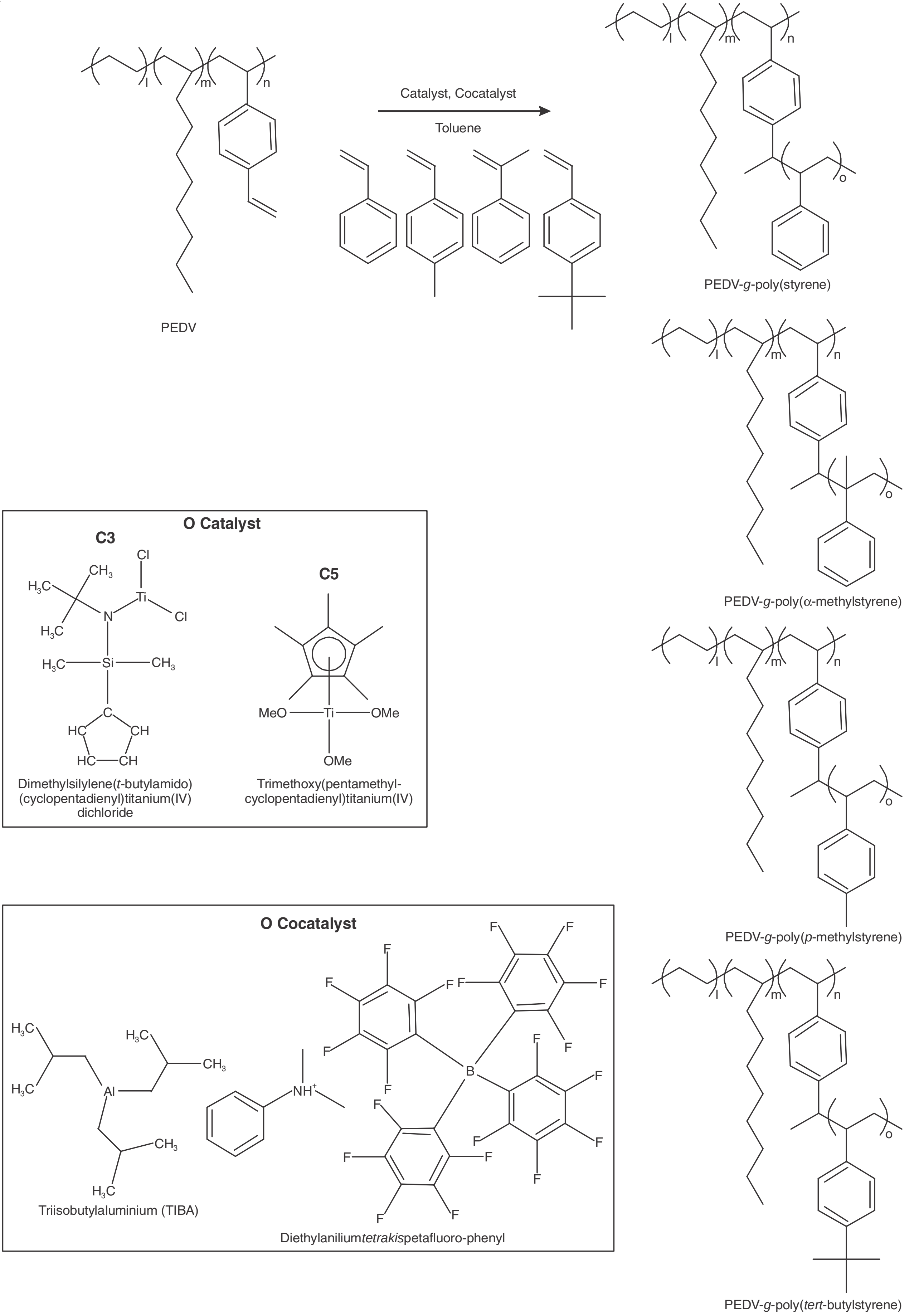


Fig. 2. ^{1}H NMR spectra for PEDV and PEDV-*g*-*tert*-butylstyrene: (a) Run 4, (b) Run 8, (c) Run 9, (d) Run 10, (e) Run 11 and (f) Run 12



Scheme-III: Synthesis of PEDV-*g*-poly(styrenic monomers) using C3 or C5 metallocene catalyst

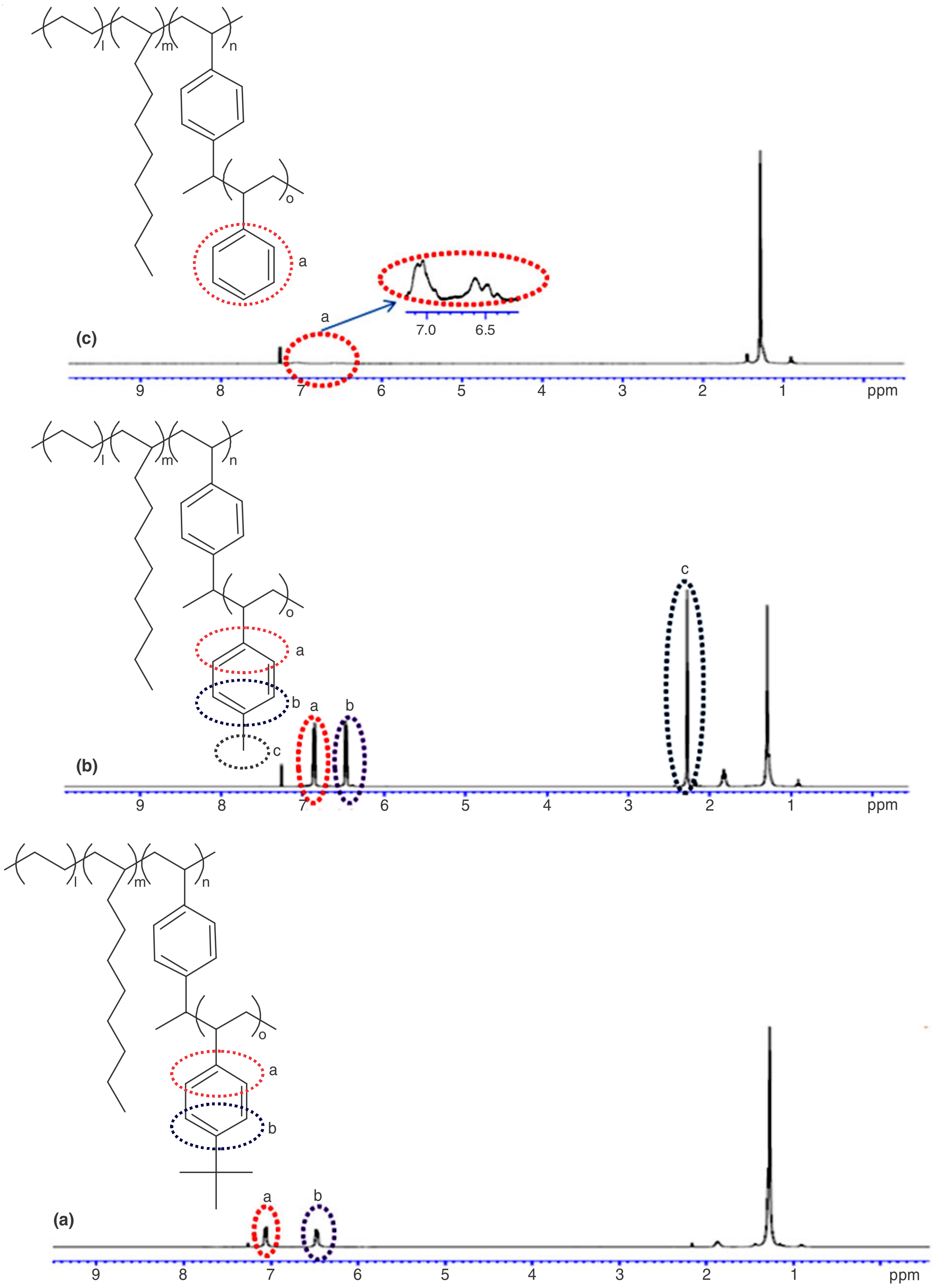


Fig. 3. ^{1}H NMR spectra for (a) PEDV-*g*-poly(*tert*-butylstyrene) (Run 20), (b) PEDV-*g*-poly(*p*-methylstyrene) (Run 19) and (c) PEDV-*g*-polystyrene (Run 17)

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 %. 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 ^{1}H 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 T_gs, which means that the prepared polymers have phase-separated structure with a soft segment and a hard segment. Of the two T_gs, 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 are 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.

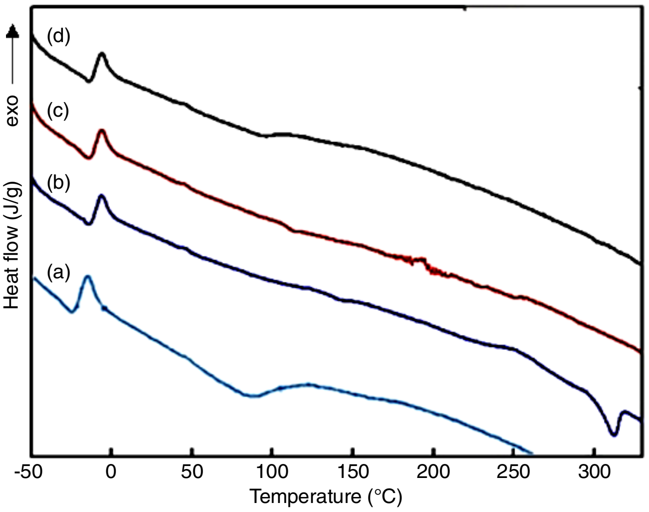


Fig. 4. DSC heating thermograms of (a) PEDV, (b) PEDV-*g*-poly(*tert*-butylstyrene), (c) PEDV-*g*-poly(*p*-methylstyrene) and (d) PEDV-*g*-poly(styrene)

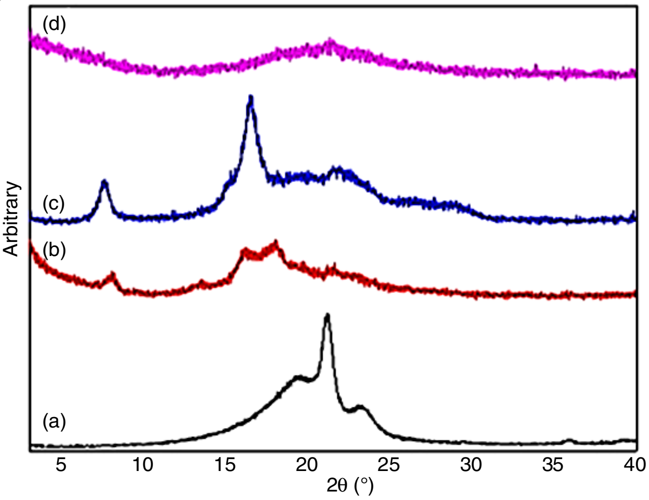


Fig. 5. Wide angle X-ray diffraction patterns of (a) PEDV, (b) PEDV-*g*-poly(*tert*-butylstyrene) (c) PEDV-*g*-poly(*p*-methylstyrene) and (d) PEDV-*g*-poly(styrene)

TABLE-3
RESULTS OF GRAFT COPOLYMERIZATION WITH VARIOUS STYRENIC MONOMERS USING C3 OR C5 CATALYST

Run[a]	Catalysts	Styrenic monomer	M_w[b] (× 10^3 g/mol)	M_n[b] (× 10^3 g/mol)	MWD[b]	Yield (g)	Composition[c] (mol %)	
							PEDV	s-PS
13	Dimethylsilylene (*t*-butylamido)(cyclopentadienyl)titanium(IV) dichloride (C3)	Styrene	188	57	3.3	0.21	95.5	4.5
14		α-Methylstyrene	161	52	3.1	–	100	0
15		*p*-Methylstyrene	165	53	3.1	0.17	98.2	1.8
16		*tert*-Butylstyrene	176	55	3.2	0.11	97.0	3.0
17	Trimethoxy(pentamethylcyclopentadienyl)-titanium(IV) (C5)	Styrene	230	62	3.7	0.22	88.6	11.4
18		α-Methylstyrene	161	52	3.1	–	100	0
19		*p*-Methylstyrene	1237	214	5.8	0.41	30.8	69.2
20		*tert*-Butylstyrene	875	178	4.9	0.45	48.1	51.9

[a]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; [b]Determined by GPC data; [c]Determined by ^{1}H NMR data.

TABLE-4
THERMAL PROPERTIES AND CRYSTALLINITY OF THE GRAFT COPOLYMERS

Run	PEDV (mol %)	PS (mol %)	Graft monomer	T_{g1}[a] (°C)	T_{g2}[a] (°C)	T_m[a] (°C)	Crystallinity[b] (%)
4	100	0	–	-16.5	–	82	20
17	88.6	11.4	Styrene	-15.7	100.5	–	29
19	30.8	69.2	*p*-Methylstyrene	-16.4	118.0	250	53
20	48.1	51.9	*tert*-Butylstyrene	-15.9	145.4	309	56

[a]Determined by DSC data; [b]Determined by WAXS 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 ^{1}H 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.

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REFERENCES

1. R. Shanks and I. Kong, Thermoplastic Elastomers, In Tech, pp. 134-154 (2012).
2. W. Radke, S. Roos, H.M. Stein and A.H.E. Müller, *Macromol. Symp.*, **101**, 19 (1996).
3. J.P. Kennedy, J.L. Price and K. Koshimura, *Macromolecules*, **24**, 6567 (1991).
4. E.J. Markel, W. Weng, A.J. Peacock and A.H. Dekmezian, *Macromolecules*, **33**, 8541 (2000).
5. Y. Chen, A.M. Kushner, G.A. Williams and Z. Guan, *Nat. Chem.*, **4**, 467 (2012).
6. K. Satoh, D.H. Lee, K. Nagai and M. Kamigaito, *Macromol. Rapid Commun.*, **35**, 161 (2014).
7. F. Jiang, Z. Wang, Y. Qiao, Z. Wang and C. Tang, *Macromolecules*, **46**, 4772 (2013).
8. D. Uhrig, R. Schlegel, R. Weidisch and J. Mays, *Eur. Polym. J.*, **47**, 560 (2011).
9. W. Kaminsky and H. Sinn, Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer-Verlag, Manasquan, NJ, USA(1988).
10. W. Apisuk, N. Suzuki, H.J. Kim, D.H. Kim, B. Kitiyanan and K. Nomura, *J. Polym. Sci. Part A*, **51**, 2565 (2013).
11. D.J. Yang, H.J. Kim and D.H. Kim, *Catalysts*, **3**, 176 (2013).
12. G.B. Galland, M. Seferin, R.S. Mauler and J.H.Z. Dos Santos, *Polym. Int.*, **48**, 660 (1999).
13. B. Wang, *Coord. Chem. Rev.*, **250**, 242 (2006).
14. J.Y. Dong, H. Hong, H.C. Wang, S. Datta and T.C. Chung, *Macromolecules*, **36**, 6000 (2003).
15. T.W. Kim, U.R. Cho and D.H. Kim, *Asian J. Chem.*, **25**, 5297 (2013).
16. G.L. Yoon, D.J. Yang, H.J. Kim, J.C. Lee, N.H. Park and D.H. Kim, *Asian J. Chem.*, **25**, 5284 (2013).
17. D.H. Kim, *Asian J. Chem.*, **25**, 5267 (2013).
18. M. Pitsikalis and A.F. Maroudas, Synthesis of Complex Macromolecular Architectures by Metallocene and Half-Metallocene Complexes, Transworld Research Network, Kerala, India, pp. 1-59 (2013).
19. R.E. Cunningham, *J. Appl. Polym. Sci.*, **22**, 2907 (1978).
20. S.L. Malhotra, P. Lessard and L.P.J. Blanchard, *Macromol. Sci. Pure Appl. Chem.*, **15**, 121 (1981).
21. F.M. Rabagliati, H. Muñoz and G. Mardones, *J. Chil. Chem. Soc.*, **55**, 111 (2010).