Synthesis of New Polyolefin Elastomers, Poly(ethylene-*ter*-propylene-*ter*-*p*-methylstyrene) and Poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene), Using Metallocene Catalysts with Constrained Ligand Geometry

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ABSTRACT: This paper discusses two new polyolefin elastomers, i.e., poly(ethylene-*ter*-propylene-*ter*-*p*-methylstyrene) (EP-p-MS) and poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene) (EO-p-MS), containing "reactive" *p*-methylstyrene (*p*-MS) groups. Both terpolymers, with a broad range of terpolymer composition, high molecular weight, narrow molecular weight, and composition distributions, have been prepared by using $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ metallocene catalyst with constrained ligand geometry. Differential scanning calorimetry (DSC) results show no detectable melting point (T_m) in both terpolymers containing less than 70 mol % ethylene units. The sharp glass transition temperature (T_g) with flat base line in each DSC curve indicates homogeneous terpolymer microstructures. In general, the T_g of EP-*p*-MS is very sensitive to the terpolymer composition (ethylene/propylene ratio and *p*-MS content). In the compositions with the ideal ethylene/propylene ratio ∼ 55/45, T_g is almost proportional to the content of *p*-MS. Only with the concentration of *p*-MS < 2 mol % does the EP-*p*-MS show a low $T_g < -45$ °C. On the other hand, the EO-*p*-MS system exhibits a low $T_g < -50$ °C in a wide range of copolymer compositions, even ones with relatively high *p*-MS contents (>7 mol %).

Introduction

By far, the most important commercial polyolefin elastomer is EPDM terpolymers,[1] i.e. poly(ethylene-*ter*-propylene-*ter*-1,4-hexadiene) and poly(ethylene-*ter*-propylene-*ter*-5-ethylidene-2-norbornene), with glass transition temperatures (T_g) usually below −45 °C. The terpolymers usually contain a few mole percent of "reactive" diene residues serving as the active sites for the subsequent vulcanization (cross-linking) reactions.[2] To subdue the potential crystallization of ethylene consecutive units and maintain a low T_g, the terpolymer with approximately equal amounts of ethylene and propylene (55/45 mole ratio) is preferred in many EP rubber products. However, due to the significant difference in comonomer reactivities[3] and multiple active sites in Ziegler−Natta catalysts, somewhat inhomogeneous comonomer distributions[4] were observed in EPDM elastomers. In other words, some short ethylene sequences exist in the polymer chains, which have sufficient length to form small crystalline domains. In fact, most commercial EPDM terpolymers are not completely soluble in hydrocarbon solvents (such as hexane) at room temperature. On the other hand, the vulcanization reactions of commercial EPDM elastomers are usually via the free radical process involving the allylic protons in diene units. The reaction results in unsaturated residues in the network, which post some concerns in long-term (UV, ozone, thermal, and chemical) stabilities.

It is interesting to note that a new generation of butyl rubber, i.e., poly(isobutylene-*co*-*p*-methylstyrene)[5] containing several percentages of "reactive" *p*-methylstyrene (*p*-MS), has been commercialized by Exxon Chemical Co. This new elastomer was found to have many superior properties over the traditional one, containing diene (i.e., butadiene and isoprene) unsaturated residues.[6] Some distinctive advantages are (i) high cross-linking efficiency under traditional vulcanization conditions, (ii) effective photo-cross-linking reaction, (iii) dramatically improved product stability (especially, for outdoor applications) due to a completely saturated polymer structure, and (iv) aromatic residues improving the very needed interactions with carbon black to further enhance desirable physical and chemical properties. In addition, the benzylic protons in the *p*-methystyrene units are very facile in many functionalization reactions, such as halogenation,[7] metalation,[8] and oxidation,[9] to form various functional groups at the benzylic position under mild reaction conditions. The metalated benzylic anions can also further serve as the anionic initiators for "living" anionic graft-from polymerization[10] to prepare polyolefin graft copolymers.

New progresses in metallocene technology[11] have opened the unprecedented opportunity for polymer chemists to prepare new polyolefins, especially copolymers containing high α-olefins with narrow composition and molecular weight distributions. The well-defined single catalytic site can be tailor-designed for incorporating high α-olefins. Several good examples, such as LLDPE,[12] long chain branching PE,[13] and ethylene/styrene copolymers,[14] have been reported.

Our research interests have been in the functionalization of polyolefins,[15] which led us to the investigation of applying metallocene catalysts to the copolymerization of α-olefins and *p*-methylstyrene (a "reactive" comonomer). In our previous paper,[16] we have reported the copolymerization of ethylene and *p*-methylstyrene by using metallocene catalysts, such as $Et(Ind)_2ZrCl_2$ and $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$. The reaction produced a new class of poly(ethylene-*co*-*p*-methylstyrene) copolymers, ranging from tough thermoplastics with high ethylene content to glassy (amorphous) copolymers with high *p*-methylstyrene content, in which the *p*-methyl-

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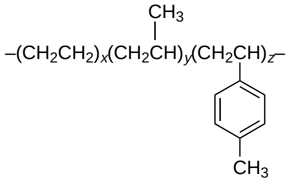
styrene units are largely isolated. The copolymerization reaction exhibited high catalyst activity, due to the combination of the cationic propagating site and favorable electronic donation of the *p*-methyl group in *p*-MS monomer. In turn, the poly(ethylene-*co*-*p*-methylstyrene) copolymers are very versatile intermediates, which can be transformed to functionalized polyethylene[16] (containing various functional groups) and graft copolymers.[10] It is interesting to note that despite the completely amorphous structure, the lowest T_g observed in this type of poly(ethylene-*co*-*p*-methylstyrene) copolymers was about −5 °C, which is too high to be useful in most of elastomer applications.

Results and Discussion

For many commercial applications elastomers with low $T_g < -45$ °C and having reactive sites (such as *p*-methylstyrene units) which can effectively form cross-linking networks and produce stable residues, are very desirable. It is certainly very interesting to expand the poly(ethylene-*co*-*p*-methylstyrene) system to polyolefin elastomers. In ethylene−propylene cases, it means preparing a random terpolymer containing close to equal molar ratio of ethylene/propylene and some *p*-methylstyrene reactive units. With the unprecedented capability of metallocene technology in copolymerization reactions, it is very interesting to expand the polyolefin elastomer to new classes containing high α-olefins, such as 1-octene (instead of propylene), which can effectively prevent the crystallization of small consecutive ethylene units and provide low-T_g properties. In chemistry, the terpolymerization reaction involving ethylene, 1-octene (high α-olefin), and *p*-methylstyrene (aromatic olefin) simultaneously, which is very difficult to achieve in Ziegler−Natta polymerization, will be an ultimate test to the metallocene technology.

In this paper, we will discuss the synthesis of two new types of polyolefin elastomers, i.e., poly(ethylene-*ter*-propylene-*ter*-*p*-methylstyrene) (EP-*p*-MS; **I**) and poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene) (EO-*p*-MS **II**) shown as follows. Their thermal transitions will also be discussed in detail.



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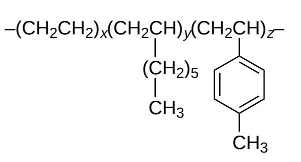

II

Poly(ethylene-*ter*-propylene-*ter*-*p*-methylstyrene). The polymerization reactions were carried out in a Parr reactor. The desirable ratio of ethylene and propylene were mixed in a steel reservoir before piping into the reactor containing a mixed solution of *p*-MS, MAO, and toluene. The polymerization reaction was initiated by charging $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ catalyst into the monomer mixture. A constant mixed ethylene/propylene pressure was maintained throughout the polymerization process. To ensure the constant comonomer ratios, the polymerization was usually terminated in 15 min by adding dilute HCl/CH_3OH solution.

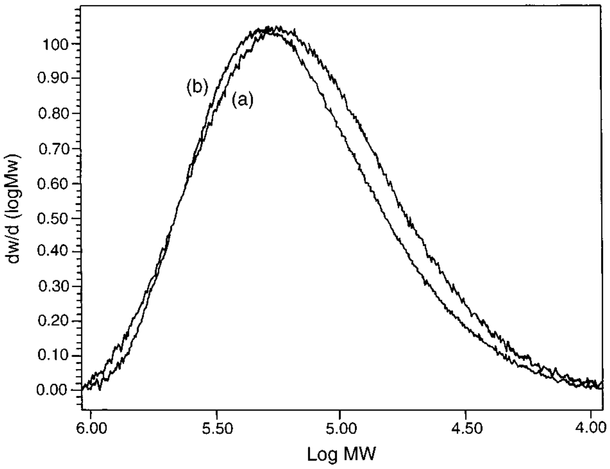

Figure 1. Comparison of two GPC curves of (a) poly(ethylene-*ter*-polypropylene-*ter*-*p*-methylstyrene) terpolymer (run p-120) and (b) poly(ethylene-*co*-polypropylene) copolymer (run p-116).

Figure 1 compares two GPC curves between poly(ethylene-*ter*-polypropylene-*ter*-*p*-methylstyrene) terpolymer (with ethylene/propylene ~54/44 mole ratio and 2 mol % *p*-MS) and the corresponding poly(ethylene-*co*-polypropylene) copolymer. Both polymers were prepared by $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$/MAO catalyst under similar reaction conditions.

Similar molecular weight and molecular weight distribution were observed, which indicate that the addition of *p*-MS did not significantly alter the polymerization process (similar propagating rate, no additional termination reaction). The high molecular weight ($M_w \sim$ 237,700 and $M_n \sim$ 107 500 and narrow molecular weight distribution ($M_w/M_n \sim 2.2$) is indicative of an ideal single-site polymerization mechanism.

Figure 2 shows the ^{1}H NMR spectrum of several poly(ethylene-*ter*-propyene-*ter*-*p*-methylstyrene) terpolymers with 1.82, 4.52, and 7.94 mol % of *p*-MS, respectively. In addition to the chemical shift at 0.8 ppm, corresponding to CH_3 in propylene units, and a band between 0.9 and 1.7 ppm, corresponding to CH_2 and CH in the polymer backbone, there are two additional chemical shifts around 2.35 and 7.0−7.3 ppm, corresponding to Ph-CH_3 and aromatic protons in *p*-MS units. The integrated intensity ratio between two chemical shifts at 0.8−1.7 and 2.35 ppm and the number of protons both chemical shifts represent determines the *p*-MS content. The mole ratio of ethylene/propylene in the terpolymer was determined by the IR technique,[17] by comparing the integrated intensity between the absorption at 1460 cm^{-1}, corresponding to the CH_2 group in the ethylene unit, and the absorption at 1379 cm^{-1}, corresponding to CH_3 group in the propylene unit. Figure 3 shows an IR spectrum of EP-*p*-MS copolymer having ethylene/propylene ratio of 46/52 (run p-119 in Table 1).

In addition to two major peaks, the absorption peak at 1513 cm^{-1} is due to the aromatic group in the *p*-MS unit. On the basis of the IR spectrum of poly(*p*-methylstyrene), two additional absorptions at 1435 and 1380 cm^{-1}, corresponding to aromatic and methyl groups in the *p*-MS unit, respectively, are overlapped with the major absorptions at 1460 and 1379 cm^{-1}. The intensity ratio among three *p*-MS absorptions at 1513, 1435, and 1380 cm^{-1} is about 16:4:1. For samples with low (<2 mol %) concentration of *p*-MS, the two overlapped absorptions have insignificant effect on the calculation of ethylene/propylene mole ratios. For the samples with >4 mol % p-MS, both intensities at 1435 and 1380 cm $^{-1}$ were taken into account by deducting

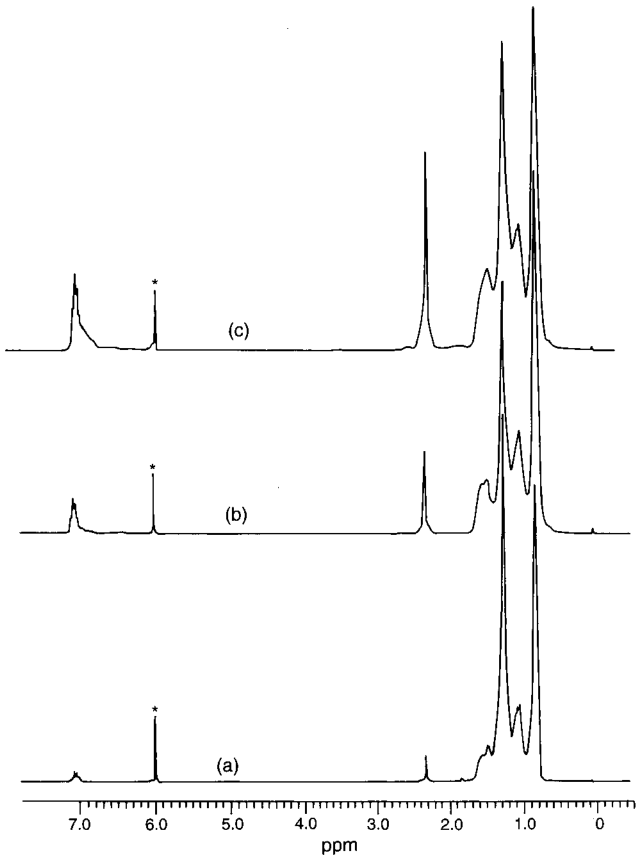

Figure 2. ^{1}H NMR spectra of poly(ethylene-*ter*-propylene-*ter*-*p*-methylstyrene) terpolymers, containing (a) 1.82, (b) 4.52, and (c) 7.94 mol % of *p*-MS comonomers. (solvent, 1,1,2,2-tetrachloroethane-d_2; relaxation delay, 5 s; temperature, 50 °C).

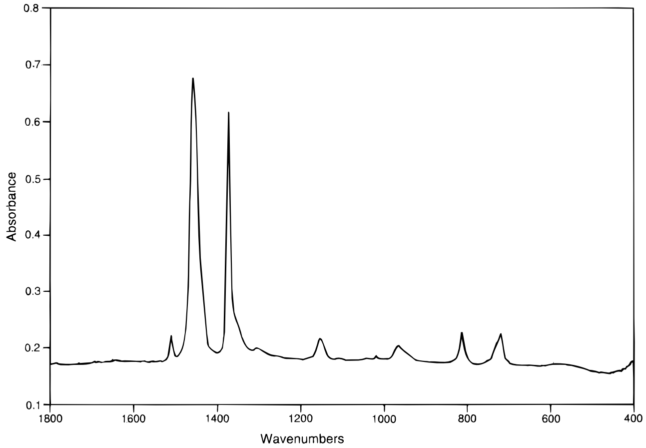

Figure 3. IR spectrum of EP-*p*-MS copolymer with an ethylene/propylene ratio of 46/52 (run p-119 in Table 1).

their intensities from the intensities at 1460 and 1379 cm $^{-1}$ before calculation.

All experimental results with various monomer feed ratios are summarized in Table 1.

Overall, the $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$/MAO metallocene catalyst shows excellent activity ((3.4−5.4) × 10^6 g of polymer/(mol of Zr h) at 50 °C) in all reactions, with comparative reactivities between ethylene and propylene and good incorporation of p-MS. Such an effective incorporation of an aromatic monomer in polyolefins is very difficult to achieve by traditional Ziegler−Natta catalysts.[18] In the control set (runs p-116, p-117, p-107, and p-115), only involving ethylene and propylene, the copolymer composition is basically governed by the monomer feed ratio. However, with *p*-MS, the incorporation of propylene seems too slow. This trend is very clearly observed in the comparative set (runs p-110, p-111, and p-112), with constant ethylene and propylene feeds and various *p*-MS concentrations; the higher *p*-MS concentration in the feed, the lower propylene/ethylene ratio in the copolymer. As discussed in our previous paper,[16] no consecutive *p*-MS incorporation was observed in $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$/MAO copolymerization reactions due to steric hindrance at the propagating *p*-MS site. The same steric hindrance may also have some effect on the subsequent propylene insertion, preferring ethylene over propylene. On the other hand, the incorporation of *p*-MS seems quiet insensitive to the ethylene/propylene feed ratio. In both comparative sets of runs p-120 vs p-119 and p-128 vs p-127, with constant *p*-MS concentration in each comparative run (0.05 and 0.03 mol/L, respectively) and varying ethylene/propylene feed ratio, the incorporation of *p*-MS is very constant at about 1.6−1.8 and 0.6−0.65 mol %, respectively.

In general, the molecular weights of these terpolymers are very high. Comparing runs p-116 vs p-120 and p-117 vs *p*-119, with the same amount of ethylene and propylene feeds and with and without *p*-MS, only a small reduction in molecular weight arises from the incorporation of *p*-MS. It is very interesting to note that the replacement of *p*-MS with styrene in the same reaction conditions significantly lowers the molecular weight of poly(ethylene-*ter*-propylene-*ter*-styrene). The results may be attributed to the relatively comparative reactivity of *p*-MS with those of ethylene and propylene. The electronic donation of the *p*-methyl group in *p*-MS is favorable in this cationic coordination polymerization mechanism.[19] It may also be possible that a weak chain-transfer reaction occurs in the terpolymerization reactions to account for the small reduction of terpolymer molecular weight.

The glass transition temperature (T_g) was examined by differential scanning calorimetry (DSC). Figure 4 shows several DSC curves of EP-*p*-MS (**I**) terpolymers (samples p-112, p-118, and p-120 in Table 1).

Each curve only has a sharp T_g transition in a flat base line, without any detectable melting point. The combination implies a homogeneous terpolymer microstructure with completely amorphous morphology. The same clean DSC curves were observed in all samples shown in Table 1, even the sample with >87 mol % of propylene content, which may have the most atactic propylene sequences incapable of crystallization. The T_g is clearly a function of the propylene and *p*-methylstyrene contents. Comparing the ethylene/propylene copolymers (without *p*-MS units) (runs p-116, p-117, p-107, and p-115), the T_g transitions shown in Figure 5 are linearly proportional to the propylene contents and level off at ~ −50 °C with the composition of ~50% of propylene content (similar results were reported for the EPDM case[2]).

The T_g transition significantly increases with the incorporation of *p*-methylstyrene in ethylene/propylene copolymers. Comparing runs p-117 and p-118, both having ~42 mol % of ethylene content and *p*-MS/propylene mole ratios of 0/58 and 10/48, respectively, the T_g increases from −43 to −20 °C. A similar result was observed in the pair of runs p-107 and p-110, with 37 mol % ethylene and a smaller difference in *p*-MS/propylene mole ratios of 0/63 and 4.5/58, respectively;

Table 1. Summary of Terpolymerization[a] of Ethylene, Propylene, and *p*-MS by Using [(C_5Me_4)$SiMe_2N$(^{t}-Bu)]$TiCl_2$/MAO

run no.	ethylene/propylene mixing ratio (psi/psi)	monomer concn in the feed (mol/L)			catalyst activity (kg mol^{-1} h^{-1})	copolymer compon (mol %)			T_g (°C)	M_w	M_n	PD
		ethlyene	propylene	*p*-MS		[E]	[P]	[*p*-MS]				
p116	80/40	0.13	0.28	0	4.9×10^3	53.9	46.1	0	−49.4	300 444	134 285	2.2
p117	70/50	0.12	0.35	0	4.7×10^3	41.8	58.2	0	−43.7	284 280	120 813	2.4
P107	50/50	0.10	0.43	0	4.8×10^3	36.2	63.8	0	−35.5			
P115	30/70	0.06	0.60	0	4.9×10^3	13.0	87.0	0	−16.4			
p110	60/60	0.10	0.43	0.1	5.4×10^3	37.0	58.5	4.5	−20.3	184 149	90 634	2.0
p111	60/60	0.10	0.43	0.3	4.9×10^3	39.2	52.9	7.9	−19.1	194 245	97 634	2.0
p112	60/60	0.10	0.43	0.5	5.3×10^3	40.3	48.6	11.1	−9.1	188 861	80 855	2.3
p118	70/50	0.12	0.35	0.3	4.0×10^3	46.4	43.6	10.0	−20.7	198 199	74 890	2.7
p113	50/70	0.08	0.50	0.3	3.5×10^3	32.4	59.2	8.4	−12.4	183 180	91 786	2.0
p120	80/40	0.13	0.28	0.05	4.1×10^3	54.4	43.8	1.8	−45.8	237 702	107 519	2.2
p119	70/50	0.12	0.35	0.05	4.0×10^3	46.1	52.3	1.6	−41.0	195 760	75 028	2.6
p128	85/35	0.14	0.25	0.03	4.4×10^3	56.3	43.1	0.6	−48.6	269 400	104 335	2.6
p127	80/40	0.13	0.28	0.03	3.8×10^3	50.7	48.6	0.7	−45.9	244 331	85 506	2.9

[a] Polymerization conditions: 100 mL of toluene; [Ti] = 2.5×10^{-6} mol; [MAO]/[Ti] = 3000; 50 °C; 15 min.

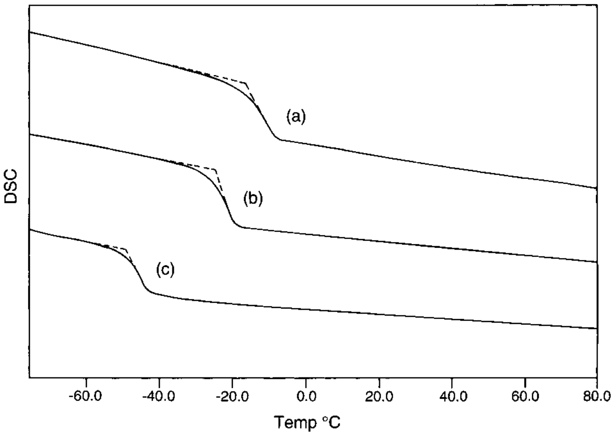

Figure 4. Comparison of DSC curves of EP-*p*-MS terpolymers from (a) run p-112, (b) run p-118, and (c) run p-120.

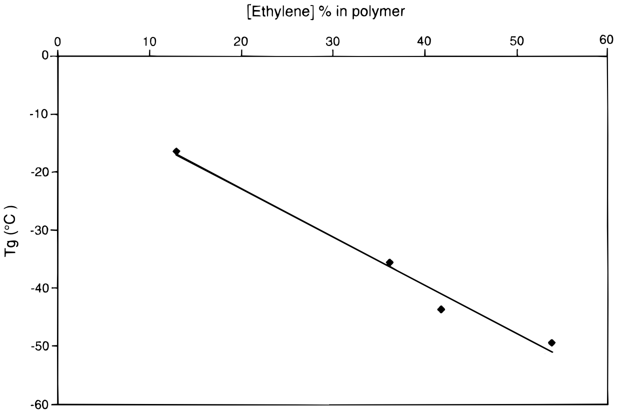

Figure 5. Plots of T_g transition of ethylene/propylene copolymer vs ethylene content.

the T_g change is smaller from −35 to −20 °C. It is very interesting to compare runs p-116 and p-120, both with ideal ~ 54 mol % ethylene content and only very small difference in *p*-MS/propylene mole ratios (0/46 vs 1.8/44); the T_g's are −50 and −45 °C, respectively. The same T_g trend holds, although much smaller. Overall, the composition of EP-*p*-MS material with low $T_g < -45$ °C is very limited, only to the composition with <2 mol % of *p*-methylstyrene content. Despite the random terpolymer structure and the ideal (~55/45) ethylene/propylene ratio, further increase of *p*-MS raises the T_g of the terpolymer to > −40 °C. Obviously, the high T_g's of both propylene (T_g of PP ~0 °C) and *p*-MS (T_g of poly(*p*-MS) ~110 °C) components preclude **I**) from achieving some desirable elastomers containing both high content of reactive *p*-methylstyrene and low T_g (< −45 °C) transition.

Poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene). In EP elastomers, the primary function of propylene units is to prevent the crystallization of ethylene sequences. In traditional Ziegler−Natta polymerization, propylene is a natural choice because it has the closest reactivity to ethylene. However, in terms of effectiveness of preventing crystallization of ethylene sequences and obtaining low T_g material, propylene is not the best comonomer, namely, due to (i) the small CH_3 side group and (ii) relatively high T_g (~0 °C) of the propylene component. In our objective to prepare polyolefin elastomers with low $T_g < -45$ °C and containing a wide concentration range of reactive *p*-MS units, the EP system clearly shows the serious limitations as discussed above. It is very interesting to replace propylene units with high α-olefins, such as 1-octene, which can effectively prevent the crystallization of ethylene sequences (as known in LLDPE[12]) and is a low T_g material[20] with no possibility of self-crystallization. Additionally, it is also very interesting to study the metallocene technology in a very complicated termonomer system, involving ethylene, 1-octene (high α-olefin), and *p*-methylstyrene (aromatic olefin).

The terpolymerization reaction of ethylene, 1-octene, and *p*-methylstyrene was usually started by adding the catalyst mixture of [C_5Me_4($SiMe_2N^tBu$)]$TiCl_2$/MAO to the monomer solution, containing 1-octene and *p*-MS monomers and partially soluble ethylene (with constant pressure) in toluene solvent. The homogeneous solution was observed through the whole copolymerization reaction. Figure 6 compares the GPC curves of the terpolymers prepared under the same ethylene (0.4 mol/L) and 1-octene (0.8 mol/L) and different *p*-methylstyrene (0.1, 0.2, and 0.4 mol/L) concentrations.

Overall, the polymer molecular weight is quiet high (M_w ~ 200 000 and is not significantly dependent on the content of *p*-methylstyrene. The molecular weight distributions (M_w/M_n) < 2.5, similar to most of metallocene-based homo- and copolymers, indicate single-site reaction with good comonomer reactivities. The detailed experimental results, under various reaction conditions, are summarized in Table 2.

Comparing runs p-471/p-470, with similar 1-octene and *p*-MS concentrations and different ethylene content, the molecular weight of the terpolymer is basically proportional to the ethylene content. On the other hand, comparing runs p-471, p-472, p-473, p-474, p-475

Table 2. Summary of Terpolymerization[a] of Ethylene, 1-Octene, and *p*-MS using [(C_5Me_4)$SiMe_2N$(^{t}-Bu)]$TiCl_2$/MAO Catalyst

	monomer concn in the feed (mol/L)				copolymer composn (mol %)						
run no.	E[a]	1-oct	*p*-MS	yield (g)	[E]	[O]	[*p*-MS]	T_g (°C)	M_w	M_n	PD
p465[b]	0.25	0.89	0	7.0	41.4	58.6	0	−61.8	134 515	60 614	2.2
p466[b]	0.25	0.89	0.13	5.2	40.0	54.5	5.6	−51.3	75 496	36 045	2.1
p470	0.20	0.80	0.10	7.3	54.2	43.0	2.7	−56.2	173 989	74 703	2.3
p471	0.40	0.80	0.10	10.1	61.1	36.0	2.9	−58.1	219 752	96 802	2.3
p472	0.40	0.80	0.20	9.8	60.3	36.3	4.4	−55.7	182 185	77 497	2.4
p473	0.40	0.40	0.20	8.2	59.6	34.0	6.4	−50.1	208 920	86 812	2.4
p477	0.40	0.20	0.20	6.4	80.2	14.1	5.7	−37.3	227 461	91 490	2.5
p476	0.40	0.80	0.40	9.0	63.4	29.3	7.3	−50.3	202 085	96 035	2.1
p475	0.40	0.60	0.40	9.1	67.2	24.7	8.1	−48.2	205 124	93 763	2.2
p478	0.40	0.40	0.40	7.9	73.3	18.5	8.1	−44.7	246 300	122 306	2.0
p474	0.40	0.60	0.15	9.0	64.7	31.3	4.0	−55.7	224 476	102 617	2.2
p396[c]	0.52	0.38	0.91	5.6	64.0	18.1	17.7	−25.8	106 954	55 825	1.9
p383[e]	0.13	0	1.82	15.9	60.0	0	40.0	38.3			

[a] Polymerization conditions (unless otherwise specified): 100 mL of toluene; [Ti] = 2.5 × 10^{-6} mol; [MAO]/[Ti] = 3000; 50 °C; 30 min. [b] Solvent, 100 mL of hexane; 60 °C. [c] Solvent, 100 mL of hexane; 30 °C; [Ti] = 2.5 × 10^{-5} mol; [MAO]/[Ti] = 2000; ethylene pressure: 45 psi. [d] Solubility of ethylene: 0.25 mol/L for 29 psi in hexane at 60 °C, 0.20 mol/L for 2 bar, 0.40 mol/L for 4 bar in toluene at 50 °C; 0.52 mol/L for 45 psi in hexane at 30 °C; 0.13 mol/L for 10 psi in hexane at 30 °C. [e] Solvent, 100 mL of hexane; [Ti] = 10 × 10^{-6} mol; [MAO]/[Ti] = 1500; 30 °C; 60 min.

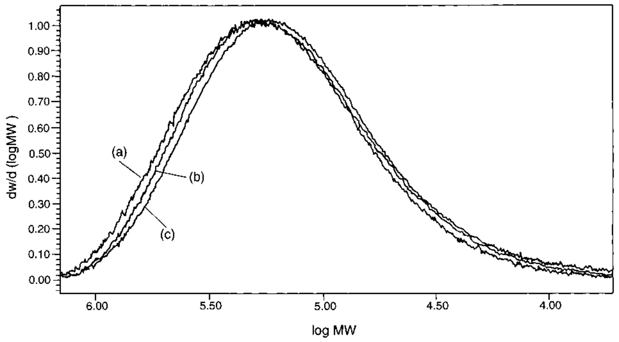

Figure 6. Comparison of GPC curves of three EO-*p*-MS terpolymers prepared from (a) run p-471, (b) run p-476, and (c) run p-472.

and p-476, with the same ethylene concentration and different 1-octene and *p*-MS ratios, the molecular weight of all terpolymers are very similar with no clear correlation pattern. The molecular weight is clearly governed by ethylene concentration, which must be due to the significantly higher reactivity of ethylene among the three monomers. It is interesting to note that the incorporation of 1-octene is also shown some reduction in high *p*-MS concentration conditions (comparative runs p-471 vs p-476 and p-475 vs p-474). Following the enchainment of p-MS, subsequent insertion of ethylene is faster than that of 1-octene, possibly due to steric hindrance at the active site.

The terpolymer composition was determined by ^1H NMR analysis. Figure 7 compares the ^1H NMR spectra of a poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene) terpolymer (run p-470) and two corresponding copolymers, poly(ethylene-*co*-1-octene) (p-465) and poly(ethylene-*co*-*p*-methylstyrene) (p-380), respectively.

The peaks at 0.87 and 2.35 ppm correspond to CH_3 in 1-octene and Ph-CH_3 in *p*-MS, respectively. The minor band 7.0−7.1 ppm is assigned to the aromatic protons in *p*-MS units. Some peaks between 1.0 and 1.7 ppm are the combined chemical shifts, corresponding to CH_2 and CH in the polymer backbone and CH_2 in the 1-octene side chains. The integrated intensity ratio, among three chemical shifts at 0.87, 1.0−1.7, and 7.0−7.1 and the number of protons each chemical shift represent, determines the mole ratio of ethylene/1-octene/*p*-MS. In run p-478, using the same comonomer concentration, the resulting terpolymer having ethylene/1-octene/*p*-MS mole ratio of 9/2/1 clearly indicates the comonomer reactivity sequence of ethylene > 1-octene > *p*-MS. In fact, the ratio is quite consistent with all results (runs p-470, p-471, p-472, p-473, p-474, p-475, and p-476) shown in Table 2, despite very different comonomer feed ratios. This reactivity ratio is very useful for predicting the composition of EO-*p*-MS terpolymer.

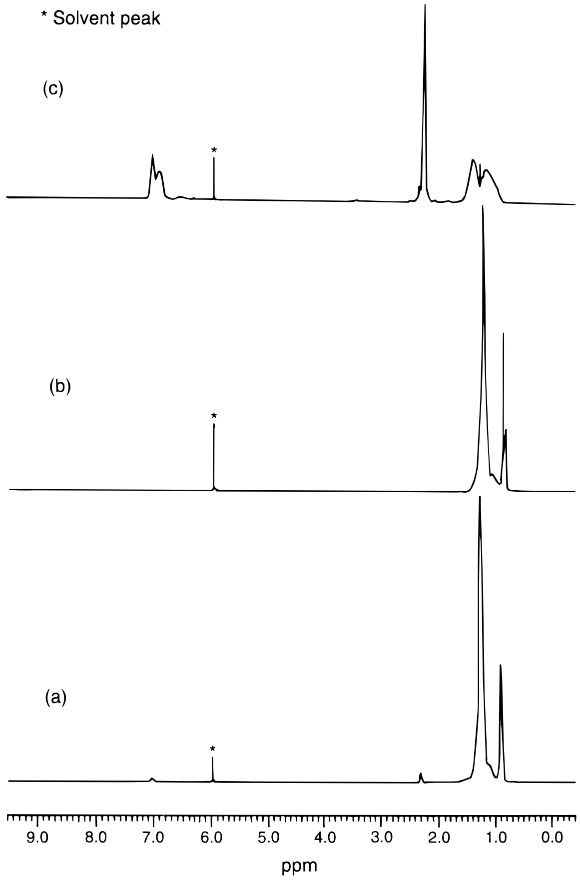

Figure 7. ^1H NMR spectra of (a) poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene) terpolymer (runs p-470) and two corresponding copolymers, (b) poly(ethylene-*co*-1-octene) (p-465), and (c) poly(ethylene-*co*-*p*-methylstyrene) (p-380). (solvent, 1,1,2,2-tetrachloroethane-d_2; relaxation delay, 5 s; room temperature).

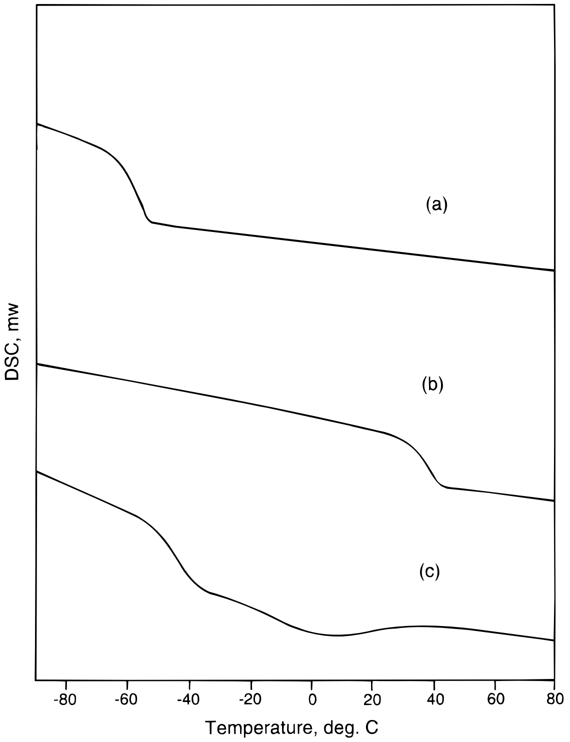

Figure 8. DSC curves of two poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene) terpolymers prepared from (a) run p-472 and (b) run p-478 and (c) poly(ethylene-*co*-*p*-methylstyrene) (run p-383).

The thermal transition temperature of PO-*p*-MS terpolymer was examined by DSC studies. Figure 8 shows the DSC curves of two PO-*p*-MS terpolymers (runs p-472 and p-478) and one poly(ethylene-*co*-*p*-methylstyrene) copolymer (run p-383).

Comparing the curves of runs 472 and 383, both having the same ethylene (~60 mol %) content but different 1-octene/*p*-MS ratios, the T_g changes from >30 °C in run 383 (with no 1-octene) to <−55 °C in run 472 (with 35 mol % 1-octene). The T_g's of co- and terpolymers are summarized in Table 2. It is very interesting to note that the EO-*p*-MS sample with even up to 8 mol % of *p*-MS still shows $T_g < -45$ °C, which is very different from the corresponding EP-*p*-MS copolymer as discussed above. These results clearly show the advantages of 1-octene comonomer (over propylene) which ensures the formation of amorphous polyolefin elastomer with low T_g and high *p*-MS content. In Figure 8c, the DSC curve of terpolymer (p-478) contains a very weak crystalline peak at ~5 °C. Apparently, a total concentration of 1-octene and *p*-MS of more than 30 mol % may be necessary to completely eliminate the crystallization of ethylene sequences.

Experimental Details

Instrumentation and Materials. All ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer with the DISNMR software. The NMR samples were prepared in 1,1,2,2-tetrachloroethane-d_2 which is a good solvent at room temperature for most of terpolymers. Only a few EP-*p*-MS samples with high ethylene content (small crystallinity) required slightly elevated temperature (50 °C) to obtain homogeneous solution and were measured at 50 °C. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution cast films on KBr windows. The molecular weight was determined by high-temperature Waters 150C GPC which was operated at 140 °C. The columns used were μStyragel HT of 10^6, 10^5, 10^4, and 10^3 Å. A flow rate of 0.7 mL/min was used, and the mobile phase was trichlorobenzene. The calibration curve was established by measuring polyethylene standards. Differential scanning calorimetry was measured (with a heating rate of 20 °C/min) on a Seiko Instrument SSC/5200.

All O_2 and moisture-sensitive manipulations were performed inside an argon filled Vacuum Atmosphere drybox equipped with a MO-40-1 dry-train. $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ was prepared as described in the literature.[14] High purity grade ethylene, propylene (MG Industries), and MAO (Albemarle) were used as received. *p*-Methylstyrene and 1-octene (Aldrich) were dried over CaH_2 before distillation. CP grade hexane and toluene were deoxygenated by argon purge before refluxing for 48 h and then distilled over potassium and CaH_2, respectively.

Terpolymerization of Ethylene, Propylene, and *p*-Methylstyrene. The terpolymerization reactions were carried out in a Parr 450 mL stainless autoclave equipped with a mechanical stirrer. In a typical reaction (p-120), the *p*-MS (5 mmol) was added into the reactor with toluene (100 mL) and methylaluminoxane (3 mL) (2.5 M in toluene). The premixed ethylene (80 psi) and propylene (40 psi) were then connected to the reactor. After saturating both ethylene and propylene gases at 50 °C (with ~1:2 ethylene/propylene mole ratio in solution), the total pressure in the reactor was controlled at 30 psi. The polymerization reaction was initiated by charging a $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ (2.5 μmol) toluene solution into the monomer mixture. A constant mixed ethylene/propylene pressure was maintained throughout the polymerization process. To ensure the constant comonomer ratio, the polymerization was terminated within 15 min by adding dilute HCl/CH_3OH solution. The polymer was isolated by filtering and washed completely with MeOH and dried under vacuum at 50 °C for 8 h. About 2.55 g of EP-*p*-MS terpolymer was obtained.

Terpolymerization of Ethylene, 1-Octene, and *p*-Methylstyrene. In a typical terpolymerization (p-478), 1-octene (40 mL) and *p*-methylstyrene (40 mmol) were mixed with 100 mL of toluene and 3 mL of methylaluminoxane (MAO) (2.5 M in toluene) in a Parr 450 mL stainless autoclave equipped with a mechanical stirrer. The sealed reactor was then saturated with 4.0×10^5 Pa (4 bar) of ethylene gas at 50 °C before adding catalyst solution $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ (25 μmol) in toluene to initiate the polymerization. Additional ethylene was fed continuously into the reactor by maintaining a constant pressure of about 4.0×10^5 Pa during the whole course of the polymerization. After 30 min, the reaction was terminated by adding 100 mL of dilute HCl solution in MeOH. The polymer was precipitated in methanol and isolated by filtering. Further purification was carried out by redissolving the polymer back in hexane solution and reprecipitating it in methanol twice. After vacuum-drying at 50 °C for 8 h, 7.94 g of EO-*p*-MS terpolymer was obtained.

Conclusion

The combination of metallocene technology and reactive *p*-methylstyrene comonomer has opened an exciting opportunity to prepare a new class of polyolefin elastomers containing reactive *p*-MS units, which would be very difficult to prepare by Ziegler−Natta catalysts. A broad composition range of new polyolefin elastomers, i.e., poly(ethylene-*ter*-propylene-*ter*-*p*-methylstyrene) and poly(ethylene-*ter*-1-octene-*ter*-*p*-methylstyrene), with relatively high molecular weight and narrow molecular weight and composition distributions have been prepared by $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ catalyst with constrained ligand geometry. In EP-p-MS cases, the T_g transition is very sensitive to the terpolymer composition, and the desirable low $T_g < -45$ °C elastomer is limited to the terpolymers with <2 mol % *p*-MS. On the other hand, the corresponding EO-*p*-MS terpolymer shows a much lower T_g transition. A broad composition range of terpolymers exhibit $T_g < -50$ °C, even the sample containing up to 7 mol % of *p*-MS.

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