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Cross-Linked Polypropylene Prepared by PP Copolymers Containing Flexible Styrene Groups

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ABSTRACT: This paper discusses an effective method to prepare cross-linked isotactic polypropylene (PP-X) with high purity (almost 100% gel content and no contamination) and high melting temperature and crystallinity. The reaction scheme involves a linear poly(propylene-*co*-*p*-(3-butenylstyrene)) copolymer (PP-BSt) containing few pendent styrene groups and the subsequent thermal treatment without any external reagent. The intermediate PP-BSt copolymers were prepared by a specific *rac*-CH$_2$(3-*tert*-butyl-Ind)$_2$ZrCl$_2$/MAO catalyst that not only performs iso-specific propylene insertion but also incorporates BSt units with a preferred α-olefin insertion over styrene moiety. The combined features permit the preparation of linear PP-BSt copolymers with high molecular weight and high catalyst activity, without the presence of hydrogen. The resulting PP-BSt copolymers having some flexible pendent styrene moieties are completely soluble in xylene at elevated temperatures, and the solution case films show active cross-linking activity at temperatures >160 °C by engaging in a Diels−Alder [2 + 4] interchain cycloaddition reaction between the pendent styrene units. Evidently, the flexibility of styrene units is important, which enhances the interchain cyclization to form a complete 3-D network, even with a very small amount of BSt units. In contrast, the corresponding poly(propylene-*co*-*p*-divinylbenzene) (PP-DVB) prepared by the same metallocene catalyst only shows moderate cross-linking efficiency under similar conditions.

Introduction

Cross-linked polyethylene (PE-X) has been widely used in heat-resisting wires, high voltage cables, heat-shrinkable tubes, and hip replacements for many years.[1] Cross-linking offers advantages of increasing temperature stability and resistance to electrical discharge, solvents, creep, and stress-cracking.[2] Although isotactic polypropylene (PP) has higher mechanical strength and a high melting point, and also shows superior heat resistance than PE, the cross-linked polypropylene (PP-X) is not currently practiced in the industry due to the lack of an effective cross-linking method. The common cross-linking processes used in the preparation of PE-X products, involving high energy irradiation (γ-rays and electron beams),[3] peroxide-induced radical reactions,[4] and silane-moisture cure mechanism,[5] are not suitable in PP case due to the inherent difficulties that the PP backbone exhibits prompt degradation[6] under free radical conditions, and the catalyst poison[7] during the transition metal mediated copolymerization of the cross-linkable silane-containing comonomers. There were many attempts to minimize the free radical chain scission by selecting a suitable PP type, and to enhance cross-linking efficiency by grafting multifunctional monomers[8] or moisture-cross-linkable silanes[9] during the free radical processes. However, the resulting PP-X products only showed minor improvement, and the gel contents (insoluble fraction after solvent extraction) were generally below 80%.[10] Both grafting and the chain scission are parallel-competing, which is slightly influenced by the process temperature, the amounts of peroxide, and cross-linking agents. Overall, despite the potential importance—especially for applications under extreme environments (high fields and high temperatures)—it is still a technological challenge to develop a new method to prepare the PP-X network. Scientifically, it would be most fascinating to identify the most suitable polymer structure and nonfree radical process for achieving a cross-linked PP network with high purity.

Experimental Details

Materials and Instrumentation. All O$_2$ and moisture sensitive manipulations were carried out inside an argon filled Vacuum Atmosphere drybox. Methylaluminoxane (MAO) (Ethyl) was purified by vacuum-pumping to remove trimethylaluminium (TMA) at 70−80 °C for 6 h. *rac*-CH$_2$(3-*tert*-butyl-Ind)$_2$ZrCl$_2$ catalyst was prepared by the published procedures.[11] Polymerization-grade propylene (from Matheson Gas) was purified by passage through a column of 4A molecular sieves and calcium carbonate. Vinylbenzyl chloride, *p*-divinylbenzene (Aldrich), and toluene (Wiley Organics) were distilled over CaH$_2$ under argon. Allyl magnesium bromide (1.0 M solution in diethyl ether from Aldrich) and diethyl ether (anhydrous, from EMD) were used as received.

All high-temperature ^{1}H spectra were recorded on a Bruker AM-300 instrument in 1,1,2,2-tetrachloroethane-*d*$_2$ at 110 °C. The melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller with a heating rate of 20 °C/min. The molecular weights of the polymers were determined by intrinsic viscosity of polymer measured in decahydronaphthalene (Decalin) dilute solution at 135 °C with a Cannon-Ubbelohde viscometer. The viscosity molecular weight was calculated by the Mark−Houwink equation: $[\eta] = KM_v^{\alpha}$ where $K = 1.05 \times 10^{-5}$ and $\alpha = 0.80$.[12]

Synthesis of *p*-(3-Butenyl)styrene. To a dry 500 mL round-bottom flask equipped with addition funnel, condenser, and magnetic stir bar was transferred 200 mL (0.2 moles) of allyl magnesium bromide solution. A 20 mL (0.14 mol) aliquot of vinylbenzyl chloride diluted with 50 mL of diethyl ether was added dropwise to allyl magnesium bromide at ice bath temperatures. After the complete addition, the mixture was refluxed and stirred for 12 h. Slowly, 200 mL of distilled water was added to the mixture. The aqueous layer was separated and washed three times with diethyl ether. The organic solvent was removed under vacuum. The obtained crude product was dried with calcium hydride and distilled under vacuum before use. Yield: 20.5 g, 93%. ^{1}H NMR spectrum (Figure S1 shown in the Supporting Information): δ 7.1−7.5 (m,

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Table 1. Summary of PP-BSt Linear Copolymers Containing Pendent Styrene Groups Prepared by *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$/MAO Catalyst[a]

run	propylene/BSt (psi/mL)	temp (°C)	catal activity (kg of PP/mmol of Zr × h)	T_m[b] (°C)	ΔH[b] (J/g)	M_v[c] (kg/mol)	styrene units[d] (mol %)
1	170/0	35	60	158	70	145	
2	170/0.5	35	46	154	61	246	0.16
3	170/1	35	44	151	57	285	0.42
4	170/2	35	38	150	54	231	0.53
5	170/3	35	30	142	49	252	0.73
6	170/4	35	30	140	45	201	0.88
7	170/20	35	18			23	8.6

[a] Catalyst: 4 μmol. Solution: toluene + BSt (50 mL). [b] T_m and ΔH are measured by DSC. [c] M_v is estimated from intrinsic viscosity of polymer/decalin dilute solution at 135 °C. [d] The pendent styrene groups in the incorporated BST units determined by ^1H NMR.

4H, aromatic H), δ 6.7 (m, 1H, aromatic−CH=C), δ 5.9 (m, 1H, C−CH=C), δ 5.7 (d, 1H, aromatic−C=CH), δ 5.3 (d, 1H, aromatic−C=CH), δ 5.1 (m, 2H, C−C=CH_2), δ 2.7 (t, 2H, aromatic−CH_2), δ 2.4 (m, 2H, CH_2).

Synthesis of Poly(propylene-*co*-*p*-(3-butenylstyrene) Copolymers. In a typical copolymerization reaction (run 5 in Table 1), 45 mL of toluene and 0.23 g of solid MAO were charged into a Parr 450 mL stainless autoclave equipped with a mechanical stirrer in a drybox. After removal from the box, the reactor was injected with 3 mL of *p*-(3-butenyl)styrene, then charged with 17 psi propylene to saturate the toluene solution at ambient temperature. About 4 × 10^{-6} mole of *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$ in 2 mL of toluene solution was then injected into the reactor with 170 psi propylene, under rapid stirring, to initiate the copolymerization. Additional propylene was fed continuously into the reactor to maintain a constant pressure (170 psi) during the entire course of the polymerization. To minimize mass-transfer and to maintain the constant feed ratio, the polymerization was carried out with rapid mixing and a short reaction time. After a 3 min reaction time elapse at 35 °C, the polymer solution was quenched with methanol. The resulting poly(propylene-*co*-*p*-(3-butenylstyrene) (PP-BSt) copolymer was washed with tetrahydrofuran (THF). A small amount of the copolymer was vacuum-dried at 50 °C overnight, then weighed in order for us to estimate the catalytic activity—the result of which was 30,250 kg of PP/mol of Zr.h. The copolymer was further analyzed by ^1H NMR (Bruker AM-300 spectrometer) and differential scanning calorimetry (Perkin-Elmer DSC-7 instrument). The DSC curves were recorded in the second heating cycle with a heating rate of 20 °C/min.

Evaluation of Cross-Linking Efficiency. Most of the resulting PP-BSt copolymer (undried) was redissolved in xylene at an elevated temperature, and the heated polymer solution was directly cased into films (thickness 10−20 um) at 100 °C. The resulting films were then heated in a vacuum oven at various temperatures for a predetermined time. The resulting PP-X films were subjected to vigorous solvent extraction by immersing the PP-X films into the boiling xylene for 5 h before removing the films from the solution. The same solvent extraction procedures were repeated at least 3 times, using fresh xylene in each solvent extraction step. This was to ensure removal of the soluble polymer fraction before drying the film and determining the gel content by the percentage of the remaining film weight.

Results and Discussion

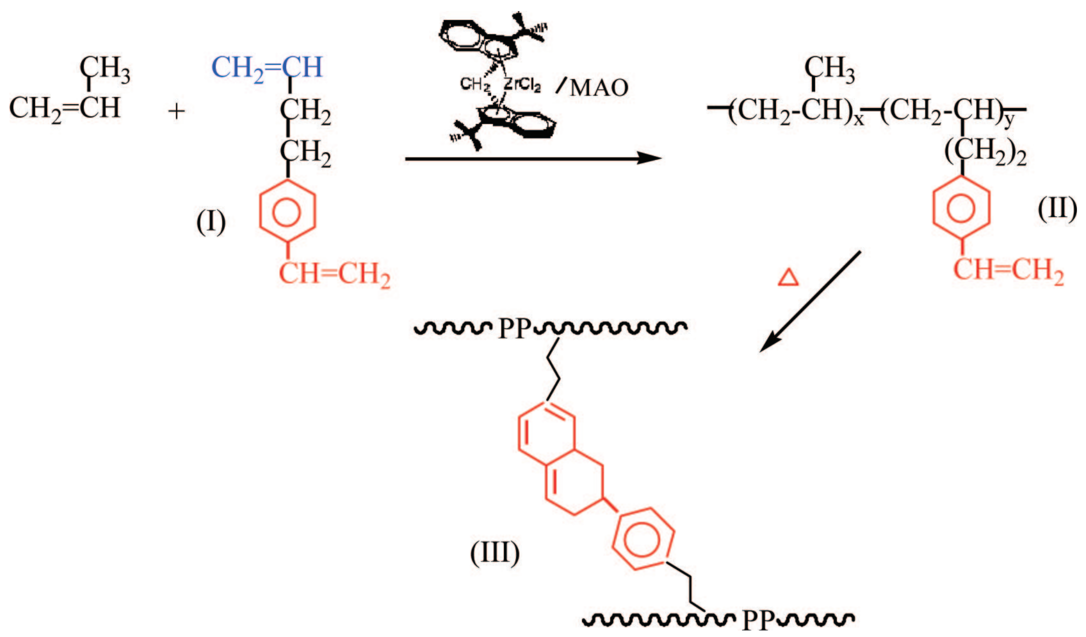
In this paper, we will discuss a new nonfree radical cross-linking mechanism for forming the PP-X network (**III**), which is centered on the poly(propylene-*co*-*p*-(3-butenylstyrene) (PP-BSt) copolymers (**II**) containing several pendent (flexible) styrene units. As first formulated by Mayo,[13] two styrene units can effectively engage in a Diels−Alder [2 + 4] cycloaddition reaction under an elevated temperature, which leads to the semibenzene dimer (cross-linking moiety) as illustrated in Scheme 1.

The poly(propylene-*co*-*p*-(3-butenylstyrene) (PP-BSt) copolymers (**II**) are prepared by a specific C_2-metallocene catalyst, i.e. *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$, which exhibits highly favorable reactivity toward α-olefin over styrene moieties. In other words, most of the BSt comonomers are incorporated through the α-olefin moiety. The incorporated BSt unit contains a pendent styrene moiety in the PP-BSt copolymer (**II**). In the Supporting Information, a control terpolymerization of propylene, 3-butenylbenzene, and *p*-methylstyrene (two comonomers that resemble the two olefinic moieties in BSt, respectively) was carried out under similar reaction conditions. The results show a 3-butenylbenzene/*p*-methylstyrene incorporation mole ratio >45 in the terpolymer. Evidently, the catalyst engages in isospecific 1,2-insertion for both α-olefin and styrene moieties to form high molecular weight PP co- and terpolymers with relatively high catalyst activities without the presence of hydrogen (chain transfer agent). These phenomena are distinctively different from most of C_2-symmetrical metallocene mediated propylene copolymerization reactions, which show almost no catalyst activity in the presence of styrene moieties (without hydrogen), due to the formation of the dormant propagating site after 2,1-insertion of styrene.[14]

Table 1 summarizes a set of experimental results for the *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$ mediated propylene/BSt copolymerizations. The reactions were started by the addition of the metallocene catalyst in the mixed solution containing two monomers and MAO in toluene. The appearance of the reacting polymer solution was highly dependent on the quantity of BSt used. In the high BSt case (run 7 in Table 1), a homogeneous solution was observed throughout the entire copolymerization reaction. In the cases of low BSt (runs 2−6), a slurry solution with white precipitates was observed right in the beginning of the reaction. The precipitation is obviously due to the crystallinity of the copolymer, which has long propylene sequences. It is interesting to note that all runs 2−6 maintain very high catalyst activities, with a notable increase in the average polymer molecular weights. These may be attributed to the relatively high reactivity of BSt in the *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$/MAO catalyst system. The better diffusibility of monomers in the copolymer structures (due to lower crystallinity) may also help to provide a good polymerization condition. On the other hand, as the BSt content increases to a very high level (run 7), the solubility of propylene in the solution may be reduced. In addition, the high concentration of bulky BSt comonomer units in the propagating chain may significantly reduce the catalyst activity and increase the chain transfer reaction that results in lower polymer molecular weight.

Figure 1a shows a typical ^1H NMR spectrum of PP-BSt copolymer (run 5 in Table 1) prepared by *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$/MAO catalyst. In addition to the major chemical shift at 0.95, 1.35, and 1.65 ppm—corresponding to the methine, methylene and methyl groups in polypropylene—there are several minor chemical shifts that are associated with the incorporated BSt comonomer units, including three distinctive olefinic proton chemical shifts at 6.7, 5.7, and 5.2 ppm and two equal intensity aromatic proton chemical shift bands at 7.1−7.2 and 7.3−7.4 ppm. With their relative chemical shift intensities, it is clear that most of the incorporated BSt units in the PP-BSt copolymer contain pendent styrene moieties. The integrated intensity ratio of the chemical shifts between 0.9 and 1.7 ppm and the chemical shifts between 7.1−7.4 ppm, and the number of protons that both chemical shifts represent, determines the concentration of BSt in the PP-BSt copolymers (**II**). It is interesting to note that this PP-BSt copolymer is very different from the long chain branched polypropylene (LCBPP)[15] prepared by the same propylene/*p*-(3-butenyl)styrene copolymerization reaction but with the presence of hydrogen and the *rac*-

Scheme 1. ***rac*-CH_2(3-*tert*-butyl-Ind)$_2$ZrCl$_2$/MAO Mediated Copolymerization of Propylene and *p*-(3-Butenylstyrene), and the Subsequent Inter-Chain Thermal Cross-Linking Reaction between Two Pending Styrene Groups in the Copolymers**



Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyst system. The resulting LCBPP polymers contain various concentrations of “T” shaped branches.[15]

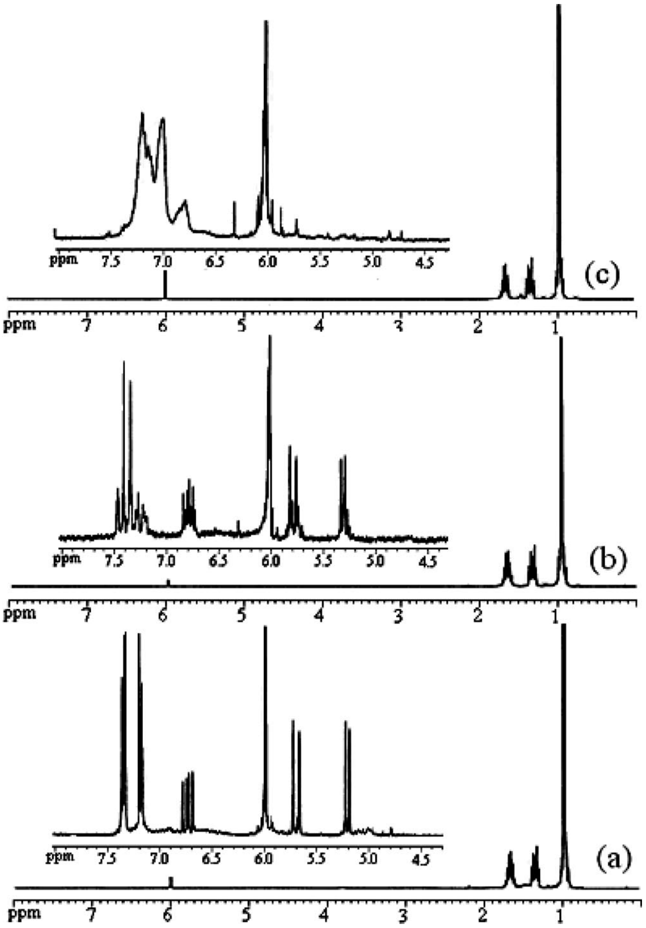
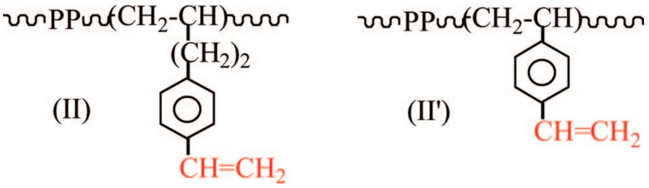


Figure 1. ^{1}H NMR spectra of (a) a PP-BSt copolymer (**II**) containing 0.73 mol % of *p*-(3-butenyl)styrene, (b) a PP-DVB copolymer (**II′**) containing 1 mol % DVB units, and (c) the soluble fraction after thermal cross-linking reaction of PP-DVB copolymer (**II′**).

Scheme 2. Molecular Structure Comparison between PP-BSt (II) and PP-DVB (II′) Copolymers



The PP-BSt copolymers (**II**) are completely soluble in xylene at an elevated temperature, and the polymer films are obtained by solution casting at the elevated temperature. The resulting films were then used to study the cross-linking reaction. For comparison, a new set of poly(propylene-*co*-divinylbenzene) (PP-DVB) copolymers were also prepared by the same *rac*-CH_2(3-*tert*-butyl-Ind)$_2$ZrCl$_2$/MAO catalyst system and were evaluated under the same thermal cross-linking condition. The detailed experimental procedures and results for the preparation of PP-DVB copolymers are discussed in the Supporting Information. As illustrated in Scheme 2, the major difference between PP-BSt (**II**) and PP-DVB (**II′**) copolymers is the flexibility of styrene cross-linkers; the former one contains two flexible methylene spacers that may be important for enhancing the interchain cycloaddition reaction during the formation of x-PP products under solid state conditions.

Both solution-cased PP-BSt (**II**) and PP-DVB (**II′**) copolymer films were heated in an oven at a specific temperature and for a predetermined time. The resulting PP-X films were subjected to a vigorous solvent extraction to remove the soluble fraction that was not fully cross-linked into the network structure. Figure 2 shows three comparative graphs—which compare the gel (insoluble) fraction of several PP-BSt (**II**) copolymers (runs 2−6 in Table 1) after thermal cross-linking at 200 °C for 5 and 60 min—and four PP-DVB (**II′**) copolymers after thermal cross-linking at 200 °C for 60 min, respectively. Evidently, the cross-linking reaction was very effective for the PP-BSt copolymer (**II**) having more than 0.7 mol % of styrene content. Within 5 min, the PP-X samples reached more than 95% gel fraction (Figure 2, parts a and b) and the longer thermal treatment achieved almost completely cross-linked PP-X products. Overall,

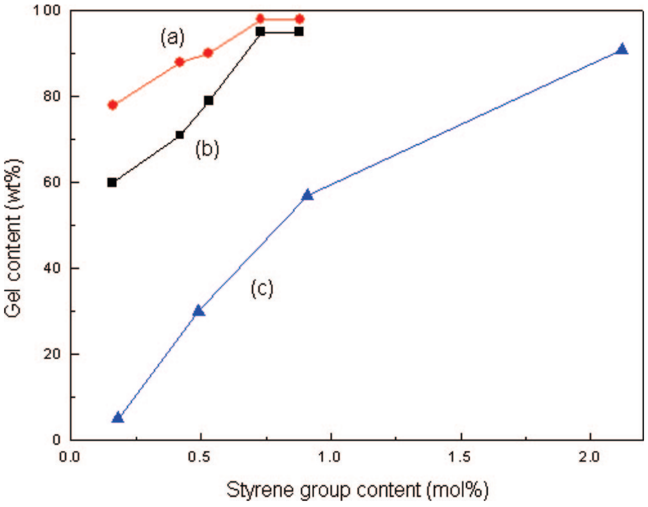


Figure 2. Gel content vs cross-linker concentration for PP-BSt copolymers (**II**) after thermal treatment at 200 °C for (a) 60 min and (b) 5 min and (c) PP-DVB copolymers (**II′**) treated at 200 °C for 60 min.

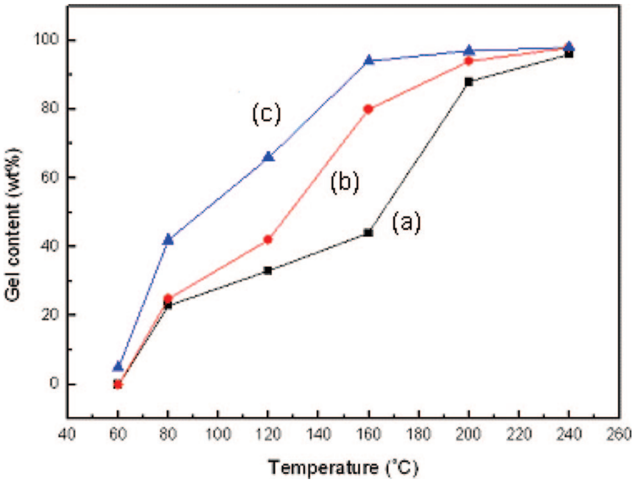


Figure 3. Gel content after thermal treatment for 1 h under various temperatures for three PP-BSt copolymers (**II**), with pendent styrene concentration of (a) 0.42 mol % (run 3), (b) 0.73 mol % (run 5), and (c) 8.6 mol % (run 7), respectively.

the cross-linking efficiency is significantly higher than the reported PP-X cases as well as commercial PE-X products prepared by free radical mediated processes.

It is interesting to understand the detailed cross-linking condition (scope and limitations) of the PP-BSt (**II**) copolymers. Figure 3 compares the gel content after thermal treatment for 1 h under various temperatures for three PP-BSt copolymers with pendent styrene contents of (a) 0.42 mol % (run 3), (b) 0.73 mol % (run 5), and (c) 8.6 mol % (run 7), respectively. The thermal regiospecific [2 + 4] cycloaddition reaction between two styrene units starts at a relatively low temperature (~80 °C). However, the rate of the cross-linking reaction is highly dependent on the temperature and copolymer composition. In the low temperature range <160 °C (below melting temperature) with limited chain motion, the cross-linking efficiency of the PP-BSt (**II**) copolymer is dependent on the concentration of pendent styrene (cross-linker) units. High cross-linker content is needed in order to observe an appreciable cross-linking reaction. It seems important to anneal the copolymer film >160 °C (beyond its melting temperature) to achieve high cross-linking efficiency, which is particularly important for the PP-BSt copolymer (**II**) with <1 mol % of pendent styrene units.

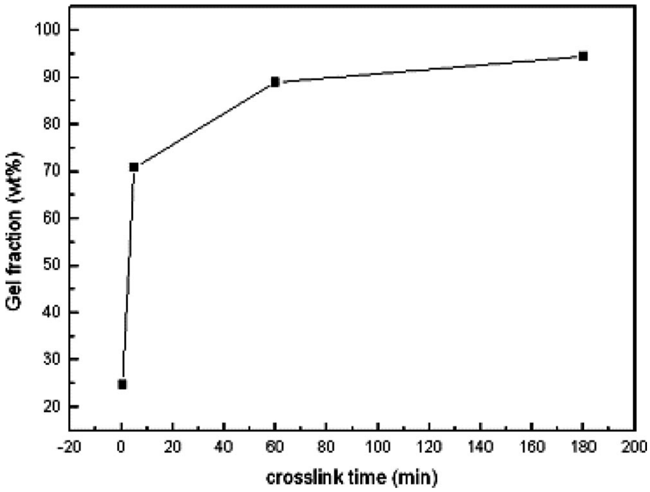


Figure 4. Gel content vs thermal treatment time at 200 °C for PP-BSt copolymer containing 0.42 mol % of pendent styrene units (run 3).

Beyond 200 °C, the interchain reaction can effectively take place. Despite very different styrene contents, all three copolymers exhibit near completely cross-linked PP-X products. Figure 4 shows the gel content vs thermal treatment time at 200 °C for a PP-BSt copolymer (**II**) having only 0.42 mol % of pendent styrene units. This copolymer achieves 95% gel content after 3 h at 200 °C.

Understanding the effect of the copolymer microstructure—especially the flexibility of styrene cross-linkers—toward the cross-linking efficiency is an interesting undertaking. Figure 2c shows the gel content of the corresponding PP-DVB (**II′**) copolymers with various vinyl contents treated under the same cross-linking condition. With the same content of styrene units and thermal treatment, the PP-DVB (**II′**) copolymers clearly show much lower gel contents and lower cross-linking efficiencies. The maximum gel content observed was ~90%, which requires that the PP-DVB (**II′**) copolymer contains more than 2 mol % of DVB units and longer thermal treatment. Furthermore, we examined the recovered soluble fraction after solvent extraction. Parts b and c of Figure 1 compare the ^{1}H NMR spectra of the PP-DVB (**II′**) copolymer containing 1 mol % DVB content and its soluble fraction after the cross-linking reaction, respectively. The three distinctive chemical shifts at 6.7, 5.7, and 5.2 ppm—corresponding to the pendent styrene moieties—completely disappeared, indicating the complete cycloaddition reaction between styrene units. Apparently, the polymer chain bonded styrene units in the PP-DVB copolymer (**II′**) have no problem in engaging in the cycloaddition reaction. However, some reactions may have occurred within the same polymer chain, which reduces the cross-linking efficiency. The flexibility of styrene cross-linkers in the PP-BSt copolymer (**II**) is very important for achieving a complete PP-X network.

Figure 5 compares two sets of DSC curves before and after thermal cross-linking reactions for runs 2 and 5 samples, respectively. The introduction of cross-linking structures slightly reduces melting temperature and crystallinity. The single (relatively shape) melting peak in the x-PP sample—with monochrometic reductions of melting temperature and crystallinity vs the cross-linking density—also implies the homogeneity of the x-PP film. Overall, the x-PP films show good crystallinity, high melting temperature, excellent mechanical strength, and high thermal stability. The detailed structure—property relationship is under investigation. We are also very interested in their electric breakdown strength under high electric field conditions.

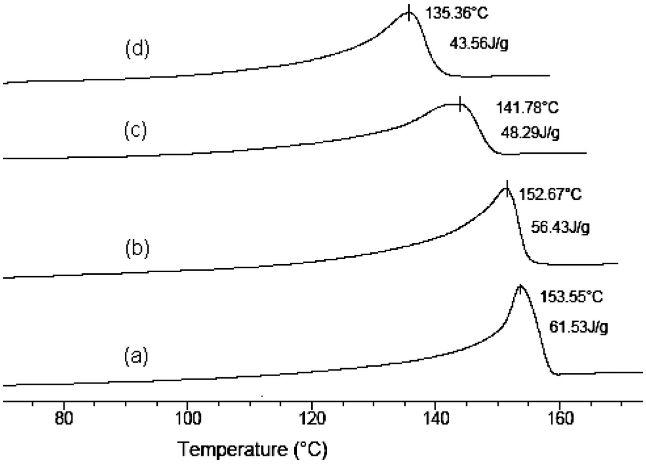


Figure 5. Comparison of DSC curves for two PP-BSt copolymers (**II**) before and after thermal cross-linking reaction at 200 °C for 60min, including (a) run 2 without cross-linking, (b) run 2 with cross-linking, (c) run 5 without cross-linking, and (d) run 5 with cross-linking.

Conclusion

The linear PP-BSt copolymers, containing some flexible pendent styrene moieties, have been prepared by a specific *rac*-CH_2(3-*tert*-butyl-Ind)$_2ZrCl_2$/MAO mediated copolymerization of propylene and *p*-(3-butenylstyrene). The resulting PP-BSt copolymers are completely soluble in xylene at elevated temperatures, and the solution-cased PP-BSt films exhibit an effective thermal cross-linking reaction via the regiospecific [2 + 4] interchain cycloaddition reaction between the pendent styrene units (without any external reagent). Clearly, the elevated temperature (>160 °C) and flexibility of styrene units (cross-linkers) are significantly advantaged through the enhancing of the interchain cycloaddition to form a 3-D network, even with a very small amount of BSt units. This self-cross-linking process prepares PP-X films with high purity (free of contaminant). For many electric applications, such as PP film capacitors, the clean PP film is essential to achieving high breakdown strength and low energy loss. The results will be discussed in the near future.

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Supporting Information Available: Figures showing the ^{1}H NMR spectra of *p*-(3-butenyl)styrene monomer, the resulting PP terpolymer, and the PP-DVB copolymer and text giving detailed experimental procedures and results of the propylene/3-butenylbenzene/*p*-methylstyrene terpolymerization reaction and the preparation of poly(propylene-*co*-divinylbenzene) (PP-DVB) copolymers including a table of results. This material is available free of charge via the Internet at http://pubs.acs.org.

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