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Communications to the Editor

Synthesis of Poly(1-octene-*g*-methyl methacrylate) Copolymers

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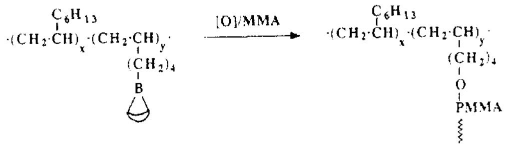
Despite many commercial applications, polyolefins have been suffering a major deficiency, mainly due to poor interaction with other materials. The inert nature of polyolefins significantly limits their end uses, particularly those in which adhesion or compatibility with other functionalized polymers is paramount. In polymer blends, the mixture of two incompatible polymers usually results in a large and irregular phase separation and poor interfacial adhesion. The physical properties of such polymer blends are usually very undesirable. It is known that addition of their block or graft copolymers as a compatibilizer[1,2] can significantly alter the morphology of the polymer blend by reducing domain sizes and increasing interfacial interaction. Despite the potential uses, the availability of graft and functionalized polyolefin copolymers is very limited, mainly due to the difficulties[3,4] in their preparation.

This paper describes a new chemistry to prepare graft copolymers of polyolefins containing a polyolefin backbone and several functionalized polymers in the side chains. The chemistry is based on a graft-from reaction using a borane-containing polymer. Under oxidation conditions, the borane group becomes a reactive site for free-radical polymerization. With the appropriate choice of borane group and reaction conditions, the free-radical-polymerized polymers are chemically bonded to the side chains of the polyolefin with controllable compositions and molecular structures. The graft-from reaction is illustrated in eq 1.

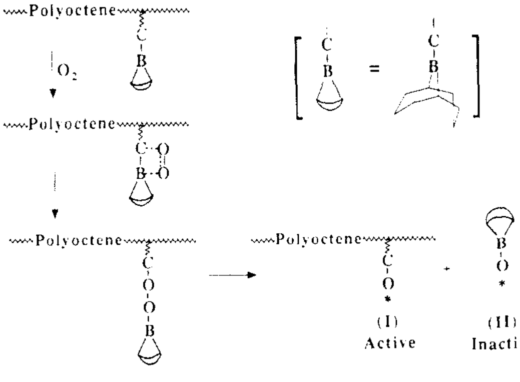


(1)

Poly(1-octene-*g*-MMA) (MMA = methyl methacrylate) is used to demonstrate the idea. One interesting aspect of polyoctene as the backbone is its elastic property, T_g = −60 °C with a low plateau modulus. In addition, the completely saturated polymer structure offers good chemical and thermal stability; its decomposition temperature is above 350 °C in air. Poly(1-octene-*g*-MMA) could be a useful new thermoplastic elastomer.

Obviously, the success of this graft-from chemistry is determined by the oxidation reaction of the borane group. It is essential to form active free-radical species selectively at the side chain of polyoctene. During the free-radical polymerization, the PMMA polymer grows from the side chain and becomes the major part of the side chain. It is known that alkylborane can be effectively oxidized to form free-radical species[5,6] such as peroxy, alkoxy, and alkyl radicals. The detailed reaction mechanism is still controversial. In the late fifties, the oxidation of triethylborane[7,8] was used as a means to initiate free-radical polymerizations. The major advantage of borane initiators is the ability to carry out free-radical polymerization at room temperature. Peroxides and azo initiators when used alone usually require considerable heat input to decompose and thereby to generate free radicals. Elevation of the temperature often causes a significant reduction in the molecular weight of the polymer accompanied by the loss of important properties of the polymer.

Our initial thinking to use alkyl-9-BBN (9-BBN = 9-borabicyclononane) in the preparation of graft copolymer is illustrated in eq 2. By exposing poly(octene-*co*-*B*-5-hexenyl-9-BBN) to oxygen at room temperature, the B–C bonds will be oxidized to the peroxide group. With a stoichiometric amount of oxygen to alkyl-9-BBN group, the peroxyl group may be selectively inserted into the B–C bond located in the side chain of poly(1-octene), instead of in the bicyclononane, which has a stable double-chair-form structure. In other words, this selectivity is due to the unfavorable ring strain increase in the insertion of the peroxyl group into the chair-form of the six-membered ring. The peroxyl group can further decompose into alkoxy radical I and borinate radical II at room temperature. The alkoxy radical I in the polymer side chain is a very active free-radical initiator. On the other hand, the radical II in the borinate group is inactive because of stabilization by the boron atom. With the coexistence of methyl methacrylate monomers, the alkoxy radicals I in the copolymer initiate free-radical polymerization and result in poly(methyl methacrylate) chains covalently bonded to the polyoctene backbone.



(2)

The poly(1-octene) containing alkyl-9-BBN was prepared by direct copolymerization[9,10] of *B*-5-hexenyl-9-BBN and 1-octene in a Ziegler–Natta polymerization. In a typical example, a 500-mL flask was charged with a Ziegler–Natta catalyst, $TiCl_3AA$ (0.4 mmol, 0.08 g) and $AlEt_2Cl$ (2.5 mmol, 0.3 g), and toluene (50 mL) under an argon atmosphere. After aging for 30 min with sufficient mixing, the monomer mixture of 1-octene (11.2 g) and *B*-5-hexenyl-9-BBN (0.101 g) in 150 mL of toluene, monomer mole

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ratio of 1000:5, was added to the catalytic solution. The copolymerization reaction was observed within 5 min with a visible increase in viscosity. The solution was stirred at room temperature for 1 h before the reaction was terminated with 2-propanol (300 mL). The precipitate was collected by filtration, washed with 2-propanol three times, and vacuum dried overnight to yield 6.5 g of copolymer. The trialkylborane in the copolymers was characterized by ^{11}B NMR with a chemical shift at $\delta = 87$ from $BF_3{\cdot}OEt_2$. Due to the slight difference in the polymerization reactivity[8] between 1-octene and *B*-5-hexenyl-9-BBN, the concentration of organoborane groups in copolymer was about 0.3 mol %.

In a typical graft-from reaction, 2 g of poly(1-octene-*co*-*B*-5-hexenyl-9-BBN) containing 0.3 mol % of hexenyl-9-BBN was dissolved in 50 mL of THF and then mixed with 10 mL of pure MMA monomer in a 200-mL flask. A septum was installed on the flask to isolate the mixture from air. The reaction occurred after injection of 5 mL of air into the flask by syringe. With constant stirring, a notable increase in solution viscosity was observed within a few minutes. The reaction was allowed to continue at ambient temperature, and the mixture became very sticky in 1 h. After 4 h, the reaction was terminated by exposing the reaction mixture to the atmosphere. The product was precipitated by adding 100 mL of 2-propanol, then collected by filtration, and finally washed with 2-propanol three times. To remove possible PMMA homopolymer from the precipitate, solvent extraction was carried out by refluxing acetone through the product for 24 h. Only a negligible amount of PMMA was obtained. The acetone-insoluble polymer is poly(1-octene-*g*-MMA) with a significant weight increase, about 3.4 g after drying. To ensure the efficiency of separation, a control experiment was also carried out by mixing equal amounts of two homopolymers, poly(1-octene) and PMMA, in THF. This polymer mixture was then precipitated in 2-propanol and was subjected to the same extraction conditions using refluxing acetone. Most of the PMMA homopolymer was recovered in the acetone-soluble fraction, with no detectable amount of PMMA left in poly(1-octene).

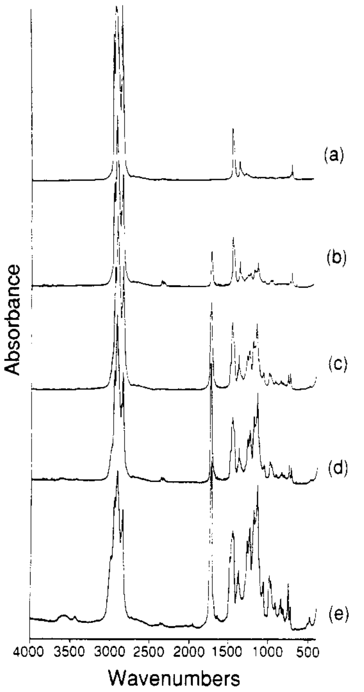

Figure 1. IR spectra of poly(1-octene-*co*-hexenol) with 0.3 mol % of hydroxyl groups (a) and poly(1-octene-*g*-MMA) with 10 (b), 30 (c), 50 (d), and 65 mol % of MMA (e).

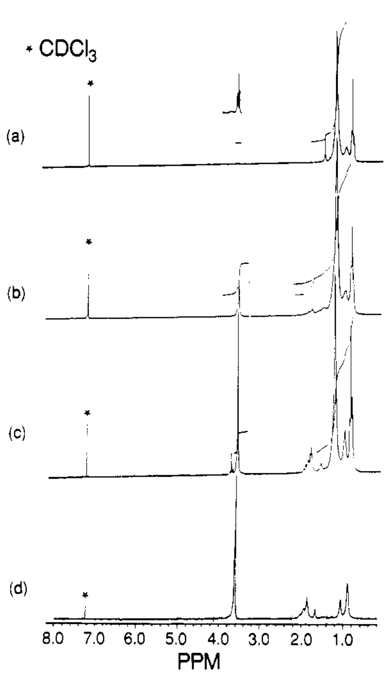

Figure 2. ^{1}H NMR spectra of homopolymer and copolymers: poly(1-octene-*co*-hexenol) with 0.3 mol % of hydroxyl groups (a), poly(1-octene-*g*-MMA) copolymers containing 21 (b) and 65 mol % of MMA (c), and PMMA homopolymer (d).

The graft copolymers are soluble in THF at room temperature, which indicates that a negligible amount of free-radical coupling reaction takes place in the termination step of PMMA polymerization. Figure 1 shows the IR spectra of four poly(1-octene-*g*-MMA) copolymers with various mole percents of MMA (10% (b), 30% (c), 50% (d), and 65% (e)). These spectra are compared with the spectrum of poly(1-octene-*co*-hexenol) (a). All polymers were prepared from poly(1-octene-*co*-*B*-5-hexenyl-9-BBN) with 0.3 mol % of *B*-5-hexenyl-9-BBN. The concentrations of PMMA in the copolymers are proportional to the reaction time. Due to the very high susceptibility of alkylboranes to air oxidation, poly(1-octene-*co*-*B*-5-hexenyl-9-BBN) was not structurally characterized, which was instead quantitatively oxidized under mild conditions, using alkaline H_2O_2, to yield poly(1-octene-*co*-hexenol). The IR spectrum of poly(1-octene-*co*-hexenol) in Figure 1a shows negligible absorption intensity of the hydroxyl group. In fact, the spectrum is almost identical to that of poly(1-octene) homopolymer. Despite the low concentration of borane groups in polyoctene, the graft-from reaction was very effective. A new absorption peak ($\nu_{C=O}$ = 1710 cm^{-1}), corresponding to the carbonyl group in PMMA, grew with reaction time. As high as 65 mol % of PMMA in poly(1-octene-*g*-MMA) copolymer (Figure 1e) was obtained. The qualitative compositions were determined by ^{1}H NMR. Figure 2 shows the ^{1}H NMR spectra of poly(octene-*g*-MMA) copolymers, poly(1-octene-*co*-hexenol), and PMMA. The pure PMMA homopolymer was obtained by a control reaction, using hexenyl-9-BBN initiator under similar free-radical polymerization conditions. In Figure 2a, a small triplet peak at 3.5 ppm, corresponding to the methylene group in primary alcohol (CH_2OH), indicates 0.3 mol % of hexenol in poly(1-octene-*co*-hexenol). The chemical shifts at δ 3.6 and 1.8 in Figure 2b,c correspond to methyl groups (CH_3O) and methylene groups, respectively, in PMMA. The chemical shifts between 1.6 and 0.7 ppm include all protons in polyoctene and three protons in the methyl group located on the PMMA backbone. The quantitative analysis of the copolymer composition was calculated by the ratio of the two integrated intensities between $\delta = 3.6$ and $\delta = 1.6$–0.7 and the number of protons both chemical shifts represent. Spectra b and c of Figure 2 indicate 21 and 65 mol % of PMMA, respectively, in poly(1-octene-*g*-MMA) copolymers.

The graft-from reaction also implies that in a GPC study only a single peak at high molecular weight will be observed in the graft copolymer, with no peak for the PMMA homopolymer, which is expected to have a molecular weight of about 60 000. Unfortunately, the molecular weight of the graft copolymer is difficult to measure by simple GPC and RI detector, especially in this case, which involves high molecular weight ($>1.5 \times 10^6$) poly(1-octene-*co*-hexenyl-9-BBN) as the starting material. The average chain length of PMMA can be estimated by the weight increase from the graft-from reaction and the moles of borane groups in poly(1-octene-*co*-B-5-hexenyl-9-BBN). Assuming all organoborane groups (0.3 mol %) are involved in the graft-from reaction after a long reaction time, the average molecular weight of PMMA in the resulting poly(1-octene-*g*-MMA) with 65 mol % of PMMA is about $M_n = 61\,000$. In a control reaction using similar reaction conditions and hexanyl-9-BBN initiator, the PMMA homopolymer has a similar molecular weight, $M_n \sim 65\,000$. It is logical that each PMMA chain has a similar molecular weight despite the reaction time. The prolongation in reaction time increases the oxidation reaction of the borane group and increases the graft density. The final graft density is dependent on the borane concentration in poly(1-octene–*co*-*B*-5-hexenyl-9-BBN) copolymer. Fortunately, our previous study[10] offers us a whole series of poly(1-octene-*co*-hexenyl-9-BBN) homogeneous copolymers with various concentrations of the borane group.

It is interesting to note that the rate of graft-from reaction can also be controlled by reaction conditions, especially the amount of oxygen introduced. The simple mixture of poly(1-octene-*co*-*B*-5-hexenyl-9-BBN) and MMA monomers does not offer any detectable amount of graft copolymer. On the other hand, excess oxygen over the stoichiometric amount of oxygen to alkyl-9-BBN groups resulted in some PMMA homopolymer. Usually, the graft-from reaction was started by adding slightly below a stoichiometric amount of oxygen (vs. borane group) in the reactor. Under unperturbed conditions, the diffusion of oxygen into polymer solution was quite slow, with no obvious change in solution viscosity observed even after 2 h of reaction time. However, the reaction became very vigorous when the reaction mixture was shaken. Within a few minutes, the polymer solution almost became a gel, and ^{1}H NMR spectrum showed a high incorporation of PMMA. Under normal agitation conditions using a stir bar, complete reaction requires 3–4 h, and the concentration of PMMA is proportional to reaction time.

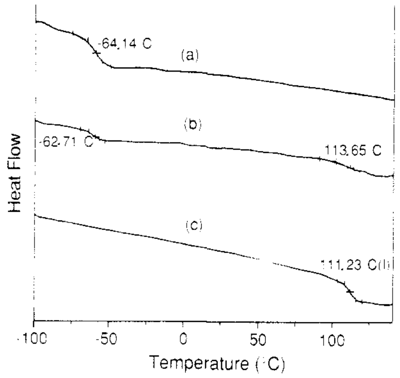

Figure 3. DSC curves of poly(1-octene-*co*-hexenol) with 0.3 mol % of hydroxyl groups (a), poly(1-octene-*g*-MMA) copolymer with 50/50 composition (b), and PMMA homopolymer (c).

The thermal properties of the copolymer were determined by DSC measurement. The samples were first heated to 170 °C and then rapidly cooled to −150 °C. The curves shown in Figure 3 are heating curves obtained from these quenched samples at a heating rate of 20 °C/min. Two glass transition temperatures (T_g), −63 and +113 °C, exist in poly(1-octene-*g*-MMA) copolymer with 50/50 composition. Both T_g's are the same as those of the two corresponding homopolymers. This indicates clear phase separation between the polyoctene backbone and the PMMA side chains. The control of graft density in the copolymer offers enough consecutive sequences of octene units in the polymer backbone to form separate domains. The detailed morphology and mechanical properties of the graft copolymer and homopolymer blends are currently under investigation.

In this paper, a novel synthetic route to a new graft copolymer, poly(1-octene-*g*-PMMA), has been described. The chemistry involves borane-containing polyoctene and graft-from free-radical polymerization. With the appropriate choice of borane group and reaction conditions, a desirable molecular structure of poly(1-octene-*g*-MMA) copolymer can be obtained with high graft efficiency. It is obvious that this chemistry can be easily applied to many polymer systems, even telechelic polymers with borane terminal end groups, to prepare multiple-phase polymer structures. Overall, the chemistry is very effective and the process is quite simple.

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Registry No. (MMA)(*B*-5-hexenyl-9-BBN)(1-octene) (graft copolymer), 142723-96-4.