LIVING RADICAL POLYMERIZATION FOR THE PREPARATION OF WELL-DEFINED FUNCTIONAL POLYOLEFIN SEGMENTED COPOLYMERS

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1. INTRODUCTION

Free radical polymerization is widely used in industry for the preparation of an extensive spectrum of materials because of the availability of a wide range of radically polymerizable monomers, mild reaction conditions, and tolerance to impurities such as moisture. The development of living radical polymerizations (LRPs)[1-3] in the 1990s provided a revolutionary broadening of the spectrum of the materials capable of being prepared by radical processes. Through LRP, it became possible to control the molecular weight (MW) and molecular weight distribution (MWD) to prepare polymers that retain chain end-functionality and exhibit well-defined architectures, such as block, graft, or star shaped copolymers,[4] from free radically polymerizable monomers using a free radical polymerization process. Three representative mechanisms have been investigated in a search for better LRP systems, nitroxide mediated polymerization (NMP),[5] reversible addition-fragmentation chain transfer (RAFT) process,[6] and atom transfer radical polymerization (ATRP).[7-10]

Atom transfer radical polymerization (ATRP)[7] has developed into one of the most robust synthetic tools within the spectrum of LRP processes.[4,11-15] The basis of ATRP is the reversible transfer of a radically transferable atom, typically a halogen atom, from a monomeric or polymeric alkyl (pseudo)halide to a transition metal complex in a lower oxidation state, forming an organic radical and a transition metal complex in a higher oxidation state. In ATRP systems the activation rate constant (k_a) is typically in the range of ~ 10^0 L mol^{-1} s^{-1} and the deactivation rate constant (k_d) is in the range of ~ 10^7 L mol^{-1} s^{-1} (Figure 1).[16] Through this fast reversible activation and deactivation procedures, the radical concentration in the system can be sufficiently lowered to minimize undesirable radical termination reaction, which leads to a living system. NMP and RAFT methods follow similar procedure to accomplish LRP system using different agent such as nitroxide and dithioester.

LRP has been used for many functional monomers, macromonomers and end-functional polymers

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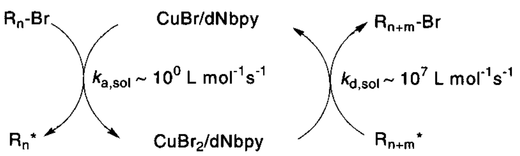

Figure 1. Typical catalyst cycle for Atom Transfer Radical Polymerization (ATRP).

to produce various kinds of polymer architectures. One of the interesting applications is offered by using macroinitiator or macromonomer prepared by other mechanisms, which offers a new way to prepare well-defined functional polyolefins.

Polyolefins are important commodity polymers with the largest volume of business due to their low cost and good mechanical properties. However, the lack of functional groups has limited many of their end uses, particularly when the interaction with other materials is important.[17] One of the approaches to solve this problem is the direct copolymerization of olefins with polar monomers through coordination mechanism using transition metal catalysts.[18] However, these catalysts generally suffered from low tolerance to polar vinyl monomer due to their oxophilic nature.[18] Instead, the preparation of segmented copolymers such as block or graft polyolefin copolymers containing functional segments has been extensively investigated. By this method, the loss of the original properties of polyolefins can be minimized while the functional segments increase the interaction with a broad range of polar materials.[17] The functional segmented polyolefins easily find its applications in many important markets as a compatibilizer, dispersant, coating materials and so on.

In this paper, examples on the preparations of polyolefin graft or block copolymers through LRP are presented. The commodity polymers such as polyethylene, polyisobutylene and ethylene-propylene-diene rubber (EPDM) are combined with more polar segments such as acrylate, methacrylate and isoprene to yield functionalized polyolefins.

2. Results and discussion

2.1 Polyethylene based copolymers

Grafting-through method using polyethylene macromonomer can be applied to prepare polyethylene graft copolymers. For example, ATR copolymerization of polyethylene macromonomers with polar monomers has been successfully conducted to prepare corresponding graft copolymers.[19] A branched polyethylene macromonomer with a methacrylate functionalized end-group was prepared through Pd-mediated living olefin polymerization. The macromonomer was then copolymerized with n-butyl acrylate by ATRP (Figure 2).

GPC traces of the graft copolymers exhibited narrow molecular weight distributions indicative of a controlled reaction. At low macromonomer concentrations, the reactivity ratios of macromonomer to n-butyl acrylate were similar to those for methyl methacrylate (active end group of polyethylene macromonomer) to n-butyl acrylate. Increased viscosity of the reaction solution resulting from increased macromonomer concentrations caused a lowering of the apparent reactivity ratio of the macromonomer to n-butyl acrylate, indicating an incompatibility between non-polar polyethylene segments and a polar poly(n-butyl acrylate) backbone.

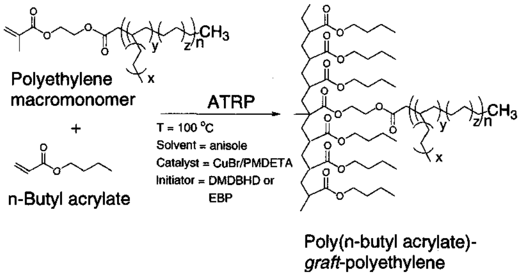

Figure 2. ATRP of n-butyl acrylate with polyethylene macromonomer for the preparation of poly(n-butyl acrylate)-*graft*-polyethylene.[19]

The incompatibility was more pronounced in the solid state, exhibiting cylindrical nanoscale morphology as a result of nanophase separation as observed by atomic force microscopy. Figure 3 presents typical height and phase images of poly (n-butyl acrylate)-*graft*-polyethylene films on bare mica recorded under various conditions. Images acquired with the increased tapping force (light tapping) revealed the presence of three types of features: (i) circular and (ii) elongated, curved domains with diameters (widths) in the range 50-100 nm and (iii) irregularly shaped "bumps". The domains appeared as depressed (darker) regions in height images and as brighter regions in phase shift images (see insets).

The bulk phase behavior of block and graft copolymers is governed by xN, the product of the binary Flory-Huggins segmental interaction parameter and number of segments in the copolymer chain.[20] Estimates based on linear polyethylene, the system in this study is characterized by xN $\approx$ 80 (>> 10), therefore the observed nanoscale morphology is a result of nano-phase separation. The observed nanoscale features can be identified as cylindrical domains of the minority component (polyethylene) oriented either (i) perpendicular or (ii) parallel to the film surface. Irregularly-shaped "bumps" represent most likely the residual macromonomer.

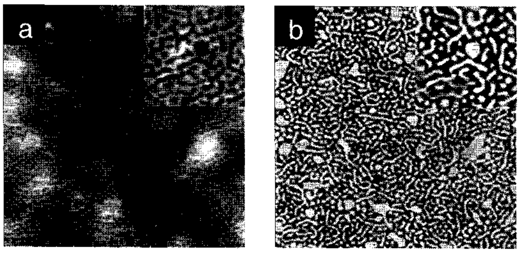

Figure 3. Tapping mode AFM height (a) and phase (b) images of poly(n-butyl acrylate)-*graft*-polyethylene films on uncoated mica. The height is encoded by gray scale with brighter values corresponding to taller features.[19]

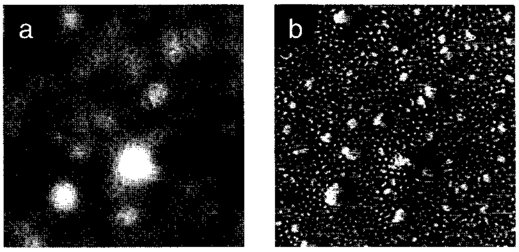

Figure 4. Tapping mode AFM height (a) and phase (b) images of poly(n-butyl acrylate)-*graft*-polyethylene films on carbon-coated mica.[19]

Preferential surface interactions with the substrate are known to influence the morphology of thin copolymer films.[21] To investigate the substrate effects, we imaged the films prepared by casting the same copolymer solution on carbon-coated mica (Figure 4). Imaging revealed the presence of circular domains with the center-to-center distances corresponding to the width of cylinders observed on uncoated mica. Such morphology is consistent with the preferential interaction of polyethylene with amorphous carbon on the surface causing the cylindrical polyethylene domains to adopt the orientation perpendicular to the surface.

2.2 Polyisobutylene based copolymers

Commercially available poly(isobutylene-*co*-*p*-methylstyrene-*co*-*p*-bromomethylstyrene) (EXXPRO™ elastomer) can be used as a macroinitiator to initiate ATRP of styrene,[22-24] MMA[24] and acrylate[22] (Figure 5). The molecular weights of the graft copolymers increased with conversion, indicating successful *grafting-from* copolymerization. Above a certain portion of vinyl monomers in the graft copolymer, the glass transition temperatures of both backbone and grafts could be seen, suggesting that the nanophase separation occurred (Table 1). The phase and dynamic mechanical behaviors were strongly affected by the compositions and to some extend by the

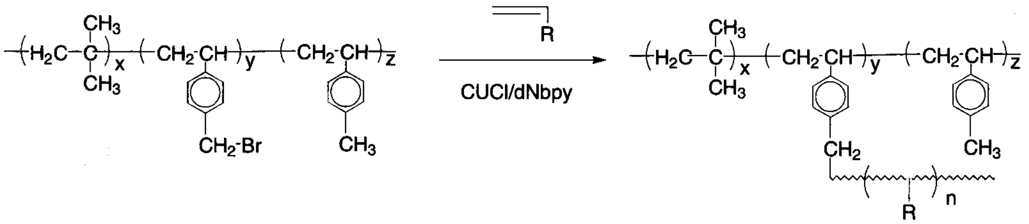

Figure 5. Preparation of polyisobutylene-*graft*-poly(vinyl monomer) using polyisobutylene macroinitiator: dNbpy, 4,4'-di(5-nonyl)-2,2'-bipyridine.

Table 1. Polyisobutylene Graft Copolymers from Polyisobutylene Macroinitiators

Macroinitiator			Monomer	Graft copolymer			
Polymer	M_n (x 10^{-3})	M_w/M_n		Monomer (wt.-%)	M_n (x 10^{-3})	M_w/M_n	T_g (℃)
PIB[a]	108	2.3	Sty[b]	69	250	2.4	-60/98
			MMA[c]	68	300	3.5	-76/100
			IBA[d]	21	181	2.5	-10

[a]PIB = poly(isobutylene-*co*-p-methylstyrene-*co*-p-bromomethylstyrene),
[b]Sty = styrene, [c]MMA = methyl methacrylate, [d]IBA = isobornyl acrylate.

side chain polydispersities. By the combination of rubbery polymers with glassy polymers, it was possible to change the properties of the graft polymer from a toughened glassy polymer to an elastomer according to their compositions. For polyisobutylene-*graft*-poly(methyl methacrylate), poly(methyl methacrylate) rich graft copolymer exhibited yielding behavior with relatively large elongation at break (about 100%) and the Young's modulus of 0.37 GPa. The polyisobutylene rich sample showed the large value of elongation at break (over 600%), no distinct yielding behavior, and low Young's modulus (0.05 GPa), indicating elastomeric characteristics. The results demonstrate that the precise control over the polymerization is possible for the preparation of functional materials with desired properties.

2.3 Ethylene-propylene-diene rubber (EPDM) based copolymers

EPDM functionalized copolymers can be prepared following two-step LRP process. EPDM was first functionalized in the presence of radical generating agent and nitroxide (e.g. 2,2,6,6-tetramethyl-4-oxopiperidine, TEMPO) to incorporate LRP initiating site on EPDM backbone. Radical generating agent abstracts allylic hydrogen from EPDM, affording macroradical that is capped with TEMPO. This EPDM macroinitiator was then adopted in the successive LRP process to generate EPDM graft copolymers (Figure 6). Following this procedure, EPDM-*graft*-polyisoprene can be prepared.[25,26]

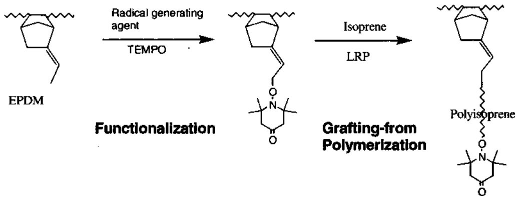

Figure 6. Preparation of EPDM-*graft*-polyisoprene.

Using different amount of radical generating agent/TEMPO in the first step and different polymerization time in the second step, the architecture of the graft copolymers such as number and length of side chains was successfully controlled.

3. Conclusions

LRP has been shown to be a versatile and robust polymerization system that allows for the preparation of wide variety of functionalized polyolefins. The incorporation of well-defined polar segments into commodity polyolefins was successfully performed. The architecture of the polymers has been extended to block or graft copolymers using polyolefin macroinitiator or macromonomers. The prepared copolymers exhibited many interesting properties like nanoscale phase separation behaviors, property change from a toughened glassy polymer to an elastomer according to the compositions, and potentially compatibilizing effect in corresponding polymer blend. These results demonstrate that the precise control over the polymerization is possible for the preparation of well-defined functional materials with desired properties, which dramatically broaden the applicability of polyolefins in many important markets.

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