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ARTICLE

RAFT/MADIX method finely regulating the copolymerization of ethylene and polar vinyl monomers under mild conditions

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RAFT/MADIX method not only can copolymerize of ethylene with a diverse range of functionally polar-monomers, but also can easily tune the polar composition and the polar monomer distribution along the produced copolymer chains. This highly versatile RAFT/MADIX copolymerization platform provides access to a diverse range of polyethylene materials.

Polyolefins account for more than half of thermoplastics' production. Among them, polyethylene (PE) is the most produced polymer, which has considerable usage in packaging films, coatings, polymer modifiers, foams, and cable materials.[1] The lack of polarity often prevents PE from exhibiting important end-use properties such as chemical compatibility with other materials (fillers, other polymers), adhesion, or dyeability. Therefore, the regulation on the incorporation of functional units into PE chain is of significant important for facilitating control over the properties to meet its wide range of applications.[2] Direct introduction of the polar functional units into PE chain could significantly change the properties and could give some functionalities.[3] Generally, the controlled free radical polymerization method[4] (including atom-transfer radical polymerization (ATRP),[5] reversible addition-fragmentation chain transfer (RAFT) polymerization,[6] nitroxide-mediated radical (NMR) polymerization[7] and organometallic-mediated radical polymerization (OMRP)[8]) can copolymerize ethylene/α-olefins and acrylate or polar vinyl acetate or acrylonitrile directly, however only the copolymers with very low ethylene incorporation have been described in most cases, for example, with methyl acrylate in a copper mediated reversible-deactivation radical copolymerization, a NMR copolymerization [7] or a RAFT copolymerization.[6] The barrier to significant ethylene incorporation arises from poor reactivation rates of dormant species in which the end of the polymer chain lacks radical-stabilization potential.[9] Recently, Brookhart and co-workers demonstrated the diimine–Pd can catalyze copolymerization of ethylene with methyl acrylate, directly incorporating methyl acrylate units into PE chain,[10] subsequently, various functional copolymers with vinyl acetate, vinyl chloride, acrylonitrile, acrylic acid, and vinyl chloride functional moieties have been prepared.[11] Though big progresses of the copolymerization of ethylene with polar vinyl monomers have been made by coordination copolymerization in recent years, the coordination copolymerization of ethylene with polar monomers remains in a very limited proportions of polar monomers.[11] Up to now, on one hand, there is no efficient method for tuning the copolymerization of ethylene and polar monomers in all proportions yet, or regulating the polar monomer arrangement along the produced copolymer chains due to that the functional groups in the polar comonomers were found to restrict the coordination of the olefin double bond to the metal catalyst,[12] which leads to very limited incorporation of the functional comonomer into the resulting polymer chain[13]. On the other hand, the copolymers of ethylene with polar N-vinyl comonomers are envisioned to have great industrial importance, however, the copolymerization of ethylene with those polar monomers containing amide moieties (including acrylamides and N-vinyl lactams) remains a challenge due to the poisoning by polar N-vinyl monomers of almost all olefin polymerization catalysts and the retarding effect of the amide functions during the reaction.[14]

RAFT polymerization is one of the versatile methods for controlling free radical polymerization, which has broad scope of monomers.[15] And recently, S. Perrier, M. Destarac, F. D'Agosto, V. Monteil, et al have reported that RAFT/MADIX (macromolecular design via the interchange of xanthates) process was one of the most versatile processes in terms of the reaction conditions, the variety of monomers for which polymerization can be controlled, tolerance to functionalities, and the range of polymeric architectures, especially, it is very effective for controlling the radical polymerization of nonconjugated vinyl monomers (vinyl acetate ethylene, etc).[16] Herein we demonstrate that RAFT/MADIX copolymerization of

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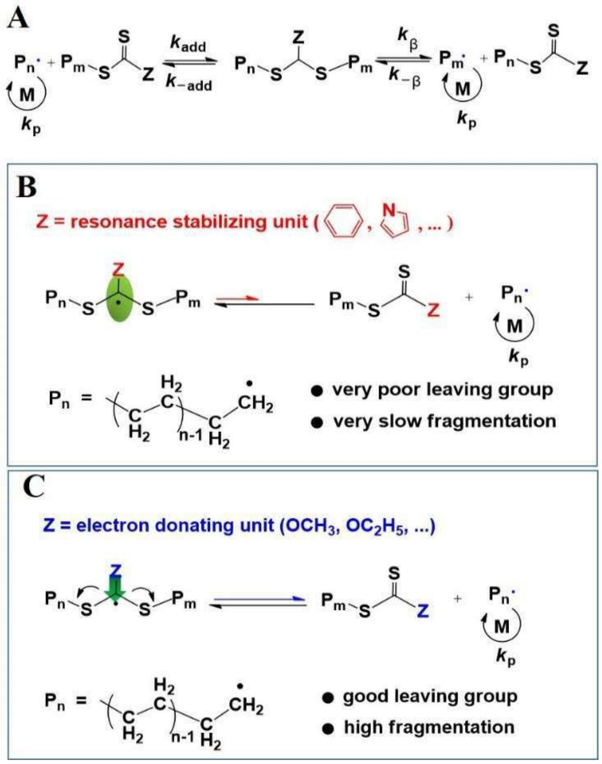
ethylene with a diverse range of functional polar monomers, in which several functional polar monomers can be directly copolymerized in all proportions with ethylene simply by varying the ethylene pressure and the amount of added polar monomers in mild conditions.



Furthermore, we also demonstrate that the potential of this RAFT/MADIX polymerization process can be used as a powerful means for the preparation of the PE copolymer with controlled arrangement of the polar monomer along the produced copolymer chains simply in a one-pot process.

Figure 1. (A) The basic reaction steps of reversible addition–fragmentation chain transfer (RAFT) process, (B) proposed mechanism of RAFT polymerization of ethylene, (C) proposed mechanism of xanthate-mediated controlled radical polymerization of ethylene.

The RAFT polymerization is generally carried out in the presence of a thiocarbonylthio compound, such as a dithioester, dithiocarbamate, trithiocarbonate, or xanthate.[9a] All of them act as reversible chain transfer agents in the free radical polymerization. Because the propagating radical of ethylene and some polar vinyl monomers are very poor homolytic leaving groups, the fragmentation of the RAFT-adduct radical (intermediate radical) is thought to be very slow when dithioesters or trithiocarbonates are used, resulting in very poor control of the copolymerization ethylene and polar vinyl monomers. To achieve good control of the radical copolymerization of ethylene and polar vinyl monomers via the RAFT/MADIX process, a delicate balance of the forward and reverse rates of addition (k_{add} and k_{-add}) and fragmentation (k_β and $k_{-\beta}$), together with the leaving rates of PE and poly(polar vinyl monomer), is necessary (Figure 1).[17] For dithiobenzoates, the presence of electron-withdrawing group in the Z moiety leads to an increase in the rate of addition and a very low fragmentation of PE, resulting in poor control over the polymerization ethylene and polar vinyl monomers. In contrast, if RAFT agent with the electron-donating group in the Z moiety is used in the polymerization ethylene and polar vinyl monomers, the presence of the electron-donating substituent increases electron density at the radical centre, which leads to the destabilization of the RAFT-adduct radicals and an increase in the fragmentation rate. On the other hand, the electron-donating substituents may lead to stabilization of the thiocarbonyl product of fragmentation through their conjugation with the C=S double bond.[17a, 17c] This increases the fragmentation of PE, and the polymerization ethylene and polar vinyl monomers may be controlled.

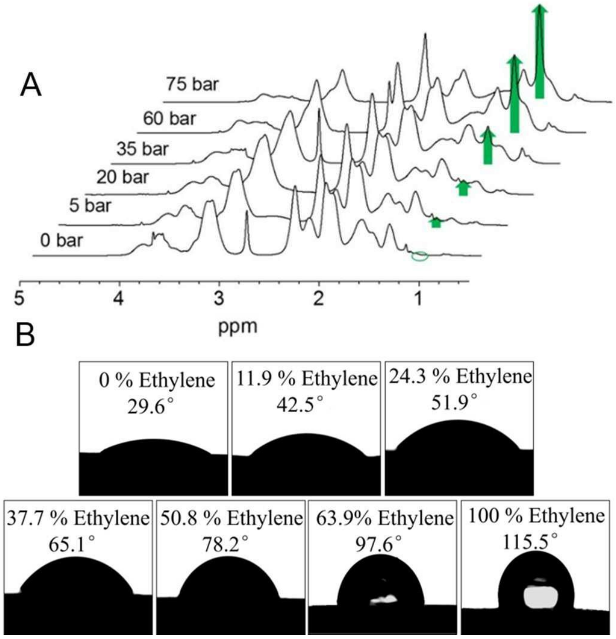


Figure 2. (A) ^{1}H NMR spectra of PE-co-PNVP under different ethylene pressure, (B) water contact angles for copolymers of different NVP content, the angles increased with ethylene content.

N-vinyl monomer has a multiplicity of chemical structures, which lead to the versatility and usability of N-vinyl monomers for the production of functional polymers with various properties and functions.[18] However, the incorporation of N-vinyl monomers into PE chain is still very difficult up to now, which is due to the fact that the generated radical species are highly reactive due to their nonconjugated nature (lack of resonance stabilization) and strong electron donating pendant groups. Here, we carried out the copolymerization of ethylene and N-vinyl lactams using O-methyl xanthate as RAFT agent. O-methyl group is an electron-donating substituent, which can increase electron density at the radical center and the fragmentation rate, thereby, controlling the RAFT polymerization of ethylene and NVP. After 10 h of copolymerization, the resulting mixtures became very viscosity, and the results are listed in Table 1. Under the specific temperature and volume of solvents, the solubility of ethylene increased with the increase of ethylene pressure.[19] Therefore, ethylene incorporation in the polymer chain can be tuned by ethylene pressure. As shown in Figure 2A, the signals coming from PE increased with the increase of the pressure of ethylene, and the incorporation of polar monomer can

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be finely tuned from 0% to 63.9% simply via changing ethylene pressure. Furthermore, the total volume of the polymerization mixture, pressure and temperature remained unchanged to ensure the constant amount of ethylene dissolved in the polymerization mixture for all experiments, the amount of NVP added will also affect the incorporation of polar monomer. When we added NVP (0.2, 0.5, 1.0 and 1.5 mL) into the polymerization system, the polar monomer incorporation is 61.5%, 62.2%, 66.4%, 74.5% as shown in Table S1, respectively. All these experiments exhibited that the incorporation of polar monomer into PE chain could be regulated in all proportions by changing ethylene pressure and the amount of NVP added.

Table 1. Copolymerization of ethylene and NVP via RAFT/MADIX process.

Entry	Pressure (bar)	Xanthate (mg)	M_w[a] (10^4 g/mol)	PDI	X[b] (%)	T_g[c] (°C)
1	0	7.5	3.01	1.43	100	84.3
2	5	7.5	4.00	1.38	90.1	44.5
3	20	7.5	4.40	1.45	75.7	42.0
4	35	7.5	4.72	1.48	62.3	41.0
5	60	7.5	5.90	1.38	47.0	22.3
6	70	7.5	6.66	1.47	36.1	20.3

[a] Determined by GPC. [b] X = polar monomer incorporation (mol%), determined by ^{1}H NMR. [c] Determined by DSC.

The controllable incorporation of polar monomer in the produced copolymers would result in tunable properties of the produced copolymers. The incorporation of polar N-vinyl pyrrolidone functionalities into PE could dramatically alter their properties. The surface properties of the copolymer products were investigated by measuring the water contact angles (Figure 2B). The water contact angle for PE is 115.5°, and the water contact angle for PNVP is 29.6°. Therefore, the water contact angle of the formed polymers could be finely tuned to 97.6, 78.2, 65.1, 51.9, 42.5° when 36.1%, 49.2%, 62.3%, 72.8%, 88.1% of the NVP comonomer was incorporated into the PE product (as shown in Figure 2B), respectively.

This RAFT/MADIX method is also effective in regulating the copolymerization of ethylene and O-vinyl monomers (e. g. vinyl acetate).[20] The molecular weight in this experiment could reach up to 10^4 g/mol and polydispersity index (PDI) remains narrow (Mw/Mn <1.4). The incorporation under different ethylene pressure was determined based on ^{1}H NMR spectra, and the results were listed in Table 2. With the increase of ethylene pressure from 5 bar to 40 bar, the incorporation of ethylene increased from 20.9% to 73.8 % in RAFT/MADIX copolymerization of ethylene and vinyl acelate. The ethylene pressure showed great control over its incorporation. Other polar monomers including N-vinylcaprolactam (NVCL), 2-hydroxylethyl vinyl ether (HOVE), vinyl trifluoroacetate (VTFAc), etc, were also used in the copolymerization with ethylene, and the results were listed in Table 2. The incorporation of HOVE under different ethylene pressure was determined by ^{1}H NMR spectra, and the results were listed in Table 2. With the increase of ethylene pressure from 10 bar to 40 bar, the incorporation of ethylene increased in RAFT/MADIX copolymerization of ethylene and HOVE. The molecular weight of the produced copolymers is above 10000, and PDI remains narrow.

Table 2. Copolymerization of ethylene and polar monomers via RAFT/MADIX process.

Entry	Pressure	Polar monomer	M_w[a] (10^4 g/mol)	PDI	X[b] (%)
1	5 bar	VAc (1 mL)	1.63	1.40	79.1
2	15 bar	VAc (1 mL)	1.55	1.37	62.7
3	20 bar	VAc (1 mL)	1.99	1.35	45.2
4	30 bar	VAc (1 mL)	1.58	1.37	34.0
5	40 bar	VAc (1 mL)	1.71	1.33	26.2
6	10 bar	HOVE (1 mL)	1.65	1.19	69.9
7	20 bar	HOVE (1 mL)	1.77	1.17	52.2
8	30 bar	HOVE (1 mL)	1.56	1.25	47.3
9	40 bar	HOVE (1 mL)	1.83	1.25	38.9
10	20 bar	VTFAc (1 mL)	0.75	1.05	32.0
11	75 bar	NVCL (1 mL)	1.96	1.31	33.8

[a] Determined by GPC. [b] X = polar monomer incorporation (mol%), determined by ^{1}H NMR.

The polar monomer arrangement along the produced copolymer chains also can be finely tuned in this RAFT/MADIX copolymerization system as shown in Figure 3. The copolymer that comprised one pure PE block and pure PNVP block was obtained in one-pot simply changing the pressure of ethylene. First, RAFT polymerization of NVP was carried out under an ethylene pressure of 0 bar for 10 h (NVP conversion > 99%), leading to the formation of homoPNVP with molecular weight of 14000 and PDI of 1.22, subsequently, the ethylene pressure was increased to 35 bar after NVP monomer was consumed up, forming diblock copolymer of PNVP and PE with molecular weight of 15200 as shown in Figure S1b. Also, via changing the pressure of ethylene, a copolymer with one PE-*r*-PNVP block containing approximately 46.3 mol% NVP/53.7mol% ethylene and a second pure PNVP block can be prepared in one-pot. First PE and PNVP random copolymer block (PE/PNVP=46.3%/53.7%, M_W=12600, PDI=1.21) was obtained after 4 h of RAFT/MADIX copolymerization of NVP and ethylene under 40 bar of ethylene pressure (NVP conversion is 35.7%), subsequently, the second pure PNVP block formed after another 4 h's RAFT/MADIX polymerization under 0 bar of ethylene, the produced "block-like" copolymer has molecular weight of 23500 and PDI of 1.47 as shown in Figure S2b and Table S2. Furthermore, the copolymer that comprised one PE-poor block containing approximately 61.3 mol% NVP/38.7 mol% ethylene and a second PE-rich block of approximately 37 mol% NVP/63 mol% ethylene was also prepared. The two blocks differ in their overall composition. RAFT/MADIX copolymerization under a working pressure of 35 bar led to the formation of a NVP-rich block with 61.3 mol% NVP/38.7 mol% ethylene, subsequently, the ethylene-rich block was then synthesized by increasing the working pressure to 75 bar with no further NVP addition, resulting in the formation of an ethylene-rich block with 37 mol% NVP/63 mol% ethylene. The GPC chromatogram (Figure S3 and Table S3) shows the molar-mass distribution of the first block (M_w=11700 g/mol, PDI=1.23), which then migrates to a region of higher molar mass (M_w=187500 g/mol) on formation of the second block, but the PDI remained narrow (PDI =1.38) as shown in Figure S3.

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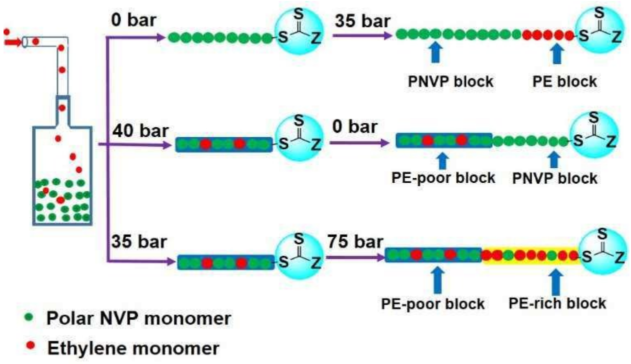

Figure 3. The scheme for tuning the polar monomer arrangement along the produced copolymer chains.

Conclusions

In summurry, enhancement of the polarity, functionality of PE chains and control over functional unit distribution in PE chain are the important challenges for the polymerization of ethylene. We addressed this important challenges by using RAFT/MADIX copolymerization system that can copolymerize ethylene with different type polar and/or functional vinyl monomers in all proportions under mild conditions, but also produce ethylene-based copolymers with controlled functional unit distribution along the produced copolymers. The RAFT/MADIX process tolerates a wide variety of functional vinyl monomers of different reactivity. Applications of the polymers produced may encompass those that can exploit their potential for adhesion, compatibility and novel processability characteristics.

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