European Polymer Journal 44 (2008) 3239–3245

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Study of amphiphilic poly(1-dodecene-*co*-*para*-methylstyrene)-*graft*-poly (ethylene glycol): Part I. Preparation of poly(1-dodecene-*co*-*para*-methylstyrene) copolymer and its molecular weight regulation ☆,☆☆

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ARTICLE INFO

Article history:
Received 30 December 2007
Received in revised form 23 June 2008
Accepted 15 July 2008
Available online 25 July 2008

Keywords:
Copolymerization
Molecular weight
Ziegler–Natta catalyst
Long chain α-olefin
P-Methylstyrene

ABSTRACT

Poly(1-dodecene-*co*-*para*-methylstyrene) copolymers with a broad composition range were prepared by an $MgCl_2$ supported $TiCl_4$ catalyst. The effects of temperature and hydrogen on catalyst activity were investigated. It was found that catalyst activity reached a maximum at around 60 °C, and then decreased with the rising temperature. Hydrogen showed an activation effect on the Ziegler–Natta catalyst. ^1H NMR and ^{13}C NMR spectra showed that *para*-methylstyrene (pMS) could be effectively and randomly incorporated into the copolymer chains. The single glass transition indicated there was no block sequence in the copolymer. The copolymerization reaction was examined by the reactivity ratios of comonomers and the relatively low reactivity ratios of 1-dodecene and pMS indicated that both of them had little tendency of consecutive insertion and should be homogeneously distributed in the copolymer chains. Furthermore, the molecular weights of copolymers were regulated by chain transfer agents (diethyl zinc and hydrogen) and temperature. The molecular weights reduced greatly with the addition of diethyl zinc and hydrogen and with the increasing temperature.

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1. Introduction

Polyolefins, such as PE, PP, EPR and EPDM, are the most widely used commercial polymer family. Despite the great success, the lack of polar groups significantly limits their application. For many years, the functionalization of polyolefins [1–5] has been a scientific interest and technologically important research subject designed to improve their poor adhesion to and compatibility with other materials. Generally, there are three approaches to the functionalization of polyolefins. The most traditional one is the chemical modification of the preformed polyolefins. However, due to the inert nature of polyolefins, this approach has to resort to high-energy sources to break the stable C–H bonds to form polymeric radicals, usually accompanied by undesirable side reactions, such as degradation and cross-linking [6,7]. The second approach is the direct copolymerization of α-olefins with functional monomers, and it has been regarded as the most ideal methods. Unfortunately, some fundamental chemical difficulties, namely catalyst poisoning and side reactions, have prevented the direct process for commercial application [8,9]. Late-transition-metal catalysts, for example, Pd- and Ni-based complexes [10–12], which have better tolerance to functional groups, have been reported as the

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☆ Contract grant sponsor: National Natural Science Foundation of China; Contract Grant No. 20604021.

☆☆ Contract grant sponsor: Excellent Youth Foundation of Zhejiang University (Zijin Program).

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doi:10.1016/j.eurpolymj.2008.07.030

best catalysts for the copolymerization of olefins with functional monomers. However, the stereotacticity of polyolefins produced by the catalysts is poor. The reactive polyolefin intermediate approach [13–15] provides another effective way to access functionalized polyolefins by first designing a reactive copolymer "intermediate" that can be effectively synthesized and subsequently interconverted to functional polymer. Obviously, the key factor in this approach is the design of a comonomer containing a reactive group. They have found three kinds of reactive comonomers, borane monomers, *para*-methylstyrene (pMS) and divinyl-benzene, which can be effectively incorporated into polyolefins.

The major advantages of pMS include its commercial availability, easy incorporation into polyolefin chains and versatility in the functionalization chemistry under various reaction mechanisms, including free radical, cationic and anionic processes. Therefore, pMS was used by Chung et al. to prepare polyolefin co- and ter-polymers, including poly(ethylene-*co*-pMS) [16,17], poly(propylene-*co*-pMS) [18], poly(ethylene-*ter*-propylene-*ter*-pMS) and poly(ethylene-*ter*-1-octene-*ter*-pMS) [19]. In addition, the incorporated pMS units are facile in many chemical reactions, such as oxidation, metallation and halogenation to form desirable functional group at the benzylic position under mild reaction conditions.

However, there are no reports to date regarding the copolymerization between long chain α-olefin and pMS. Since poly(long chain α-olefin) can be readily dissolved in alkanes, amphiphilic copolymers containing long chain α-olefin can be forecasted to show special properties in selective solvents, especially in alkanes. In this paper, we will discuss the kinetic aspects of the copolymerization reaction of 1-dodecene and pMS and the resulting molecular structure of poly(1-dodecene-*co*-pMS) copolymers. According to Chung's study [18], metallocene catalysts are not very effective in producing PP-*co*-pMS copolymers as measured by catalyst activity and pMS incorporation because of steric jamming. The comonomers have different insertion fashions, 1,2-insertion for propylene and 2,1-insertion for pMS. While the copolymerization of propylene and pMS can only proceed *via* 1,2-insertion over Ziegler–Natta catalysts. They found many advantages of using Ziegler–Natta catalysts. Specifically, the $MgCl_2$ supported $TiCl_4$ catalysts show high catalyst activity, high copolymer molecular weight and no formation of pMS homopolymer. In this work, a $TiCl_4$/ID/$MgCl_2$ type Ziegler–Natta catalyst is used in the copolymerization of 1-dodecene and pMS.

Based on the synthesized poly(1-dodecene-*co*-pMS) copolymers, we intend to prepare a novel amphiphilic graft copolymer in our future work. Considering the possible applications of the amphiphilic graft copolymer, e.g., polymeric emulsifier for emulsified fuel, the molecular weights of the amphiphilic graft copolymers should be controlled at a proper range to obtain good solubility in alkanes. Therefore, the molecular weight of the precursor poly(1-dodecene-*co*-pMS) should also be regulated. So the molecular weight regulation of poly(1-dodecene-*co*-pMS) will also be discussed in this paper.

2. Experiment part

2.1. Materials

1-Dodecene was purchased from Aldrich, purified by refluxing and distillation over sodium, and kept under a dry N_2 atmosphere. pMS (Aldrich) was distilled over CaH_2 before use. The supported catalyst $TiCl_4$/ID/$MgCl_2$ (Ti content = 3 wt%) was donated by Beijing Research Institute of Chemical Technology. Triisobutylaluminium (Aldrich, Al(i-Bu)$_3$) and diethyl zinc (Aldrich, $ZnEt_2$) were used as received. An external electron donor diphenyl dimethoxysilane (Hubei Huabang Chemical Co., $Ph_2(MeO)_2Si$ or DDS) was dried over CaH_2 and distilled before use. *n*-Heptane as solvent was purified over sodium/benzophenone ketyl and distilled under a dry N_2 atmosphere prior to use. Nitrogen (99.999%) was purified by passing through two columns of deoxygen catalyst and preactivated 4 Å molecular sieves to remove the residual moisture and oxygen.

2.2. Copolymerization procedures of 1-dodecene and pMS

All manipulations were carried out under a nitrogen (N_2) atmosphere with standard Schlenk techniques. A typical copolymerization was conducted as follows. The designed amounts of *n*-heptane (40 mL), pMS (0.0014 mol), 1-dodecene (0.0442 mol), Al(i-Bu)$_3$ (1.61 mmol), DDS (0.0644 mmol) and $ZnEt_2$ (0.228 mmol) were injected into a 100 mL glass flask connected to a Schlenk line and equipped with a magnetic stirrer under N_2 atmosphere. Then, the flask was immersed in a thermostat at 50 °C. Finally, the supported catalyst $TiCl_4$/ID/$MgCl_2$ (ID = internal donor) (42.8 mg) was added into the mixture to initiate the polymerization. In all reactions, Al/Ti (molar ratio) = 60 and Al/Si (molar ratio) = 25 were used. After 2 h, polymerization was terminated by the addition of HCl acidified methanol. The resulting polymer was precipitated by adding isopropanol, washed with methanol and dried in vacuum at 50 °C. The polymer was placed in a Soxhlet extractor and allowed to undergo extraction in ethyl acetate for 24 h to remove homopoly(pMS). Finally, the copolymer was dried *in vacuo* at 50 °C for 12 h.

2.3. Instruments

NMR spectra were recorded in deuterated tetrachloroethane on a Varian Mercury 300 Plus instrument at room temperature. Molecular weight and polydispersity index (PDI) were measured with gel permeation chromatography on a PL-GPC220 at 150 °C with 1,2,4-$C_6H_3Cl_3$ as the eluent. Three PLgel (10 μm) mixed B columns (7.5 mm × 300 mm) were used. Differential scanning calorimetry (DSC) was performed under a N_2 atmosphere on a Perkin Elmer DSC-7 at a heating rate of 10 °C min^{-1}.

3. Results and discussion

The copolymerization of 1-dodecene and pMS was illustrated in Fig. 1. The molecular structure of copolymers and

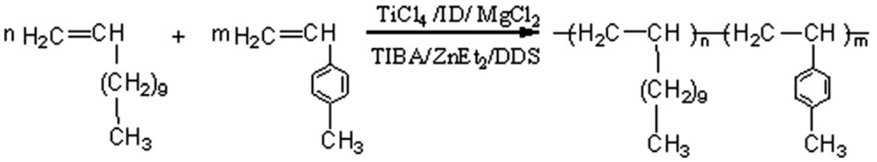

Fig. 1. Synthesis of poly(1-dodecene-*co*-pMS) copolymer.

the kinetic aspects of copolymerization will be discussed in detail.

3.1. Synthesis of poly(1-dodecene-co-pMS)

In our previous work, Wang et al. [20] studied the copolymerization of ethylene and styrene catalyzed by $MgCl_2$-supported-$TiCl_4$ catalyst with Al(i-Bu)$_3$ as cocatalyst and DDS as external donor, and $TiCl_4$/ID/$MgCl_2$/Al(i-Bu)$_3$/DDS catalyst was proved to be a high-efficiency catalytic system. Furthermore, Al(i-Bu)$_3$ is more beneficial for polymerization of aryl substituted ethylene than $AlEt_3$ [21]. Alkoxysilanes are the most commonly used external donors for Ziegler–Natta catalyst. $Ph_2(MeO)_2Si$ (DDS) bearing less bulky alkoxy groups with respect to $Ph_2(EtO)_2Si$, gives a better equilibrium between selective poisoning of the nonstereospecific sites and activation of the isospecific sites. The addition of $Ph_2(MeO)_2Si$ can increase the first-step stereoregularity and the molecular weights of copolymers [22–26]. So the catalytic system was used in this work.

It is well known that in the Ziegler–Natta catalytic polymerization, both 1-dodecene and pMS predominately proceed *via* a 1,2-insertion [18]. Table 1 summarizes the experimental results. Overall, polymer productivity is similar in the reactions with or without pMS. Namely, pMS monomer does not reduce the catalyst activity. It is observed that the molecular weights of the copolymers slightly increased with the increase of pMS consumption. Similar phenomena have also been reported in other literature [18]. The broad molecular weight distribution $\overline{M}_w/\overline{M}_n = 4-5$ is indicative of multiple active centers of the heterogeneous Ziegler–Natta catalysts. As shown in Table 1, very small quantity of pMS homopolymer was detected and poly(1-dodecene) homopolymer was not observed. So the presence of homopolymer was neglected when the conversion for each monomer was calculated. The conversion of pMS was always higher than that of 1-dodecene, indicating the higher reactivity of pMS. It was found that the pMS contents of the copolymers increased with the increasing pMS contents in feed molar ratios.

The effects of temperature and hydrogen on catalyst activity were also investigated. The reactions were conducted for 2 h at different temperatures with the feed ratio of $M_1/M_2 = 8$ (mol/mol), and with addition of the same amount of $ZnEt_2$ in each experiment. As shown in Fig. 2, temperature has a significant influence on catalyst activity in the absence or presence of H_2. Catalyst activity reaches a maximum at around 60 °C, but rapidly decreased with further increase in temperature. This is due to irreversible deactivation of some active centers under high temperatures. Moreover, the catalyst activity of the reactions with H_2 addition is higher than that without H_2 at the same temperature. Hydrogen shows an activation effect on the copolymerization, similar to the hydrogen effects observed in propylene polymerization by supported Ziegler–Natta catalyst [27].

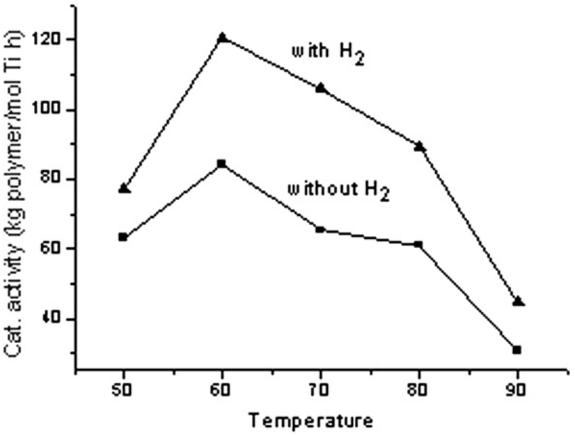

Fig. 2. The effects of temperature and hydrogen on catalyst activity.

Table 1
Copolymerization of 1-dodecene and pMS[a]

Run	M_1[b] (mol)	Feed ratio M_1/M_2[c]	Yield (%)	M_2 in copolymer (mol %)	Conversion of M_1 (%)	Conversion of M_2 (%)	Catalyst activity kg polymer (molTi h)$^{-1}$	$\overline{M}_n \times 10^3$ g mol^{-1}	PDI	M_2 homopolymer (wt%)
1	0.0450	1/0	56.6	0	56.6	0	100.97	133.0	4.3	0
2	0.0442	32/1	68.6	3.3	68.5	73.8	103.86	149.7	4.7	0.30
3	0.0434	16/1	54.4	6.5	54.2	60.5	95.70	173.7	4.4	0.51
4	0.0419	8/1	62.9	12.1	62.3	69.1	93.34	196.9	4.5	0.82

[a] Other conditions: reaction temperature, 50 °C; reaction time, 2 h; 40 mL, heptane; Al/Ti, 60; Al/Si, 25.

[b] M_1 = 1-dodecene.

[c] M_2 = pMS.

3.2. Microstructure of poly(1-dodecene-co-pMS) copolymers

Fig. 3 shows the ^{1}H NMR spectra of two typical poly(1-dodecene-*co*-pMS) copolymers containing 34.2 and 45.9 mol % of pMS units, respectively. In addition to the major chemical shifts at 1.56, 1.21 and 0.83 ppm, corresponding to the methine, methylene and methyl groups in 1-dodecene units, there are two additional chemical shifts around 2.23 and 6.8–7.1 ppm, corresponding to Ph-C**H**$_3$, and aromatic protons in pMS units, respectively. The integrated intensity ratio between the chemical shifts in the region from 0.83 to 1.56 ppm and chemical shifts in the region from 6.8 to 7.1 ppm, as well as the number of protons both chemical shifts represent determines the pMS content in the copolymers. The pMS content of the synthesized copolymers covers a broad composition range, varying from 3.02 to 58.5 mol %. Krauss and Rollmann [28] and Smith and Ashraf [29] proposed that NMR resonances from 6.1 to 6.8 ppm result from block styrene sequences, while the resonances from 6.8 to 7.4 ppm occur in random polystyrene sequences. Therefore, the resonances between 6.8 and 7.1 ppm of the typical copolymers imply that there is no detectable block pMS sequence in copolymer chains.

The chain structure of a typical poly(1-dodecene-*co*-pMS) copolymer was examined by means of ^{13}C NMR spectrum. The assignment of the peaks in the ^{13}C NMR spectrum is determined with reference to the calculation by Grant–Paul method [30]. In the aromatic region, the resonances are observed at 129.25, 130.18, 136.03 and 141.18 ppm, which are attributable to phenyl carbons from pMS units. The chemical shift assignments in the aliphatic region are shown in Fig. 4.

Furthermore, the copolymer composition, dyad sequence distribution and number-average sequence length $\overline{n}$ can be estimated according to the following equations [31]

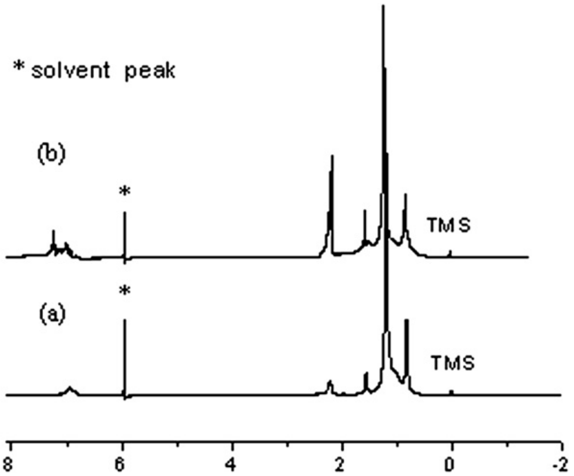

Fig. 3. ^{1}H NMR spectra of poly(1-dodecene-*co*-pMS) copolymers, containing (a) 34.2 mol % and (b) 45.9 mol % of pMS units.

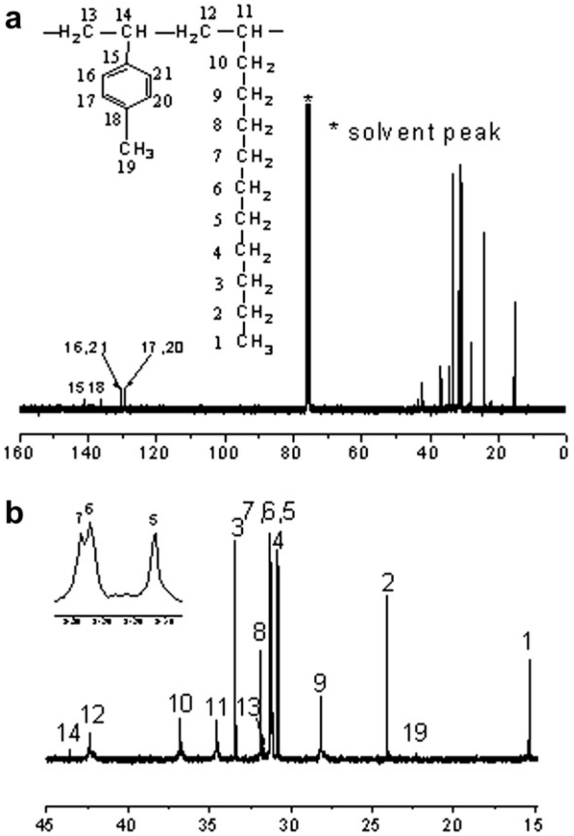

Fig. 4. The ^{13}C NMR spectrum of the copolymer (a) and the expanded aliphatic region (b).

$$M_1M_1 = A_{\alpha\alpha-M_1M_1} \quad M_1M_2 = A_{\alpha\alpha-M_1M_2} \quad M_2M_2 = A_{\alpha\alpha-M_2M_2} \tag{1}$$

$$\overline{n}_{M_1} = \frac{M_1M_1 + \frac{1}{2}M_1M_2}{\frac{1}{2}M_1M_2} \quad \overline{n}_{M_2} = \frac{M_2M_2 + \frac{1}{2}M_1M_2}{\frac{1}{2}M_1M_2} \tag{2}$$

$$M_2\% = \frac{M_2M_2 + \frac{1}{2}M_1M_2}{M_1M_1 + M_1M_2 + M_2M_2} \times 100\% \tag{3}$$

The letter A represents the area of corresponding peak.

The results are listed in Table 2. The nomenclature used for carbon atoms follows the suggestion of Carman and coworkers [32]. Each methylene carbon (S) of the copolymer backbone has been labeled by two Greek letters, indicating the number of bonds separating it from the nearest tertiary carbons along the chain in both directions. The estimated copolymer composition M_2% is 48.4%. Comparing the calculated chemical shifts of $S_{\alpha\alpha}$ and $S_{\alpha\beta}$ of the three different dyads with the observed values, it is clear that only signals for $S_{\alpha\alpha}$ are observable, which suggests there are predominantly head-to-tail connections of monomer units and no

Table 2
Dyad sequence distribution and their relative abundance

Dyad	Calculated $S_{\alpha\alpha}$ (ppm)	Calculated $S_{\alpha\beta}$ (ppm)	Observed δ (ppm)	Abundance (%)
M_1M_1	40.66	33.76	42.11	5.46
M_1M_2	40.88	34.29	42.36	93.43
M_2M_2	43.11	45.29	43.53	1.11

detectable tail-to-tail couplings. This can be explained by the large steric hindrance between the substituents of 1-dodecene and pMS. The M_1M_2 dyad sequence is much richer than the others, and the corresponding $\overline{n}_{M_1}$ and $\overline{n}_{M_2}$ are 1.12 and 1.02, respectively, indicating the pMS units and 1-dodecene units are mainly connected in alternative mode. The results clearly demonstrate that pMS units are distributed uniformly in the copolymer chains with almost no consecutive insertion, and the copolymer is a random copolymer with high alternation inclination.

3.3. Thermal behavior of the copolymer

DSC measurements were carried out to evaluate the macroscopic structure of the copolymer. Fig. 5 compares the DSC curves of poly(1-dodecene) and three poly(1-dodecene-*co*-pMS) copolymers with different pMS contents. Poly(1-dodecene) has a glass transition (T_g = 33.2 °C) and a melting peak (T_m = 43.8 °C). As to the three copolymers, they have only one T_g transition, respectively, which is indicative of homogeneous copolymer structure with no detectable block sequences. Furthermore, the T_g shifts to higher temperature as the pMS content increases, as shown in Table 3. Meanwhile, every copolymer has one small melting peak resulting from the crystallizable side alkyls (with 9 consecutive methylene sequence for each side group) of 1-dodecene units. There is a tendency that the melting point decreases with the increasing pMS content, which suggests that the incorporation of pMS prevents to a certain degree the crystallization of 1-dodecene units.

3.4. Reactivity ratios

One of the best ways to investigate a copolymerization system is to determine its reactivity ratios of the comonomers. In order to get meaningful results, a series of copolymerization were carried out by changing monomer feed ratio and comparing the resulting copolymers' compositions under conversion of 10%. Table 4 gives the experimental results.

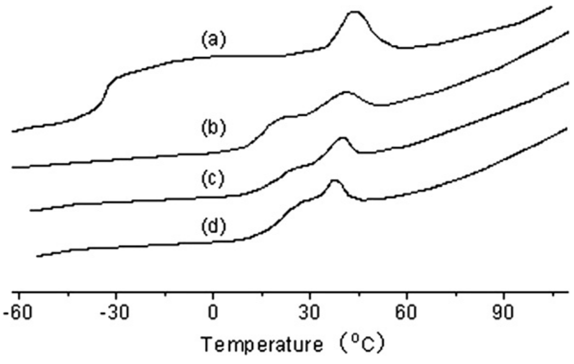

Fig. 5. DSC curves of poly(1-dodecene) (a) and the copolymers with (b) 3.3, (c) 16.4 and (d) 34.2 mol % of pMS comonomer.

Table 3
DSC results of poly(1-dodecene) and three copolymers

Sample	pMS (%)	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})
Poly(1-dodecene)	0	−33.2	43.8	35.6
copolymer 1	3.3	17.1	41.2	21.6
copolymer 2	16.4	21.2	39.5	17.9
copolymer 3	34.2	23.2	37.6	11.2

The reactivity ratios of 1-dodecene and pMS are estimated by Kelen–Tüdös linearization method. The calculation [33] is based on the following composition equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \tag{4}$$

where $[M_1]$ and $[M_2]$ are the concentration of monomers, and $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the monomer reactivity ratios. After the introduction of

$$G = \frac{x(y-1)}{y}, \quad F = \frac{x^2}{y}, \quad \alpha = \sqrt{F_m \times F_M} \tag{5}$$

$$\eta = \frac{G}{\alpha + F}, \quad \xi = \frac{F}{\alpha + F} \tag{6}$$

where F_m and F_M are the lowest and highest values of F, the composition equation is transformed into

$$\frac{\eta}{\xi} = r_1 - \frac{1-\xi}{\alpha\xi} \cdot r_2 \tag{7}$$

Plotting $\frac{\eta}{\xi}$ versus $\frac{1-\xi}{\alpha \cdot \xi}$, a straight line is obtained by linear regression, as shown in Fig. 6. The calculated values of r_1 and r_2 can be estimated from the intercept and slope of

Table 4
Copolymerization results under different feed ratios at 60 °C

Run	x	Conversion (%)	M_2 content (mol %)	y
5	1	8.51	50.8	0.97
6	2	7.58	42.3	1.36
7	4	5.32	34.2	1.92
8	8	6.97	24.5	3.08
9	16	7.93	16.4	5.10
10	32	7.21	9.62	9.40

Note. $x = [M_1]/[M_2]$, $y = d\,[M_1]/d[M_2]$.

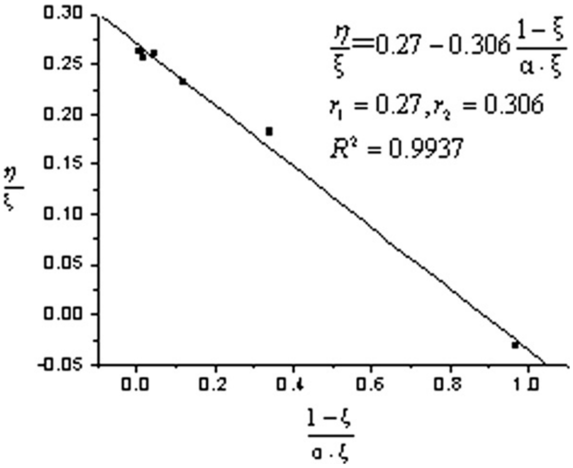

Fig. 6. Plot for the calculation of r_1 and r_2.

the straight line. The obtained values of reactivity ratios are $r_1 = 0.27$ and $r_2 = 0.306$. The relatively low r_1 and r_2 indicate that both comonomers have low tendency of consecutive insertion. So there is very low probability for the formation of homopolymer. In other words, both of the 1-dodecene and pMS units shall be randomly and homogeneously distributed in the copolymer chains.

3.5. Regulation of molecular weight

Molecular weight and molecular weight distribution are key parameters in the preparation and application of copolymers. So the influences of feed ratio and chain transfer agent (H_2 and $ZnEt_2$) on molecular weights of copolymers are studied to have a better understanding of the copolymerization.

As shown in Table 5, the feed ratios showed only an insignificant influence on molecular weight, the molecular weights increased slightly with the rising concentration of pMS. But the molecular weights of copolymers were strongly dependent on the amount of H_2 and $ZnEt_2$. In general, the addition of H_2 and $ZnEt_2$ obviously reduced the molecular weights and broadened the molecular weight distribution, compared with the data in Table 1. In addition, increasing the amount of $ZnEt_2$ caused further decrease in molecular weight. For example, in run 11, 12 and 14, the amount of $ZnEt_2$ increased from 1 to 5 mol ‰, the molecular weights dropped from 73.8×10^3 to 16.8×10^3 g mol^{-1}. The results clearly demonstrate that $ZnEt_2$ is an effective chain transfer agent. The same conclusion can be drawn from the results of run 15, 16, 18 groups, and run 19, 20, 22 groups. The dependence of molecular weight on the concentration of $ZnEt_2$ is attributed to chain transfer reactions. As proposed by Natta G., $ZnEt_2$ exchanges an ethyl group for a propagation chain, as shown in the following equation [34]

$$[\text{cat}] - \text{Pn} + \text{ZnEt}_2 \rightarrow [\text{cat}] - \text{Et} + \text{PnZnEt} \tag{8}$$

where [cat] is the catalyst complex on which the polymer chain Pn is growing. The resulting PnZnEt does not further participate in the polymerization, and it is called a dead polymer. While the [cat]-Et formed at the same time is a new active site, which has the capacity to initiate monomers to continue the propagation. As shown in Table 5, the addition of hydrogen can further reduce the molecular weights of copolymers. These results obviously show that the molecular weights of the copolymers can be adjusted by varying the consumption of H_2 and $ZnEt_2$.

Table 5
The results of molecular weight regulation

Run	M_1/M_2 (mol)	Chain transfer agent	$\overline{M}_n \times 10^3$ g mol^{-1}	PDI
11	32:1	$ZnEt_2$ (1 mol ‰)[a]	73.8	6.1
12	32:1	$ZnEt_2$ (2 mol ‰)	60.6	10.0
13	32:1	H_2 + $ZnEt_2$ (2 mol ‰)[b]	51.0	6.9
14	32:1	$ZnEt_2$ (5 mol ‰)	16.8	6.6
15	16:1	$ZnEt_2$ (1 mol ‰)	73.7	4.9
16	16:1	$ZnEt_2$ (2 mol ‰)	66.5	6.8
17	16:1	H_2 + $ZnEt_2$ (2 mol ‰)	53.5	7.1
18	16:1	$ZnEt_2$ (5 mol ‰)	22.6	4.9
19	8:1	$ZnEt_2$ (1 mol ‰)	99.0	4.7
20	8:1	$ZnEt_2$ (2 mol ‰)	84.5	5.1
21	8:1	H_2 + $ZnEt_2$ (2 mol ‰)	72.7	5.6
22	8:1	$ZnEt_2$ (5 mol ‰)	17.8	5.6

[a] The amount of $ZnEt_2$ is presented by mole permillage to the comonomers.

[b] The volume of H_2 is 20 vol% of the gas phase over the reaction solution.

Table 6
The effect of temperature on molecular weight

Temperature (°C)	$ZnEt_2$ (mol ‰)	$\overline{M}_n \times 10^3$ g mol^{-1}	PDI
50	2	99.0	4.7
60	2	41.2	5.7
70	2	40.1	5.4
80	2	36.1	5.1
90	2	35.6	5.4

Note. The amount of $ZnEt_2$ is presented by mole permillage to the comonomers.

In order to investigate the effect of temperature on molecular weight, a group of experiments were performed, which were summarized in Table 6. The molecular weights decrease greatly with the increasing temperature, while the molecular weight distribution does not change much with temperature.

In all, the molecular weight of the copolymer can be effectively regulated by adding certain amount of $ZnEt_2$ and H_2 in the polymerization system.

4. Conclusion

A new class of poly(1-dodecene-*co*-pMS) random copolymer with a broad composition range was synthesized by $TiCl_4/ID/MgCl_2$ catalyst. ^1H NMR, ^{13}C NMR and DSC analysis clearly show that pMS can be effectively and randomly incorporated into copolymer chains. The reactivity ratios of the copolymerization at 60 °C were found to be $r_1 = 0.27$ and $r_2 = 0.306$. Moreover, the molecular weights of copolymers can be regulated in a wide range by changing the amount of $ZnEt_2$. The copolymers may be used as a precursor for the preparation of novel functional graft polymers with main chain comprised of long chain α-olefin units. Amphiphilic graft copolymers synthesized based on poly(1-dodecene-*co*-pMS) copolymers will be discussed in part II.

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