

Effect of Catalyst Type on the Copolymerization of Styrene/1-Hexene and Exploring of Their Structural and Thermal Properties

M. R. Rostami Daroukola^{a,*}, N. Bahri-Laleh^a,
M. Nekoomanesh-Haghighi^a, and S. Rahmatiyani^a

^aPolymerization Engineering Department, Iran Polymer and Petrochemical Institute (IPPI),
Tehran, 14975/112 Iran

*e-mail: m.rostami@ippi.ac.ir

Received August 8, 2019; revised October 28, 2019; accepted November 11, 2019

Abstract—The effect of catalyst type on styrene/1-hexene copolymerization reactions was investigated. The copolymerization reactions were performed using conventional free radical polymerization, atom transfer radical polymerization (ATRP) and Ziegler-Natta polymerization methods. Copolymers containing different 1-hexene compositions were synthesized and characterized by ¹H NMR, GPC and DSC methods. The monomer reactivity ratios for free radical copolymerization were calculated using linear methods and found to be $r_1 \sim 25$ and $r_2 \rightarrow 0$ for styrene and 1-hexene, respectively. The increases of 1-hexene mole fraction in ATRP synthesized copolymers showed that CuCl/L promotes 1-hexene cross propagation significantly. Furthermore, 1-hexene cannot participate in self-propagation reaction. In the polymerization assisted by supported Ziegler-Natta catalyst, the conversion of the reaction was increased with mole fraction of 1-hexene in the feed, which indicated the higher reactivity of this monomer. Finally, the thermal properties of copolymers were studied by DSC.

DOI: 10.1134/S1560090419070029

INTRODUCTION

In recent years, the synthesis of different classes of copolymers with α -olefins and other monomers by using various catalyst systems has been considered [1–4]. The microstructure and architecture prediction of these copolymers can significantly enhance the final polymer properties [3–7]. Among various types of the polymerizations, conventional free radical copolymerization is one of the most important methods, which can copolymerize wide variety of monomers under convenient conditions. However, due to the low reactivity of the 1-alkene monomers [8–10], it is important to estimate the reactivity ratio of this monomer against the second monomer. In another type of the reactions, the atom transfer radical polymerization (ATRP) can provide active species allow predicting and controlling the structure and properties of the resulting polymers [8, 12, 13]. It is well known that in copolymerization reactions, the copolymer composition is affected by the reactivity ratios (r_1 and r_2) of the monomers. The catalyst type has a significant influence on the reactivity ratio of the monomer pair during the copolymerization reaction [8, 9, 11, 14–16]. The effect of Lewis acid catalyst on the reactivity ratios of (meth)acrylate/1-hexeneradical copolymerization was investigated. The

reactivity ratio for methyl methacrylate decreases in the presence of Lewis acids, and 1-alkene reactivity ratio is close to zero [9]. Homogeneous copolymerization of styrene and 1-hexene was carried out in toluene at room temperature using bis-indenyl ethane zirconium dichloride/methylaluminumoxane (MAO) system. The results showed that this catalyst system is highly active for 1-hexene and less effective for styrene polymerization [11]. The ATRP and free radical copolymerization of methyl acrylate with 1-octene using ethyl 2-bromoisobutyrate as initiator was investigated in details. The reactivity ratios of the monomers were determined and a gradient trend in the sequence distribution of monomers was observed due to the rapidity of cross-propagation of 1-octene-terminated polymeric radicals with methyl acrylate [8]. The copolymers of vinyl monomers with 1-alkenes with predictable and controlled architectures are of great interest because the combination of these monomers can significantly enhance the final properties of the polymers [13, 17–20]. The existence of 1-alkenes units in polystyrene backbone can decrease polystyrene glass transition temperature and improve mechanical properties [1, 5, 11, 17].

It is well known that α -olefins reactivity in coordination polymerization is much higher than in radical polymerization. However, this difference was not quantified, yet. Furthermore, the monomers reactivity ratios in the abovementioned polymerizations were not determined so far. To shed light on these issues, in this article we were targeted to do comprehensive study on the copolymerization behavior of styrene/1-hexene monomers using different radical and coordination polymerization systems. It is worth to mention that styrene/1-hexene copolymers have commercial importance, since neat polystyrene is a rigid polymer.

EXPERIMENTAL

Materials

Styrene (St) and 1-hexene (1-He) monomers (Tabriz and Aryasol petrochemical, Iran) were purified by distillation under reduced pressure over CaH_2 . Tetrahydrofuran, THF (Merck; $\geq 99.5\%$), ethylbenzene (Merck; $\geq 99.5\%$), toluene (Merck; $\geq 99.5\%$), and benzoyl peroxide, BPO (Aldrich; 98%), were used as the solvents and initiator, respectively. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (Merck; 99.8%), carbon tetrachloride (Merck; 99.5%) and copper (I) chloride (Aldrich; 99%) were used as the ligand, initiator and catalyst, respectively. $\text{Mg}(\text{OEt})_2$ based Ziegler-Natta catalyst, with the trade name of THT, and triethyl aluminum (Maroon petrochemical, Iran) were used as catalyst and co-catalyst, respectively.

Styrene/1-Hexene Radical Copolymerization

The mixtures containing various ratios of St/1-He were introduced to glass tubes equipped with a magnetic stirrer. A required amount of BPO initiator was added and the glass tube was sealed with a rubber septum and degassed by argon purging for 10 min. The sealed tube was immersed in a preheated oil bath at the desired temperature. The tube then was removed from oil bath and reaction mixture was dissolved in THF, filtered and then dried under vacuum at 50°C to reach a constant weight. The copolymer compositions of the synthesized copolymers were determined by ^1H NMR spectroscopy.

Styrene/1-Hexene Copolymerization via ATRP

A required amount of CuCl was introduced to a glass tube equipped with a magnetic stirrer. The glass tube was sealed with a rubber septum and was undergone vacuum and then nitrogen for three times. The mixtures containing various ratios of St/1-He, ligand (PMDETA) and initiator (CCl_4) were degassed by argon purging for 10 min before adding to the glass tube. The sealed tube was immersed in a preheated oil

bath at the desired temperature. The tube was then removed from oil bath and reaction mixture was dissolved in THF, filtered and then dried under vacuum at 50°C to reach a constant weight.

The dried polymer or copolymer was then dissolved in THF and passed through a neutral alumina column to remove the remaining copper catalyst. The sample was then dried again under vacuum up to a constant weight and studied by ^1H NMR spectroscopy to determine the reactivity ratio of the monomers.

Synthesis of Poly(1-hexene) and Its Copolymers via Ziegler-Natta Process

A two-neck 50 mL glass reactor was sealed and purged with dry nitrogen. The mixture containing purified styrene and 1-hexene monomers was weighed in glove box and added to the reaction vessel. A required amount of triethylaluminum ($\text{Al}/\text{Ti} = 130$) and then $\text{TiCl}_4/\text{Mg}(\text{OEt})_2$ catalyst in dried toluene was injected to the reaction medium at 60°C . After 90 min, the reaction mixture was precipitated in methanol and then dissolved in toluene, filtered and dried under vacuum at 60°C to reach a constant weight. The obtained product was studied by ^1H NMR spectroscopy, GPC and DSC techniques.

In situ Polymerization of Styrene in the Presence of Poly(1-hexene) or St/1-He Copolymers

At the first stage, appropriate amount of poly(1-hexene) or 1-He/St copolymers was dissolved in styrene and 30% v/v of ethylbenzene. The process of dissolving was performed at room temperature in a glass tube with magnetic stirrer to reach a uniform solution. Then BPO initiator (0.2 wt % of styrene) was added and temperature was raised to 120°C . The reaction mixture was dried under vacuum up to a constant weight and studied by DSC method.

Characterization Methods

The ^1H NMR spectra of the copolymer were recorded in CDCl_3 with a Bruker DRX500 spectrometer operated at 500 MHz. Molecular weights and PDI were measured by a Waters 150C gel permeation chromatography (GPC) equipped with a refractive index detector in THF at room temperature. Polystyrene standards were used for calibration. The glass transition temperature of the synthesized polymers was determined with a Perkin Elmer (Diamond7, USA) DSC under N_2 atmosphere with a heating rate of 10 grad/min. Glass transition temperatures were

Table 1. Styrene/1-hexene copolymerization reaction conditions and obtained copolymer compositions via radical copolymerization at 80°C

Run	Styrene in feed (molar part)	Time, min	Conversion, %	Styrene in copolymer, mol %
1	0.2	120	6	95.5
2	0.4	120	7.1	97.7
3	0.6	120	11.3	98.1
4	0.8	60	15.6	99.1

The molar ratio of benzoyl peroxide to monomers was 0.08.

reported from the first heating scans as the midpoint of the temperature range bounded by the tangents to the two flat regions of the heat flow curve.

RESULTS AND DISCUSSION

Radical Copolymerization of Styrene and 1-Hexene

Copolymerization reaction of styrene and 1-hexene was conducted using 0.2–0.8 molar ratio of styrene in the feed at 80°C for 1–2 h. As shown in Table 1, the conversion increased with the mole percent of styrene in the feed. These results are attributed to higher reactivity of styrene in copolymerization.

¹H NMR spectroscopy was used to determine the mole fraction of the styrene and 1-hexene in the synthesized copolymers. According to Fig. 1, all spectra showed peaks at 0.7–1.5 ppm, assigned to various protons in the 1-hexene units [7, 11]. Also, styrene units displayed two groups of peaks at 0.8–2.4 and 6.45–7.25 ppm corresponding to the protons in the main chain (alkyl moieties) and phenyl ring, respectively [7, 11, 21]. Compositions of the synthesized copolymers were determined using the following equations:

$$\text{St, \%} = \frac{I_{\text{St}}}{I_{\text{St}} + I_{\text{1-He}}} \times 100, \quad (1)$$

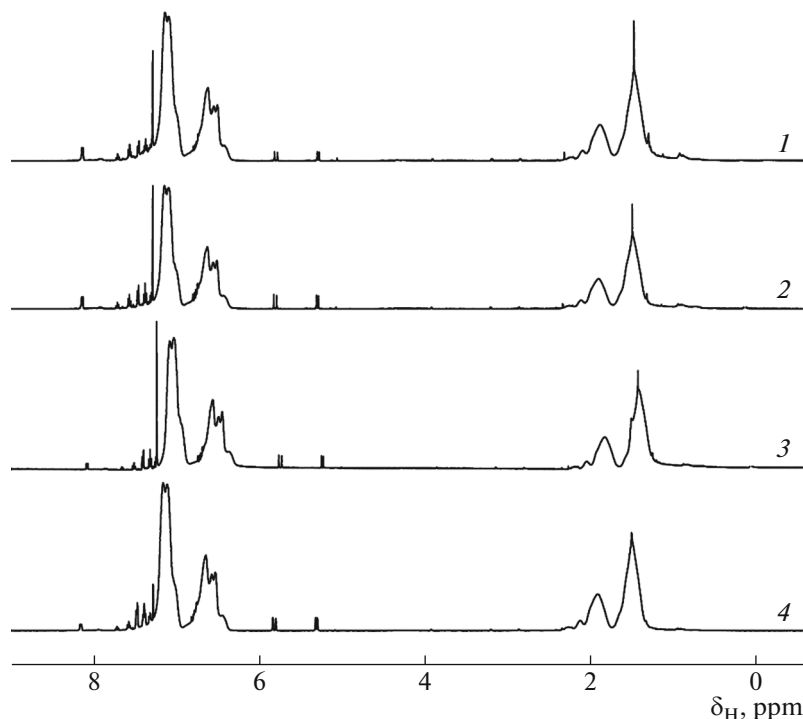


Fig. 1. ¹H NMR spectra of the synthesized St/1-He copolymers via radical copolymerization at various mole fractions of styrene monomer in the feed $f(\text{St}) = (1) 20, (2) 40, (3) 60, \text{ and } (4) 80$.

Table 2. Fineman-Ross parameters of radical copolymerization of styrene and 1-hexene

Run	M_1	m_1	$X = M_1^2(1 - m_1)/m_1(1 - M_1)^2$	$\Psi = M_1(2m_1 - 1)/m_1(1 - M_1)$
1	0.2	0.955	0.003	0.24
2	0.4	0.977	0.010	0.65
3	0.6	0.981	0.044	1.47
4	0.8	0.991	0.145	3.96

Table 3. Kelen-Tüdös parameters of radical copolymerization of styrene and 1-hexene

Run	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\xi = H/(\alpha + H)$
1	0.25	21.2	0.24	0.003	10.1	0.12
2	0.67	42.5	0.65	0.010	20.9	0.34
3	1.5	51.6	1.47	0.044	22.9	0.68
4	4	110	3.96	0.145	23.9	0.88

$$\alpha = (H_{\min} \times H_{\max})^{0.5} = (0.0029 \times 0.1453)^{0.5} = 0.020687.$$

$$I_{\text{St}} = \frac{I_{6.45-7.25}}{5}, \quad (2)$$

$$I_{1\text{-He}} = \frac{|I_{(0.7-2.4)} - I_{(6.45-7.25)} \times 0.6|}{12}. \quad (3)$$

In these equations, St% and 1-He% are the molar percent of styrene and 1-hexene in copolymers, respectively. I_{St} and $I_{1\text{-He}}$ are the integrated intensities of the styrene and 1-hexene protons, respectively. The copolymer compositions of the synthesized copolymers were calculated and summarized in Table 1.

As shown in Table 1, the mole percent of styrene in the copolymer progressively increased with its increase in the feed composition. It may be supposed that the reactivity of 1-hexene in free radical copolymerization is less than that of styrene. The reactivity ratio of monomers was calculated using linear method of Fineman-Ross (Eq. (4)).

$$\left(\frac{M_1(2m_1 - 1)}{m_1(1 - M_1)} \right) = r_1 \left(\frac{M_1^2(1 - m_1)}{m_1(1 - M_1)^2} \right) - r_2 \rightarrow \psi = r_1 \times X - r_2. \quad (4)$$

In this equation, the mole fraction of styrene in the feed and copolymer is M_1 and m_1 respectively. The constants in Eq. (4) are calculated and summarized in Table 2.

Kelen-Tüdös method was also employed to determine the reactivity ratio of styrene and 1-hexene (Eq. (5)).

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}. \quad (5)$$

The coefficients in Eq. (5) are constant which are described and calculated in Table 3.

Figure 2 shows the plots of ψ versus X for Fineman-Ross and η versus ξ for Kelen-Tüdös methods. The

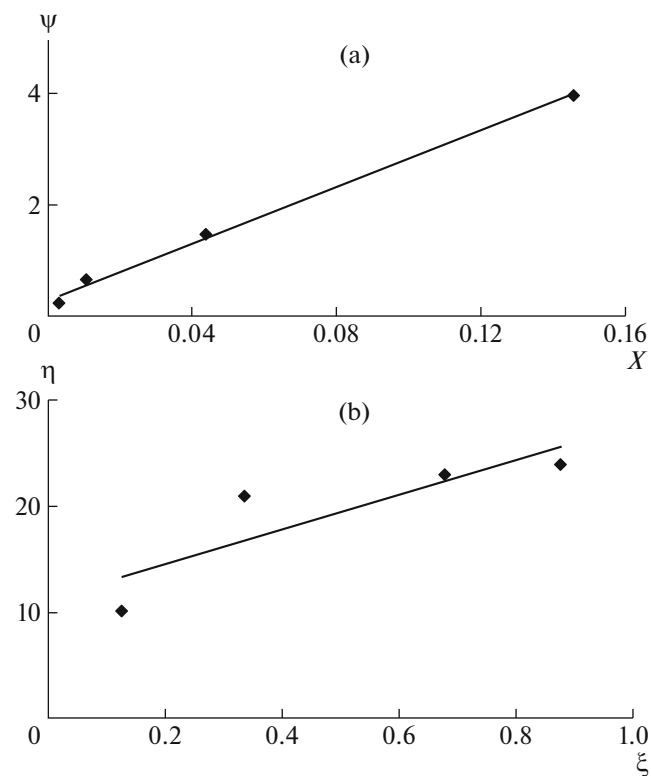


Fig. 2. The plots of (a) Fineman-Ross ($y = 25.4x + 0.296$, $R^2 = 0.996$) and (b) Kelen-Tüdös ($y = 16.31x + 11.22$) for conventional free radical copolymerization of styrene and 1-hexene.

Table 4. Styrene/1-hexene copolymerization via ATRP at 80°C

Run	Styrene in feed	Time, min	Conversion, %	Styrene in copolymer, mol %
1	0.2	120	6.8	83.8
2	0.4	120	10.9	93.3
3	0.6	120	–	94.3
4	0.8	60	9.8	95.4

Table 5. Fineman-Ross parameters of ATRP copolymerization of styrene and 1-hexene

Run	M_1	m_1	$X = M_1^2(1 - m_1)/m_1(1 - M_1)^2$	$\Psi = M_1(2m_1 - 1)/m_1(1 - M_1)$
1	0.2	0.84	0.202	0.012
2	0.4	0.93	0.619	0.032
3	0.6	0.94	1.41	0.136
4	0.8	0.95	3.81	0.771

reactivity ratios of the styrene r_1 and 1-hexene r_2 (Fig. 2b), respectively. These values indicate that were calculated from the slope and intercepts of the linear line to be 25.4 and 0 (Fig. 2a) and 27.5 and 0 (Fig. 2b), respectively. These values indicate that the reactivity of the styrene is much higher than that of 1-hexene.

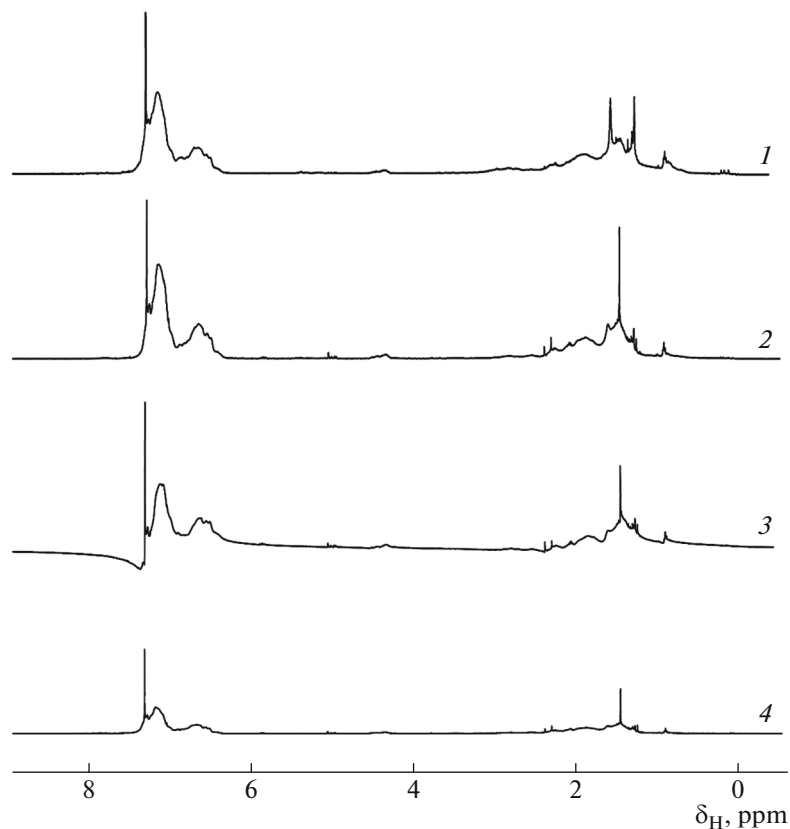


Fig. 3. ^1H NMR spectra of the synthesized St/1-He copolymers via ATRP at various mole fractions of monomers in the feed $r(\text{St}) = (1) 20, (2) 40, (3) 60, \text{ and } (4) 80$.

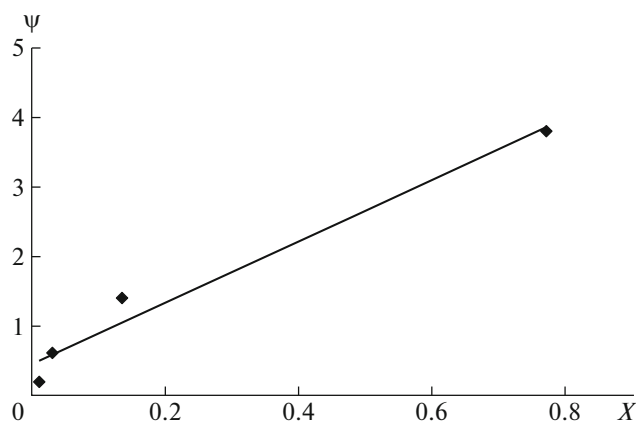


Fig. 4. The plots of Fineman-Ross for the ATRP of styrene and 1-hexene ($y = 4.414x + 0.459$, $R^2 = 0.971$).

Atom Transfer Radical Copolymerization of Styrene and 1-Hexene

The atom transfer radical copolymerization of styrene and 1-hexene was performed for the similar range of styrene molar fraction (0.2–0.8) in the feed. In all reactions the mole ratios of monomers, CuCl, CCl₄ and PMDETA were kept constant at 100/1/1/2; copolymerization was conducted at 80°C. As shown in Table 4, conversion increased with rise of styrene content in the feed. In order to determine the reactivity ratio of the monomers in ATRP, the copolymer compositions were determined by ¹H NMR spectroscopy [22, 23] (Fig. 3). As shown in Table 4, the mole percent of styrene in copolymers is above 80–90 mol % independently of monomer feed.

These results were used to calculate the reactivity ratio of the styrene and 1-hexene. The corresponding coefficients for Fineman-Ross equation are summa-

Table 6. Reaction conditions and copolymer compositions obtained from Ziegler-Natta process¹

Run	Styrene in feed, mol %	Conversion, %	Styrene in copolymer, mol %
1	0	40	0
2	10	27	1.7
3	19.4	19.6	3
4	50	10.7	5.4
5	80.6	5.2	72
6	100	1	100

¹Reaction conditions: $t = 90$ min, Al/Ti = 200 mol/mol, $T = 60^\circ\text{C}$.

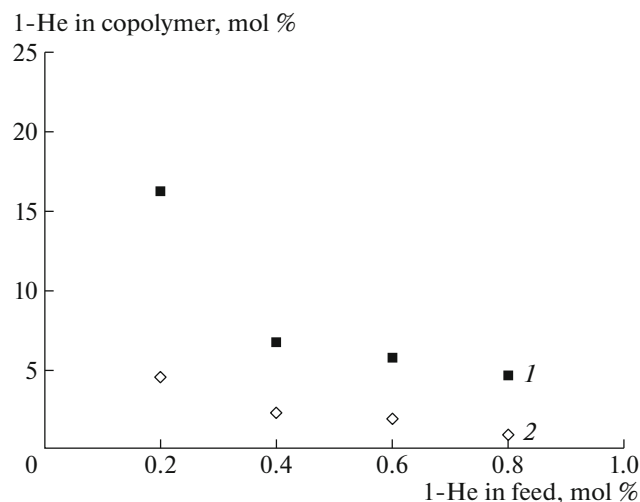


Fig. 5. The mole fraction of 1-hexene in synthesized copolymers via (1) ATRP and (2) free radical copolymerization.

rized in Table 5. Figure 4 shows the plots of ψ versus X . From the slope and intercept values, the reactivity ratio of styrene and 1-hexene were calculated to be 4.41 and 0, respectively.

Thus, the calculated values of the reactivity ratios for styrene and 1-hexene in free radical and ATRP techniques allow concluding that in both cases, styrene is much more active, i.e. the rate of addition of styrene to the macroradical with styrene terminal unit (self-propagation, k_{11}) is much higher than the addition of the 1-hexene to the similar active site (cross-propagation, k_{12}). The mole fraction of 1-hexene in the synthesized copolymers via both ATRP and free radical polymerization was compared. As shown in Fig. 5, the mole fraction of 1-hexene in copolymers synthesized via ATRP is higher than in the copolymers obtained via conventional mechanism. The slight difference between reactivity ratios obtained for various radical polymerization methods has been already described earlier [7–10]. For example, the ATRP of methyl acrylate and 1-octene was studied and their reactivity ratios were found as 3.36 and 0, respectively [8]. The similar characteristics for conventional free radical polymerization are 7.52 and close to zero.

Ziegler-Natta Polymerization Reactions of Styrene and 1-Hexene

The polymerization reactions of 1-hexene and styrene using Ziegler-Natta catalyst were conducted at 60°C. As shown in Table 6, the copolymerization rate decreases with rise of styrene content in monomer feed. This indicates the higher activity of catalyst sites for the polymerization of 1-hexane rather than sty-

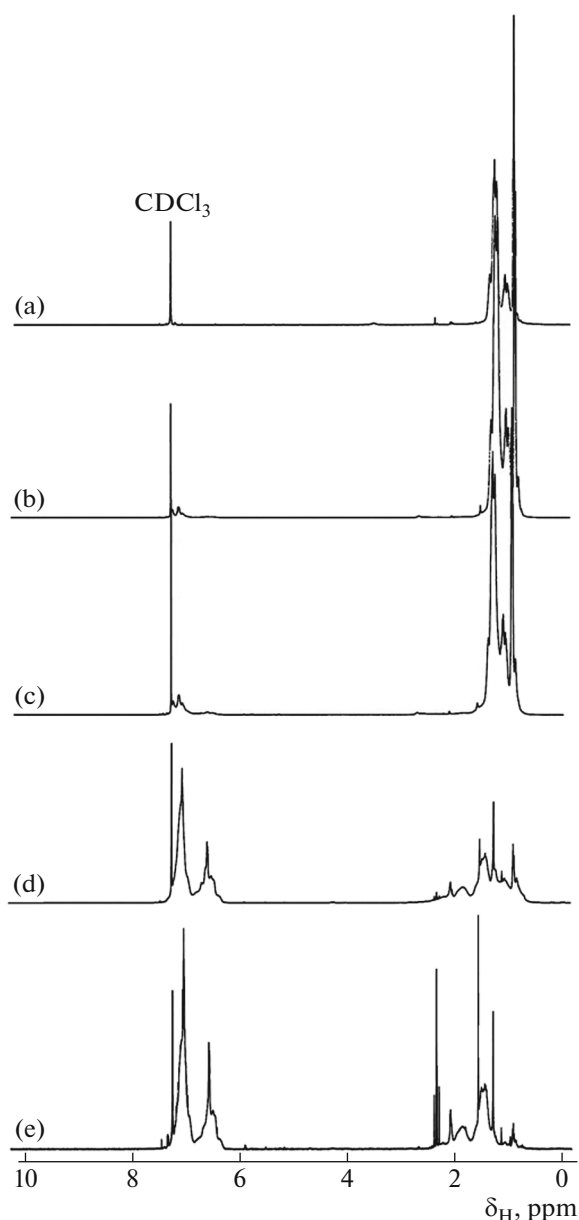


Fig. 6. ^1H NMR spectra of (a) neat poly(1-hexene), synthesized copolymers of 1-hexene and styrene via Ziegler-Natta catalyst: P1-Hex/PS = (b) 80.6/19.4, (c) 50/50, (d) 19.4/80.6, (e) neat polystyrene.

rene. This can be attributed to different electron donating behavior of the pendent group in the monomers [22].

^1H NMR spectroscopy was used to characterize the synthesized copolymers. As shown in Fig. 6, the peaks at 0.7–1.5 ppm are assigned to 1-hexene protons [7, 11]. Furthermore, styrene unit has two peaks at 0.8–2.4 and 6.45–7.25 ppm which correspond to the protons in main chain and phenyl side group, respectively [7, 11, 21]. These peaks appeared at 6.45–7.25 ppm are slightly increased with an increment of styrene

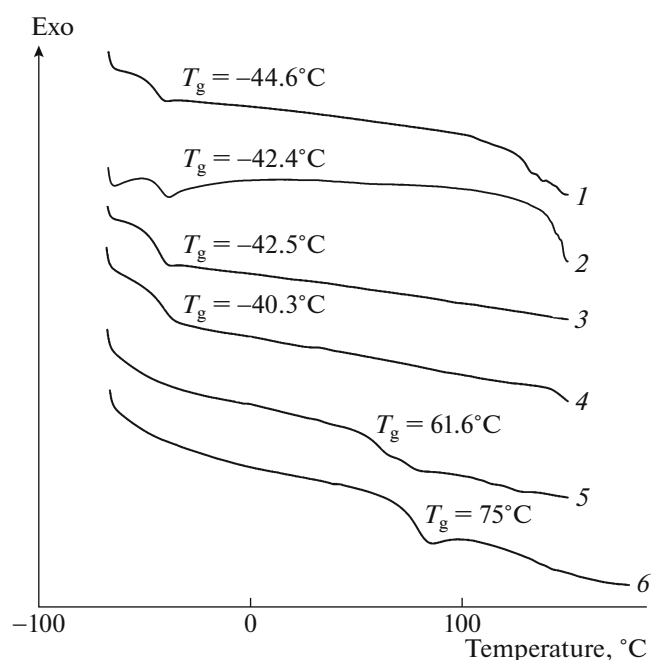


Fig. 7. DSC thermograms of (1) neat poly(1-hexene), synthesized copolymers of 1-hexene and styrene via Ziegler-Natta catalyst: P1-Hex/PS = (2) 90/10, (3) 80.6/19.4, (4) 50/50, (5) 19.4/80.6, (6) neat polystyrene in N_2 atmosphere. Rate 10 grad/min.

molar percent in the feed. The copolymer compositions are summarized in Table 6. The mole percent of styrene in copolymers slightly increased by increasing the mole percent of styrene in the feed. This can be attributed to the special effects of styrene on the activity of Ziegler-Natta catalysts.

As shown in Table 7, the molecular weights of synthesized polymers are relatively low, while dispersity is rather high. By increasing the 1-hexene content, the rate of polymerization affects the fragmentation of the catalyst and creates more active sites; these factors led to broad molecular weight distribution of the synthesized copolymer [17, 23, 24].

Thermal behavior of the synthesized 1-hexene/styrene (co)polymers was studied by DSC. As shown in Fig. 7, the glass transition temperatures of polystyrene and poly(1-hexene) were obtained 75 and -44.6°C , respectively. T_g of the copolymers decreases with increase of 1-hexane content in copolymer [11].

To improve the polystyrene properties, it was prepared by free radical polymerization initiated by BPO in the presence of poly(1-hexene) or copolymers of styrene and 1-hexane (Table 8). As is shown in Table 8, the amount of poly(1-hexene) or copolymers lies in the range of 4–8% by weight of styrene in the feed. Under similar polymerization reaction conditions, the estimated conversion decreases with increasing the weight percent of poly(1-hexene) and

Table 7. Characteristics of the copolymers synthesized via Ziegler-Natta catalyst

Run	Styrene in feed, mol %	Styrene in copolymer, mol %	M_n	PDI	T_g , °C
1	0	0	15300	5.85	-44.6
2	10	1.7	—	—	-42.4
3	19.4	3	11000	17.96	-42.5
4	50	5.4	19300	6.87	-40.3
5	80.6	72	8500	5.4	61.6
6	100	100	4800	2.34	75

Table 8. In situ polymerization reaction of styrene in the presence of 1-hexane, poly 1-hexene and its copolymers at 120°C

Reaction	Polymer, g	Conversion, %	Styrene content in product, wt %	T_g , °C
1	—	71.3	100	89
2	—	71.6	100	87.6
3	Poly(1-hexane), 0.0687	65.2	94.5	77.9
4	Poly(1-hexane), 0.1435	45.5	85.2	68.5
5	Poly(1-hexane/styrene) (98.3/1.7), 0.1435	37.4	82.6	56.6
6	Poly(1-hexane/styrene) (97/3), 0.1435	36.1	82.1	58.7

All reactions carried out in 30% v/v of ethyl benzene solvent, with 0.2 weight percent of benzyl peroxide initiator respect to styrene and time of the reactions was 5 h.

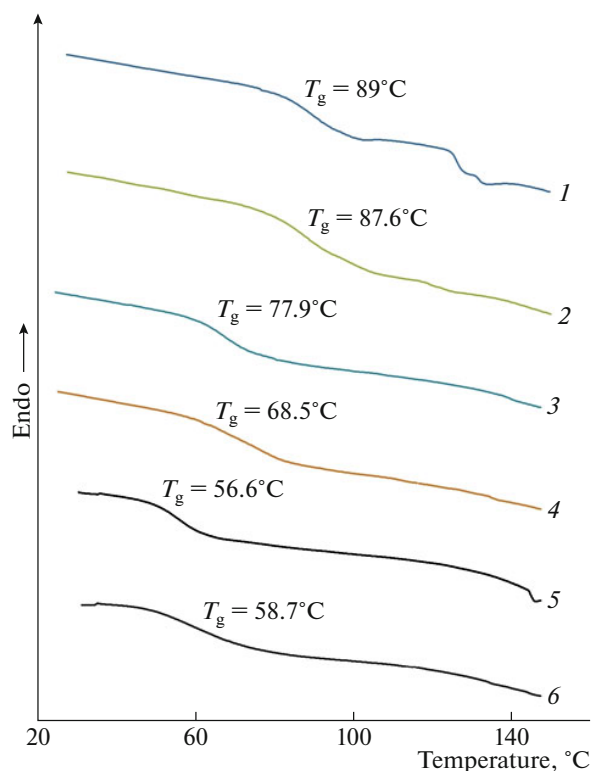


Fig. 8. DSC curves of (1) neat polystyrene, (2) PS/P1-He copolymer and synthesized PS containing different weight percents of poly(1-hexene): (3) PS + 5.5 wt % P1-He, (4) PS + 14.8 wt % P1-He, and its copolymers: (5) PS + 17.4 wt % P(1-He-co-St) (98.3/1.7), (6) PS + 17.9 wt % P(1-He-co-St) (97/3).

its copolymers. DSC method was used to estimate T_g of the prepared polymers (Fig. 8). As shown in Table 8, the T_g of polystyrene containing a small amount of 1-hexene is slightly less than that of neat polystyrene. The increase of the content of poly(1-hexene) or its copolymers led to decrease of T_g of polystyrene due to plasticizing effect of 1-hexane [26–29].

CONCLUSIONS

In this research, different styrene/1-hexene copolymers were synthesized via conventional free radical polymerization, ATRP and Ziegler-Natta catalyst polymerization. In radical copolymerization both via conventional and ATRP mechanisms 1-hexene has low activity. In polymerization with Ziegler-Natta catalyst, the conversion of the reaction was increased with mole fraction of 1-hexene in the feed confirming high activity of catalyst sites toward 1-hexene. The copolymer composition, molecular weights and MWD have considerable influence on glass transition temperature of the synthesized copolymers.

FUNDING

The authors are thankful to Iran Polymer and Petrochemical Institute (IPPI) for financial support of this work under the grant no. 43794102.

REFERENCES

1. Z. Mohamadnia, L. Azimnavahsi, and M. Soheili, *Polym. Sci., Ser. B* **60**, 172 (2018).
2. F. M. Rabagliati, D. E. Yañez, D. Canales, R. Quijada, and P. A. Zapata, *Polym. Bull.* **70**, 2111 (2013).
3. F. F. Karbach, T. Macko, and R. Duchateau, *Macromolecules* **49**, 1229 (2016).
4. I. E. Nifant'ev, A. A. Vinogradov, G. N. Bondarenko, S. A. Korchagina, A. V. Shlyakhtin, V. A. Roznyatovskii, and P. V. Ivchenko, *Polym. Sci., Ser. B* **60**, 469 (2018).
5. S. Camadanli, U. Decker, Ch. Kühnel, I. Reinhardt, and M. R. Buchmeiser, *Molecules* **16**, 567 (2011).
6. F. Martínez, E. Uribe, and A. F. Olea, *J. Macromol. Sci. A* **42**, 1063 (2005).
7. F. M. Rabagliati, R. A. Cancino, A. Martínez de Iar-duya, and S. Muñoz-Guerra, *Eur. Polym. J.* **41**, 1013 (2005).
8. R. Venkatesh, S. Harrison, D. M. Haddleton, and B. Klumperman, *Macromolecules* **37**, 4406 (2004).
9. Y. Chen and A. Sen, *Macromolecules* **42**, 3951 (2009).
10. Zh. Fu, Y. Fan, and Zh. Fan, *Iran. Polym. J.* **20**, 223 (2011).
11. S. Rahmani, M. Abbasian, P. N. Moghadam, and A. A. Entezami, *J. App. Polym. Sci.* **104**, 4008 (2007).
12. K. Tanaka and K. Matyjaszewski, *Macromol. Symp.* **261**, 1 (2008).
13. K. Tanaka and K. Matyjaszewski, *Macromolecules* **40**, 5255 (2007).
14. E. Mishima, T. Tamura, and Sh. Yamago, *Macromolecules* **45**, 8998 (2012).
15. K. Koumura, K. Satoh, and M. Kamigaito, *Macromolecules* **42**, 2497 (2009).
16. E. Mishima, T. Tamura, and Sh. Yamago, *Macromolecules* **45**, 2989 (2012).
17. I. V. Vasilenko, S. V. Kostjuk, L.V. Gaponik, and F. N. Kaputskii, *Polym. Sci., Ser. A* **49**, 395 (2007).
18. Sh. Liu, B. Gu, H. A. Rowlands, and A. Sen, *Macromolecules* **37**, 7924 (2004).
19. L. Guo, W. Liu, and Ch. Chen, *Mater. Chem. Front.* **1**, 2487 (2017).
20. R. Luo and A. Sen, *Macromolecules* **39**, 7798 (2006).
21. H. Zhang and K. Nomura, *J. Am. Chem. Soc.* **127**, 9364 (2005).
22. M. A. Semsarzadeh and M. R. Rostami Daronkola, *Iran. Polym. J.* **15**, 829 (2006).
23. M. A. Semsarzadeh, M. R. Rostami Daronkola, and M. Abdollahi, *J. Macromol. Sci. A* **44**, 953 (2007).
24. N. Nabizadeh, G. H. Zohuri, M. Khoshsefat, N. Ramezani, and S. Ahmadjo, *Polym. Sci., Ser. B* **60**, 122 (2018).
25. T. Xu, H. Yang, Zh. Fu, and Zh. Fan, *J. Organomet. Chem.* **798**, 328 (2015).
26. N. Senso, P. Praserttham, B. Jongsomjit, T. Taniike, and M. Terano, *Polym. Bull.* **67**, 1979 (2011).
27. A. Hanifpour, N. Bahri-Laleh, M. Nekoomanesh-Haghighi, and S. A. Mirmohammadi, *J. Appl. Polym. Sci.* **133**, 43882 (2016).
28. D. Nazari, N. Bahri-Laleh, M. Nekoomanesh-Haghighi, S. M. Jalilian, R. Rezaie, and S. A. Mirmohammadi, *Polym. Advan. Technol.* **29**, 1603 (2018).
29. A. Hanifpour and N. Bahri-Laleh, *J. Appl. Polym. Sci.* **136**, 47169 (2019).