



Effects of Styrenic Comonomers in the Metallocene Catalyzed Terpolymerization†

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Various terpolymers consisting of ethylene, 1-hexene and styrenic monomer were synthesized using a metallocene catalyst and cocatalyst system. The styrenic monomer, as the third monomer, was styrene, *p*-methyl styrene or 4-*tert*-butyl styrene. The structures of the terpolymers were examined by ¹³C NMR and ¹H NMR spectroscopy. The catalytic activity, polymer yield and molecular weights of the terpolymers were compared. The effects of each alkyl substituent of the styrenic monomer on the kinetics and thermal properties of the terpolymers, which were synthesized under identical polymerization conditions, were examined. The mechanical properties of the terpolymers were observed using a universal testing machine. The Shore A hardness, scratch resistance, permanent tensile strain, glass transition, crystallization temperature and the density of the terpolymers were also measured.

Key Words: Terpolymerization, Ethylene, 1-Hexene, Styrenic monomer, Metallocene catalyst.

INTRODUCTION

In the 1950s, it was reported that metallocene catalysts can be used for olefin polymerization along with Cp₂TiCl₂ and co-catalyst (divalent Et₃Al or Et₂AlCl). High activity was observed during olefin polymerization in the presence of methylaluminoxane, which was developed further by Kaminsky in the 1980s¹.

Several groups have examined polymerization according to the types of metallocene catalyst/co-catalyst and polymerization conditions. On the other hand, many studies focused on a homopolymer or copolymer containing ethylene or propylene with a high α -olefin, a diene monomer, cycloolefin, or styrene, *etc.* Nevertheless, there are no reports on terpolymerization²⁻⁴.

In this study, a metallocene catalyst/co-catalyst system was used for terpolymerization, where different third monomers were used. As the third monomer, styrene, *p*-methyl styrene or 4-*tert*-butyl styrene, which have an increasing number of methyl groups in the order of 4-*tert*-butyl styrene > *p*-methyl styrene > and styrene, was used.

EXPERIMENTAL

All manipulations were carried out in an inert nitrogen atmosphere. Toluene (SAMCHUN, 99.5 %) and 1-hexene (Aldrich, 97 %) were purified by refluxing over sodium using benzophenone as an indicator.

Styrene (Aldrich, 97 %), *p*-methyl styrene (Alfa Aesar, 98 %, *p*-MS) and 4-*tert*-butyl styrene (Alfa Aesar, 98 %, *t*-BS) were obtained using a standard purification process. *rac*-Et(Ind)₂ZrCl₂ was purchased from Aldrich. Trityl *tetrakis*(pentafluorophenyl) borate and *tri*-*iso*-butylaluminum as the co-catalyst were purchased from Acros and Tosho, respectively.

Typically, all polymerization reactions were carried out under a nitrogen atmosphere in a 300 mL stainless steel autoclave with a mechanical stirrer. Polymerization was carried out at a fixed pressure of ethylene gas at 50 °C. The polymerization reaction was initiated by the injection of toluene, 1-hexene, styrenic monomer, *rac*-Et(Ind)₂ZrCl₂ and co-catalysts. After several minutes, the polymer solution was poured into a diluted HCl/EtOH solution. The resulting polymer was washed with EtOH (600 mL) and dried *in vacuo*. Using a Soxhlet apparatus and *n*-hexane as the solvent, each soluble terpolymer was separated from the insoluble polyethylene (some type of by product). A pure terpolymer could be obtained after drying the soluble fractions.

The terpolymer was analyzed based on the ¹³C NMR spectra recorded at 50 °C using a Bruker AVANCE 500 MHz spectrometer. Sample solutions of the polymer were prepared in a CDCl₃ solvent. Deuterated solvent was used to provide an internal lock signal.

The ¹H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. The NMR samples were prepared in

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TABLE-1
SUMMARY OF TERPOLYMERIZATION OF ETHYLENE, 1-HEXENE AND STYRENIC MONOMER

Name ^a	Monomer (mol/L)			Yield (g)		Catalytic activity ^d	M _w ^e (×10 ⁻⁴)	M _n ^e (×10 ⁻⁴)	MWD ^e	Composition ^f			
	E ^b	H ^c	Styrenic monomer	Before soxhlet	After soxhlet (soluble in n-hexane)					E ^b	H ^c	Styrenic monomer	
PEHS	0.4	0.8	Styrene 0.4	12.1	9.2	7384	287	12.5	2.3	87.1	12.7	Styrene	0.2
PEHM			<i>p</i> -MS 0.4	10.3	5.2	4320	298	12.4	2.4	89.7	9.5	<i>p</i> -MS	0.8
PEHB			<i>t</i> -BS 0.4	10.2	2.7	2160	287	13.0	2.2	87.2	11.7	<i>t</i> -BS	1.1

^aPolymerization conditions: catalyst = 2.5 μmol, [Borate]/[Zr] = 1.5, [Al]/[Zr] = 500, 50 °C, 30 min; ^bEthylene; ^c1-hexene; ^dCatalytic activity = kg; of polymer/(mol of catalyst · h); ^eDetermined by gel permeation chromatography; ^fDetermined by ¹H NMR

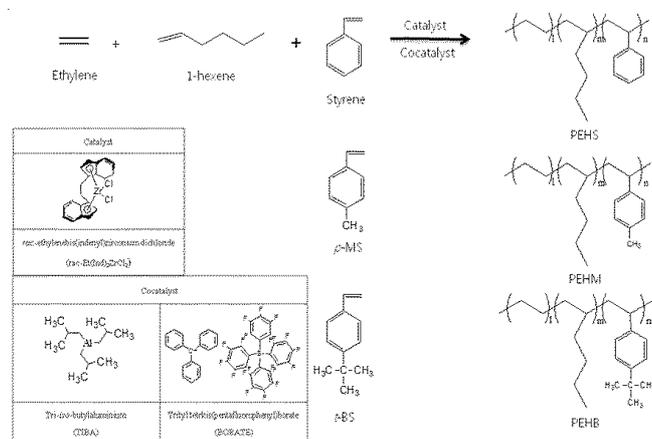
CDCl₃ solvent. The catalytic activity, polymerization rate, molecular weight and molecular weight distribution of the terpolymers were also examined.

Differential scanning calorimetry data for the terpolymer were recorded using a differential scanning calorimetry Q100 V8.2 Build 268 (TA Instruments). The samples were heated from 0 °C to 150 °C and cooled to 0 °C at 10 °C/min. Subsequently, they were reheated to 150 °C at 10 °C/min. The crystallization temperature (T_c), melting temperature (T_m) and enthalpy of melting (ΔH_m) were derived from the second and third run curves. The measured ΔH_m values were converted to the degree of crystallinity (1-λ)_{ΔH} using 290 J/g as the enthalpy of fusion of a perfect polyethylene crystal.

The elastic modulus, tensile strength and elongation at break were determined using a UTM (Tinius Olsen Co. Ltd., H5K-T) at a crosshead speed of 10 mm/min. The measurements were carried out on five specimens obtained from the same sample and the mean of their results is reported. The samples were also analyzed to determine the Shore A hardness, anti-scratch property and density (Alfa Mirage Co., MD-300S).

RESULTS AND DISCUSSION

Scheme-I presents the synthetic scheme for the terpolymers consisting of ethylene, 1-hexene and styrenic monomer: styrene, *p*-methyl styrene (*p*-MS), or 4-*t*-butyl styrene (*t*-BS). *rac*-Et(Ind)₂ZrCl₂ was used as the metallocene catalyst. Trityl tetrakis(pentafluorophenyl) borate (BORATE) and *tri*-isobutylaluminium (TIBA) was also used as a cocatalyst. Three types of terpolymers, poly(ethylene-*ter*-1-hexene-*ter*-styrene) (PEHS), poly(ethylene-*ter*-1-hexene-*ter*-*p*-MS) (PEHM) and poly(ethylene-*ter*-1-hexene-*ter*-*t*-BS) (PEHB), were obtained using this system.

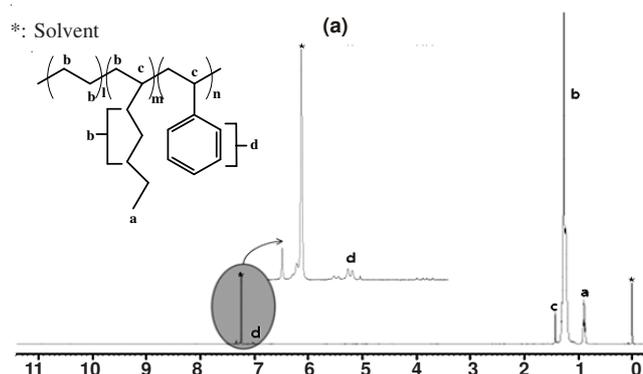


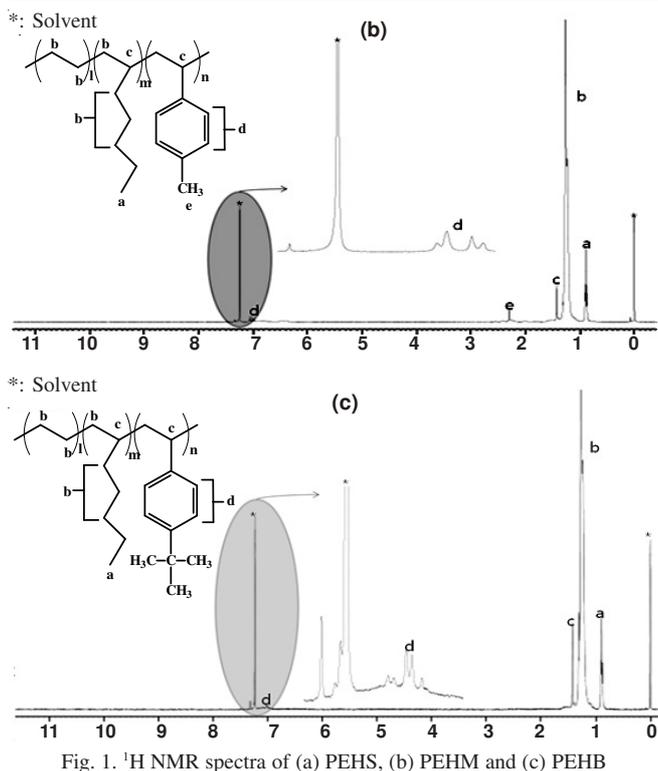
Scheme-I: Synthetic procedures for the terpolymers

Table-1 lists the polymer yield, catalytic activity, molecular weight, molecular weight distribution and compositions of PEHS, PEHM and PEHB.

As shown in Table-1, the catalytic activity of PEHB was the lowest among the three terpolymers. This is might due to the highest composition of the *t*-BS in the terpolymer, compared to that of the other styrenic monomer in PEHS or PEHM. During terpolymerization, *t*-BS could be inserted relatively easily into the terpolymer *via* an electron donating 4-*t*-butyl group, which provides very favourable polymerization conditions in cationic coordination. On the other hand, *t*-BS, which was already inserted into the terpolymer, inhibited the additional incorporation of ethylene and 1-hexene caused by the steric effect, which leads to the lowest catalytic activity of the terpolymerization for PEHB⁴⁻⁶. The molecular weight of the terpolymers was similar.

Fig. 1 presents the ¹H NMR spectra of the terpolymers. (a) shows the ¹H NMR spectra of PEHS. The peak at 0.9 ppm was assigned to the CH₃ of 1-hexene. The CH₂ peaks of ethylene and 1-hexene appeared at 1.1-1.3 ppm. The CH aliphatic peak of 1-hexene and styrene appeared in 1.4 ppm. The CH aromatic peaks of styrene were observed at approximately 7 ppm. (b) shows the ¹H NMR spectra of PEHM. The peaks at 0.9 and 2.3 ppm were assigned to the CH₃ of 1-hexene and *p*-methyl styrene, respectively. The CH₂ peaks of ethylene and 1-hexene were observed at 1.1-1.3 ppm. The CH aliphatic peak of 1-hexene and *p*-methyl styrene was observed at 1.4 ppm. The CH aromatic peaks of the *p*-methyl styrene were noted at approximately 7 ppm⁷. (c) shows the ¹H NMR spectra of PEHB. The peak at 0.9 ppm was assigned to the CH₃ group of 1-hexene. The CH₂ peaks of ethylene and 1-hexene were observed at 1.1-1.3 ppm. The CH aliphatic peak of 1-hexene and *t*-BS was noted at 1.4 ppm. The CH peaks of the aromatic ring in the *t*-BS appeared at approximately 7 ppm. The peaks had a very broad base line, which might be due to the side effects of the three CH₃ group in the *t*-BS.



Fig. 1. ^1H NMR spectra of (a) PEHS, (b) PEHM and (c) PEHB

The structure of the terpolymers was also analyzed by ^{13}C NMR. Fig. 2 shows the ^{13}C NMR spectra of the terpolymers⁸⁻¹⁹. The appearance of the CH aromatic peaks (125-130 ppm) of styrenic monomers, which were inserted into the terpolymers, was confirmed. In the case of PEHM and PEHB, the appearance of a CH_3 peak of the *p*-methyl styrene (21 ppm) and *t*-BS (31 ppm) was also confirmed.

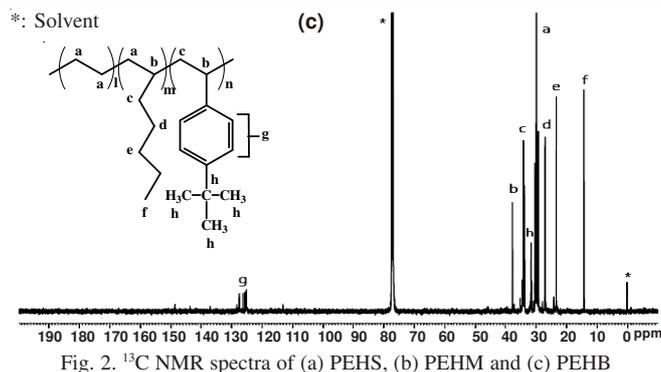
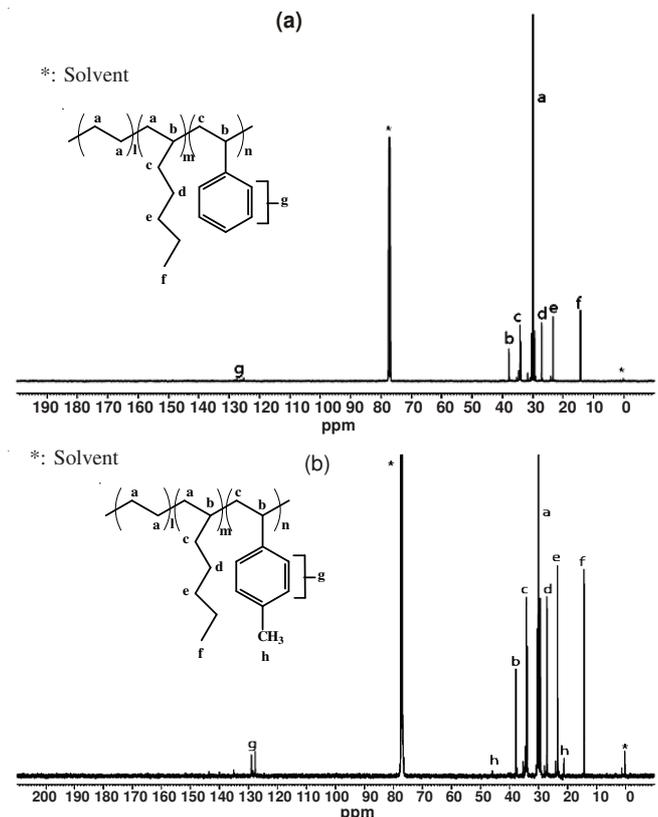
Fig. 2. ^{13}C NMR spectra of (a) PEHS, (b) PEHM and (c) PEHB

Fig. 3 shows differential scanning calorimetry curves of the terpolymers: PEHS, PEHM and PEHB. The variations in the second cooling and third heating curves of the terpolymers were observed in the lower and upper areas, respectively. The crystallization temperature (T_c) and melting temperature (T_m) of the terpolymers were confirmed. The T_m values of the terpolymers were 80-90 $^{\circ}\text{C}$. As expected, the T_c of the polymers showed similar trends to their T_m .

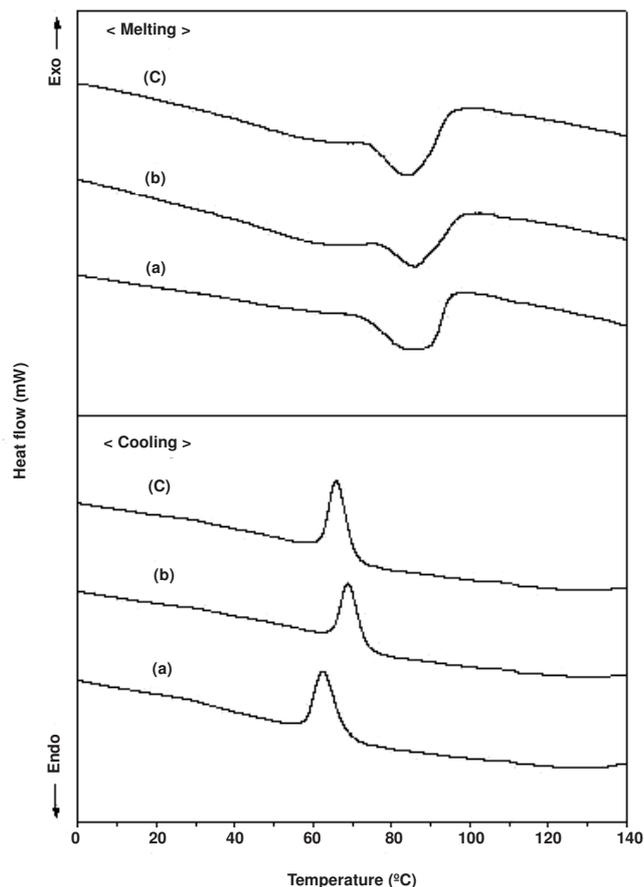


Fig. 3. DSC melting and cooling thermograms of (a) PEHS, (b) PEHM and (c) PEHB

The T_m values of the terpolymers increased in the order of PEHM > PEHB and > PEHS. This is consistent with the ethylene contents in the terpolymers. The T_m value of the terpolymers in this system was influenced mainly by the ethylenic contents in the terpolymer, not by the crystallinity of the terpolymers. Table-2 lists the T_m , T_c and crystallinity

values measured by differential scanning calorimetry. The crystallinity was calculated from their enthalpies of fusion. The crystallinity of PEHS was highest²⁰.

Name ^a	Monomer (mol/L)			T _m (°C)	T _c (°C)	X _c (%)	
	E ^b	H ^c	Styrenic monomer				
PEHS			Styrene	0.4	73.3	68.1	3.81
PEHM	0.4	0.8	<i>p</i> -MS	0.4	78.2	72.2	2.34
PEHB			<i>t</i> -BS	0.4	75.1	70.4	3.40

^aPolymerization conditions: catalyst = 2.5 μmol, [Borate]/[Zr] = 1.5, [Al]/[Zr] = 500, 50 °C, 30 min; ^bEthylene; ^c1-hexene

Fig. 4 shows the polymerization rate curves of the terpolymers, *i.e.* the ethylene polymerization rate as a function of the polymerization time. All polymerizations were marked by the very high initial rates for which the maximum rate (R_p , max) was reached within 1-2 min. The R_p of PEHM was higher than those of PEHS and PEHB. This phenomenon means that the consumption of ethylene gas was highest throughout terpolymerization. This result is closely related to the highest concentration of ethylene in PEHM, as shown in Table-1.

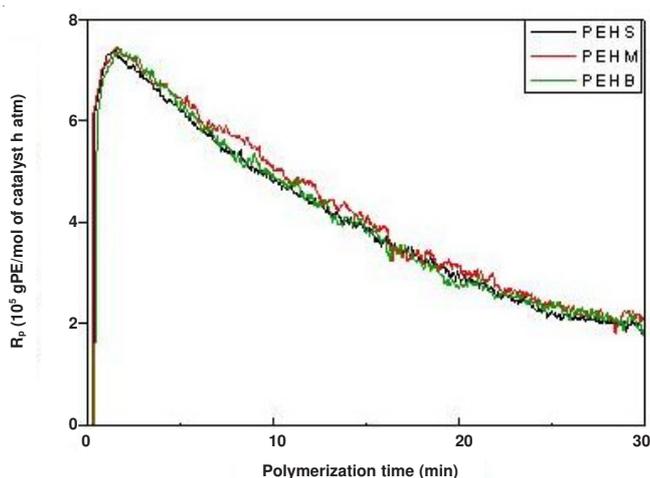


Fig. 4. Rate of polymerization (R_p) of the terpolymers

Table-3 summarizes the physical properties of terpolymers. The Shore A hardness and density of PEHB were highest. In the case of the permanent tensile strain and scratch resistance, PEHM had the highest value.

Fig. 5 shows the stress-strain curves of the terpolymers. Table-4 lists the various stress-strain data of the terpolymers. The Young's modulus, yield stress, maximum stress and strain at break of the terpolymers increased with increasing number of methyl (CH_3) groups in the styrenic monomers²¹.

Name ^a	Monomer (mol/L)			Shore A hardness	Scratch resistance (N)	Permanent tensile strain (%)	Density (g/cm ³)	
	E ^b	H ^c	Styrenic monomer					
PEHS	0.4	0.8	Styrene	0.4	66.9	7.0	18.3	0.878
PEHM			<i>p</i> -MS	0.4	76.4	7.8	26.7	0.883
PEHB			<i>t</i> -BS	0.4	82.1	7.5	25.6	0.892

^aPolymerization conditions: catalyst = 2.5 μmol, [Borate]/[Zr] = 1.5, [Al]/[Zr] = 500, 50 °C, 30 min; ^bEthylene; ^chexene

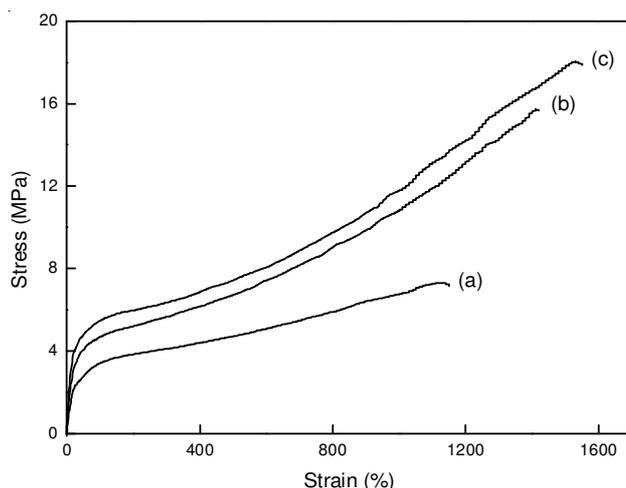


Fig. 5. Stress-strain curves of the terpolymers: (a) PEHS, (b) PEHM and (c) PEHB

Name ^a	Young's modulus	Yield stress (MPa)	Max. stress (MPa)	Strain at break (%)
PEHS	0.048	1.7	3.6	1150
PEHM	0.056	2.4	7.8	1420
PEHB	0.062	2.8	8.9	1550

^aPolymerization conditions: catalyst = 2.5 μmol, [Borate]/[Zr] = 1.5, [Al]/[Zr] = 500, 50 °C, 30 min

Conclusion

Terpolymers were synthesized using a catalyst and cocatalyst system consisting of *rac*-Et(Ind)₂ZrCl₂, BORATE and TIBA. The catalytic activity decreased with increasing number of methyl groups in the styrenic monomer of the terpolymers. The compositions of the terpolymers were analyzed by ¹H NMR. The incorporation of the styrenic monomers into the terpolymer was confirmed by the appearance of the CH aromatic peaks (125-130 ppm) of the styrenic monomers in the terpolymers using ¹³C NMR.

The crystallization temperature (T_c) and melting temperature (T_m) of the terpolymers by the differential scanning calorimetry thermographs were observed. The R_p of PEHM was higher than those of PEHS and PEHB. This is consistent with the highest composition of ethylene in PEHM. In terms of the physical properties, PEHB with *tert*-butyl groups showed the highest stress and strain values among the three samples.

REFERENCES

1. W. Kaminsky, *Metalorganic Catalysts of Synthesis and Polymerization: Recent Results by Ziegler-Natta and Metallocene Investigations*, Springer-Verlag, Berlin (1999).
2. R. Marconi, L. Boggioni, A. Ravasio, F.D. Colo, I. Tritto and U.M. Stehling, *Macromolecules*, **44**, 795 (2011).

3. F.G. Sernetz, R. Mulhaupt and R.M. Waymouth, *Macromol. Chem. Phys.*, **197**, 1071 (1996).
4. G.W. Theaker, C. Morton and P. Scott, *J. Polym. Sci., Part A: Polym. Chem.*, **47**, 3111 (2009).
5. K. Nomura, H. Fukuda, S. Katao, M. Fujiki, H.J. Kim, D.H. Kim and S. Zhang, *J. Chem. Soc., Dalton Trans.*, **40**, 7842 (2011).
6. K. Nomura, N. Suzuki, D.H. Kim and H.J. Kim, *Macromolecules*, (Communicated).
7. H.L. Lu, S. Hong and T.C. Chung, *Macromolecules*, **31**, 2028 (1998).
8. G.B. Galland, F.F. Nunes Escher, L.F. Silva, M.M. Camargo Forte and R. Quijada, *J. App. Polym. Sci.*, **104**, 3827 (2007).
9. M.L. Ferreira, G.B. Galland, D.E. Damiani and M.A. Villar, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 2005 (2001).
10. S. Martinez, M.T. Exposito, J. Ramos, V. Cruz, M.C. Martinez, M. Lopez, A. Munoz and J. Martinez, *J. Polym. Sci. Part A: Polym. Chem.*, **43**, 711 (2005).
11. J.C. Randall, *J. Polym. Sci., Part B: Polym. Phys.*, **13**, 889 (1975).
12. T. Shiono, S.M. Azad and T. Ikeda, *Macromolecules*, **32**, 5723 (1999).
13. F. Zhu, Y. Fang and S. Lin, *J. Appl. Polym. Sci.*, **74**, 1851 (1999).
14. L. Caporaso, L. Izzo, I. Sisti and L. Olive, *Macromolecules*, **35**, 4866 (2002).
15. F.F.N. Escher and G.B. Galland, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 2474 (2004).
16. W. Liu, D.G. Ray and P.L. Rinaldi, *Macromolecules*, **32**, 3817 (1999).
17. D.H. Lee and J.Y. Jho, *Polym. Bull.*, **38**, 665 (1997).
18. K. Nomura, H. Okumura, T. Komatsu and N. Naga, *Macromolecules*, **35**, 5388 (2002).
19. G.B. Galland, R. Quijada, R. Rojas, G. Bazan and Z.J.A. Komon, *Macromolecules*, **35**, 339 (2002).
20. T.C. Chung and H.L. Lu, *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1017 (1998).
21. R. Quijada, J. Guevara, G.B. Galland, F.M. Rabagliati and J.M. Lopez-Majada, *Polymer*, **46**, 1567 (2005).