Available online at www.sciencedirect.com

ScienceDirect

Polymer 49 (2008) 1180–1184

polymer

www.elsevier.com/locate/polymer

Bulk polymerization of vinyl chloride with half-titanocene/MAO catalyst

Yoshikatsu Tsuchiya, Tsuyoshi Nomaguchi, Kiyoshi Endo*

Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received 12 November 2007; received in revised form 13 January 2008; accepted 16 January 2008
Available online 20 January 2008

Abstract

Bulk polymerization of vinyl chloride (VC) with Cp*Ti(OPh)$_3$/MAO catalyst was investigated. The bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst proceeded to give poly(vinyl chloride) (PVC) with high molecular weight in good yields. The M_n of the polymer increased in direct proportion to polymer yields and the line passed through the origin. The M_w/M_n of the polymer decreased with an increase of polymer yield. The GPC elution curves were unimodal and the whole curves shifted clearly to the higher molecular weight as a function of reaction time. This indicates that the control of molecular weight can be achieved in the polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst even in bulk. The structure of PVC obtained from the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst consists of a regular structure. The thermal stability of the polymer obtained with Cp*Ti(OPh)/MAO catalyst was higher than that of PVC obtained from radical polymerization and depended on the molecular weight of the polymer. In contrast to that, the initial decomposition temperature of the polymer obtained from a radical polymerization did not depend on the molecular weight. We presumed that the decomposition of the polymer obtained with Cp*Ti(OPh)$_3$/MAO catalyst initiated at the chain end.

Keywords: Half-titanocene; Poly(vinyl chloride); Bulk polymerization

1. Introduction

Many processes such as bulk, solution, suspension, emulsion, mini-emulsion and dispersion polymerizations are known in the production of polymers and each process has its own characteristics [1]. Among them, bulk polymerization has an advantage from the viewpoints of not only simple process but also wide range of generable molecular weight of a polymer. Such process has been achieved in the field of polyolefin industry. On the other hand, poly(vinyl chloride) (PVC) is predominantly manufactured by a radical suspension polymerization of vinyl chloride (VC). In such polymerization, molecular weight may be limited by the chain transfer to the monomer because of large transfer constant [2]. In contrast, such limit may not be considered in the polymerization of VC with transition metal catalyst.

We have investigated the solution polymerization of VC in CH_2Cl_2 with transition metal complexes, especially half-titanocenes [3–7], and found that the control of both the main chain and the molecular weight of the polymer is possible in the polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst [7]. If the bulk polymerization in the production of polyethylene and polypropylene is applied to transition metal catalyzed polymerization of VC, it will be expected to produce a high molecular weight polymer. However, the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst was not investigated.

In this article, we study the controlled polymerization and the synthesis of high molecular weight PVC in the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst. Thermal stability of PVC related to the molecular weight was also investigated.

2. Experimental

2.1. Materials

Commercially available vinyl chloride (VC) was used after distillation over calcium hydride. MAO (pure methylaluminoxane)

---

* Corresponding author. Tel./fax: +81 6 6605 2697.
E-mail address: endo@a-chem.eng.osaka-cu.ac.jp (K. Endo).

0032-3861/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.01.032

purchased from Tosoh-Fine Co. was used as-received. Cp*$TiCl_3$ (Strem Chem. Inc.) was used without further purification. Cp*$Ti(OPh)_3$ was synthesized from Cp*$TiCl_3$ according to the literature [8,9]. PVC samples obtained with lauroyl peroxide (LPO) were kindly supplied from Taiyo Enbi Co. Ltd. The polymers were purified by reprecipitation from tetrahydrofuran (THF) to methanol. Other reagents were used after purification by conventional methods.

2.2. Polymerization procedure

Polymerization was carried out in a sealed glass tube method. A Y-shaped glass tube with a rubber septum for introducing the reagents into the tube by a syringe and with a connection to a vacuum system was used. VC (total volume was 10 mL) was charged into the tube at −78 °C by vacuum distillation. Cp*$Ti(OPh)_3$ and MAO diluted with toluene were introduced into the tube by a syringe. After the reaction of Cp*$Ti(OPh)_3$ and MAO for several minutes at room temperature, toluene was evacuated from the solution under high vacuum. After that, solvent and monomer were introduced into the tube. After all reagents were charged, the tube was sealed off under high vacuum. After polymerization, the contents of the tube were poured into an excess of methanol containing a small amount of hydrochloric acid to precipitate the polymer formed. The polymers were washed well with an excess of methanol and dried under high vacuum overnight. Polymer yields were determined by a gravimetric method.

2.3. Characterization of the polymers

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) and the polydispersity (M_w/M_n) of the polymer were determined by gel permeation chromatography (GPC) using a Tosoh RE-8800 series system in THF as calibrated with polystyrene standards. The ^1H and ^{13}C NMR spectra of the polymer were taken using a JEOL A-400 spectrometer in C_6D_6/*o*-dichlorobenzene (30/70 vol%/vol%) at 120 °C with hexamethyldisiloxane (HMDS) as an internal standard. Thermogravimetric analysis (TGA) measurement was carried out using a SEIKO TG/DTA 6200 under nitrogen atmosphere at a heating rate of 10 °C/min in the range from 25 to 500 °C.

3. Results and discussion

3.1. Polymerization of VC in CH_2Cl_2 and bulk

We have reported that the polymerization of VC with half-titanocene/MAO catalysts in CH_2Cl_2 gives a polymer consisting of only regular head-to-tail units [5,7]. PVC does not dissolve in VC monomer, although low molecular weight PVC is able to dissolve in CH_2Cl_2. The bulk polymerization behavior of VC may be different from the solution polymerization in CH_2Cl_2 with respect to an initiation efficiency and a polymerization rate. To elucidate these points, the polymerization of VC with Cp*$Ti(OPh)_3$/MAO catalyst was carried out in bulk. The results are listed in Table 1, in which the results for the polymerization in CH_2Cl_2 are also indicated for comparison. The initiation efficiency (I.E.: estimated from ($[VC]_0 \times$ yield (%) $\times 62.5$)/([Ti] $\times M_{n,obv}$) $\times 100$, where $[VC]_0$ and [Ti] are the concentrations of VC and Cp*$Ti(OPh)_3$/MAO catalyst, respectively) in bulk was lower than that in CH_2Cl_2, and the M_n of the polymer obtained from the bulk polymerization was higher than that from the solution polymerization. The results may be attributed to the heterogeneity in bulk polymerization.

Table 1
Comparison of PVC from the polymerization of VC in bulk and CH_2Cl_2 with Cp*$Ti(OPh)_3$/MAO catalyst at 20 °C for 48 h

Solvent	[VC] (mol/L)	Yield (%)	M_n[a] $\times 10^{-4}$	M_w/M_n[a]	I.E.[b] (%)
–	15.2	30.0	25.3	2.0	37.5
CH_2Cl_2	3.0	53.0	3.1	1.7	106.9

$[Ti] = 3.0 \times 10^{-3}$ mol/L, [MAO]/[Ti] = 10 mol ratio.

[a] M_n and M_w/M_n were determined by GPC analysis with polystyrene standards.

[b] I.E.: initiation efficiency = $\{([VC]_0 \times \text{yield} \times 62.5)/([Ti] \times M_n)\} \times 100$.

High molecular weight PVC was usually difficult to synthesize from a radical polymerization of VC, since the molecular weight of the polymer should be restricted by large chain transfer constant to the monomer ($C_m = 3.2 \times 10^{-4}$ at 20 °C [2]). However, such limitation may be ignored in the polymerization of VC with Cp*$Ti(OPh)_3$/MAO catalyst, leading to the synthesis of high molecular weight PVC.

3.2. Kinetic study

To elucidate a kinetic profile in the bulk polymerization of VC with Cp*$Ti(OPh)_3$/MAO catalyst, the bulk polymerization of VC was conducted. The results are shown in Fig. 1. The polymer yield increased with an increase of reaction time along with molecular weight of the polymer, although the polymerization rate was very slow. At the initial stage of the polymerization, some retard of the polymer yield and the M_n of the polymer was observed. This may be explained by a slow initiation as well as by the solution polymerization [7].

To estimate the stability of the active site for the bulk polymerization, the M_n of the polymer was plotted against polymer yield. The results are also shown in Fig. 1. The M_n of the polymer increased in direct proportion to polymer yields and the line passed through the origin. In addition, the M_w/M_n value decreased with increasing polymer yield. If the side reactions such as termination reaction are not occurred in the chain polymerization, the M_w/M_n of the polymer is known to decrease in reverse proportion to increase of number-average degree of polymerization (DP) $\{M_w/M_n \approx 1 + 1/DP\}$ [1]. The results suggest that side reactions such as termination reaction may be ignored even in the bulk polymerization as well as in the solution polymerization [7].

The GPC elution curves of the polymers obtained from the polymerization of VC with Cp*$Ti(OPh)_3$/MAO catalyst are shown in Fig. 2. The elution curves were unimodal and the whole curves shifted clearly to the higher molecular weight

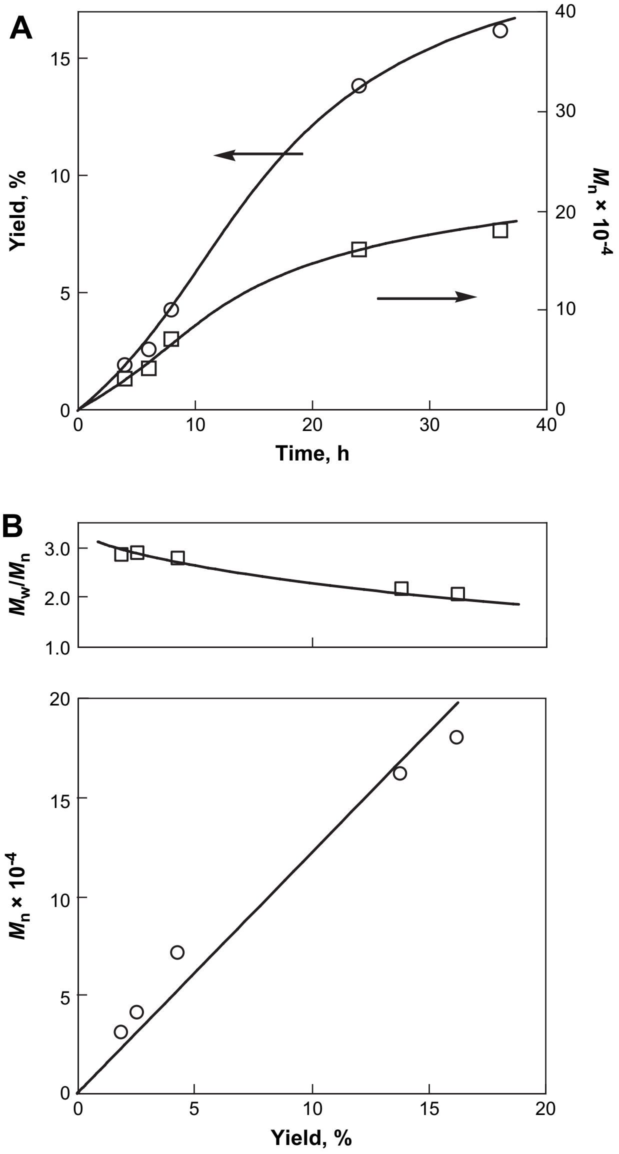

Fig. 1. (A) Kinetic studies and (B) relationship between the polymer yield and the M_n of PVC on the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst at 20 °C; [VC] = 15.2 mol/L, [Ti] = 3.0 × 10^{-3} mol/L, [MAO]/[Ti] = 10 mol ratio, total volume = 10 mL.

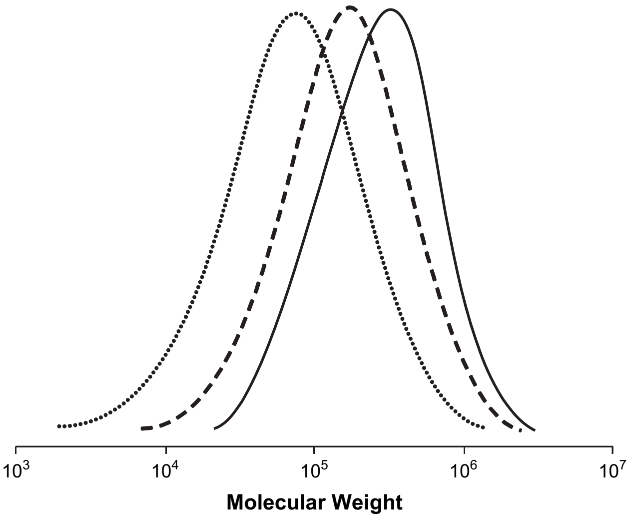

Fig. 2. GPC elution curves of PVC obtained from bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst at 20 °C for 6 h (···), 16 h (—), and 36 h (—).

as a function of reaction time, suggesting that the active site for the polymerization is stable even in the bulk polymerization. On the basis of these results, it is clear that the molecular weight control of PVC is possible even in the bulk polymerization as well as in the solution polymerization.

3.3. Structure of PVC

Fig. 3 shows the ^{1}H NMR spectrum of the polymer obtained from the bulk polymerization with Cp*Ti(OPh)$_3$/MAO catalyst, in which the spectrum of the polymer obtained from the radical polymerization with LPO is also indicated for comparison. The peaks at 2.0 and 4.3 ppm based on methylene proton and methine proton in the main chain were observed in both polymers. Although the peaks at 3.9–4.0, 4.0–4.1 and 5.7–5.8 ppm based on the anomalous units such as the head-to-head structure [10], $-CH_2-CH{=}CH-C\mathit{H}_2Cl$ and $-C\mathit{H}{=}C\mathit{H}-CHCl-$ [11] appeared in PVC obtained from radical polymerization, such peaks were not observed in PVC obtained with Cp*Ti(OPh)$_3$/MAO catalyst. This suggests that the polymerization proceeds by non-radical mechanism, but that detail mechanism is still obscure.

The tacticity of PVC obtained from bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst was estimated by ^{13}C NMR spectra of the polymer. The results are listed in Table 2, in which the results obtained from the solution polymerization in CH_2Cl_2 are also indicated for comparison. The mm contents of PVC obtained from the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst were somewhat higher than that obtained from the solution polymerization. This may be explained by either the polarity of the solvent or the uniformity of the polymerization system.

3.4. Thermal stability of PVC

As described above, PVC obtained from the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst has no anomalous structures. It will be expected to show more thermal stability than that obtained from radical polymerization. The thermal decomposition of PVC obtained with Cp*Ti(OPh)$_3$/MAO catalyst was carried out and the results are shown in Fig. 4, in which the results of PVC obtained with radical initiator are also indicated for comparison. The initial decomposition temperature ($T_{-5\%}$) of PVC obtained from the bulk polymerization with Cp*Ti(OPh)$_3$/MAO catalysts was higher than that obtained with LPO.

In the bulk polymerization, the molecular weight of PVC can be changed widely and synthesized up to high molecular weight rather than the solution polymerization, and the main chain structure is controlled. These factors may influence the thermal property. The effect of molecular weight on the thermal decomposition was examined. Fig. 5 shows the molecular

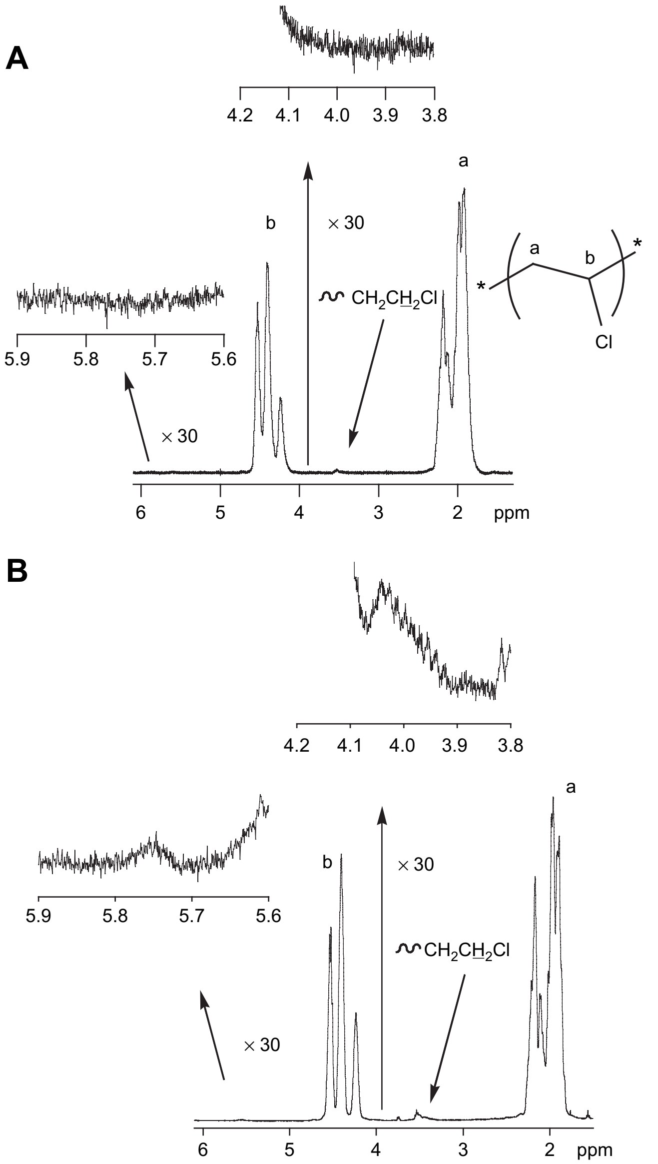

Fig. 3. ^{1}H NMR spectra of PVC obtained from the polymerization of VC with (A) Cp*Ti(OPh)$_3$/MAO catalyst ($M_n = 6.0 \times 10^4$) and (B) LPO ($M_n = 3.2 \times 10^4$).

Table 2
Tacticity of PVC obtained from polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst at 20 °C[a]

Solvent	mm	mr	rr
CH_2Cl_2[b]	18.3	45.1	36.6
–[c]	22.7	43.8	33.9

[a] [Ti] = 3.0×10^{-3} mol/L, [MAO]/[Ti] = 10 mol ratio.

[b] [VC] = 3.0 mol/L.

[c] [VC] = 15.2 mol/L.

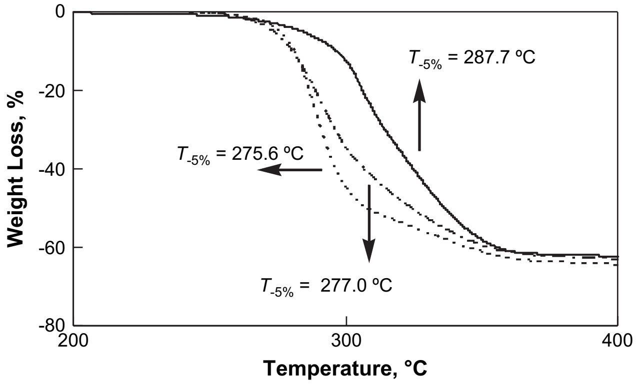

Fig. 4. TG curves of PVC obtained with Cp*Ti(OPh)$_3$/MAO catalyst (solid line, $M_n = 12.2 \times 10^4$; chain line, $M_n = 7.5 \times 10^4$) and radical initiator (broken line; $M_n = 17.1 \times 10^4$) at a heating rate of 10 °C/min. $T_{-5\%}$ indicates the temperature of 5% weight loss.

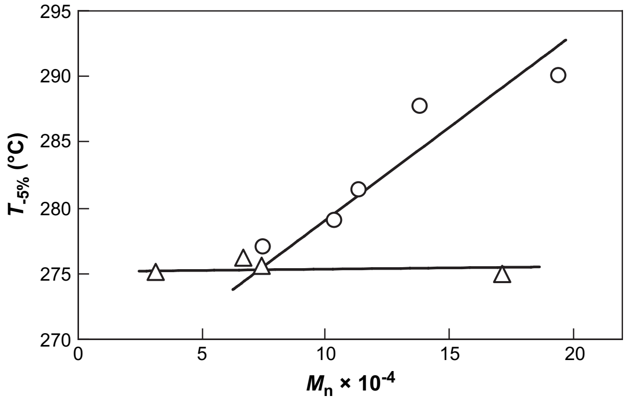

Fig. 5. Molecular weight dependence of initial decomposition temperature ($T_{-5\%}$) of PVC obtained with Cp*Ti(OPh)$_3$/MAO catalyst (○) and LPO (△).

weight dependence on $T_{-5\%}$ of PVC obtained with Cp*Ti(OPh)$_3$/MAO catalyst, in which the results for PVC obtained with radical polymerization are also indicated. The $T_{-5\%}$ of the polymer obtained from bulk polymerization with Cp*Ti(OPh)$_3$/MAO catalyst increased with an increase of the molecular weight of PVC, in contrast to that PVC obtained with LPO did not depend on the molecular weight of the polymer. It was also reported that thermal decomposition of PVC obtained from radical polymerization did not depend significantly on the molecular weight of the polymer [12]. Although the terminal structure of PVC were known to influence the thermal decomposition temperature of the polymer [13], the thermal decomposition of the polymer is generally believed to initiate at the anomalous units in the chains followed by chain reaction of dehydrochlorination [14]. PVC obtained with Cp*Ti(OPh)$_3$/MAO catalyst did not have such anomalous structures in the chain. Thus, the thermal decomposition of the polymer may be initiated at the chain end because of decrease of initiating point of thermal decomposition per chain with increase of the molecular weight of the polymer.

4. Conclusion

The molecular weight of PVC obtained from the bulk polymerization of VC with Cp*Ti(OPh)$_3$/MAO catalyst was higher than the polymer obtained from solution polymerization with the same catalyst and radical polymerization. In the ^{1}H NMR spectrum, the anomalous structures of the polymer obtained from the bulk polymerization with Cp*Ti(OPh)$_3$/MAO catalyst were not observed as well as that obtained from the solution polymerization in CH_2Cl_2. Namely, the structure of the polymer obtained from the bulk polymerization can be regulated even in the bulk polymerization. The thermal stability of the polymer was superior to that of PVC obtained with radical initiator. The initial decomposition temperature of the polymer obtained with Cp*Ti(OPh)$_3$/MAO catalyst depended on the molecular weight, in contrast to that the thermal decomposition of the polymer obtained with radical initiator did not depend on the molecular weight.

References

[1] Ordian G. Principle of polymerization. 3rd ed. New York: Wiley Interscience; 1991.

[2] Danusso F, Sianesi D. Chim Ind (Milan) 1955;37:695–701.

[3] Endo K, Saitoh M. Polym J 2000;32(3):300–2.

[4] Endo K, Saitoh M. Macromol Rapid Commun 2002;23(15):913–6.

[5] Endo K, Saitoh M. J Polym Sci Part A Polym Chem 2003;41(2):248–56.

[6] Endo K, Saitoh M. Polym Bull 2003;49(6):411–6.

[7] Endo K, Nomaguchi T, Tsuchiya Y. J Polym Sci Part A Polym Chem 2007;45(17):3872–6.

[8] Wade SR, Wallbridge MGH, Willey GR. J Chem Soc Dalton Trans 1982;2:271–4.

[9] Chien JCW, Salajka Z. J Polym Sci 1991;A-29(9):1253–63.

[10] Darricades-Llauro MF, Michel A, Guyot A, Waton H, Petiaud R, Pham QT. J Macromol Sci Chem 1986;A23(2):221–69.

[11] Benedikt GM, Cozens RJ, Goodall BL, Rhodes LF, Bell MN, Kemball AC, et al. Macromolecules 1997;30(1):10–21.

[12] Xu P, Zhou D, Zhao D. Eur Polym J 1989;25(6):581–3.

[13] Park GS, Skene CL. J Polym Sci Part C 1971;33:269–79.

[14] Starnes Jr WH. Prog Polym Sci 2002;27(10):2133–70.