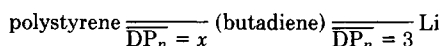


Ethylene–Styrene Diblock Copolymers: Synthesis by Ziegler–Natta Catalysis and Identification

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Synopsis

A new way of directly synthesizing ethylene–styrene diblock copolymer by Ziegler–Natta catalysis was studied. It consists of using a soluble complex prepared by the reaction of



with TiCl_4 in the ratio $r = [\text{Li}]/[\text{Ti}] = 2$ to initiate the formation of the polyethylene block. The well-defined linear diblock structure was established both by GPC of the polyethylene block and by ^{13}C NMR and DSC analyses of the copolymer. Moreover, by using such a catalytic system, the efficiency was found to be 0.88 with respect to carbon–titanium bond. This value is relatively high compared to those of conventional Ziegler–Natta catalytic systems.

INTRODUCTION

ABA triblock copolymers with elastomeric B block have been intensively studied in order to be used as thermoplastic elastomers. Diblock copolymers, although easier to prepare, have not aroused the same interest until recently.

The diversification of properties of polymeric materials obtained by using polymer blends has permitted researchers to expect the use of these diblock copolymers as emulsifying additives.

Block copolymers based on an olefin and another monomer have already been prepared by several workers. One process for their synthesis consists of using Ziegler–Natta polymerization, taking advantage of favorable reactivity ratios.¹ Unfortunately, both this method of polymerization and the insolubility of the catalyst during the reaction lead to high molecular heterogeneity of the obtained copolymers. Since then, it has been shown that such heterogeneity decreases the mechanical properties of blends compatibilized by such additives.² Another way has been used recently. It consists of synthesizing copolymer with one polystyrene block and one polybutadiene block. The latter is subsequently selectively hydrogenated, leading to a polyethylene block.^{3,4} This method induces a better definition of the copolymers prepared, although the existence of 1,2 butadiene units (before hydrogenation) results in the fairly low melting temperature of the polyethylene block.

This paper describes a new route of directly synthesizing such diblock copolymers: It consists of using a soluble Ziegler–Natta complex prepared by the reaction of a macromolecular organolithium compound with TiCl_4 . Previously this method was used to prepare poly(ethylene-*b*-butadiene) copolymers^{5,6}; however, side reactions occurring during the formation of the polyethylene block led to a slight crosslinking of the copolymer. Since these side reactions were due to the presence of double bonds in the 1,2 butadiene units, this work has been

turned towards the realization of poly(ethylene-*b*-styrene) copolymers.

Recently, Cohen et al.⁷ claimed to have prepared both poly(ethylene-*b*-isoprene) and poly(ethylene-*b*-styrene) copolymers by a method similar to this one. Some of the results published by these authors appear to be surprising; others disagree with the findings corresponding to this work. The polymer samples characterization could explain these disagreements.

RESULTS AND DISCUSSION

Synthesis of the Copolymer Poly(ethylene-*b*-Styrene)

The method is derived directly from the one usually used for the preparation of block copolymers from living systems. It consists of reacting a macromolecular organolithium compound with TiCl_4 . By mixing the reactants the substitution of Ti(IV) and the subsequent reduction of Ti(IV) to Ti(III), lead to the formation of a Ziegler-Natta complex whose composition is



When the solvation energy of the polymer chains by the solvent of the reaction medium is sufficiently high, the complex obtained is soluble,⁶ and the addition of ethylene monomer in the solution leads to the polymerization of the olefin. Previous studies of this system showed a kinetic behavior similar to that of living polymers.⁹ Nevertheless, when the initial organolithium polymer is the polybutadienyllithium, the obtained copolymer is slightly crosslinked.⁸ In order to avoid such a disadvantage, the polybutadiene block is replaced by a polystyrene block. However, in so doing, a β hydrogen elimination reaction disactivates the polystyryl-titanium ends and leads to the formation of linear polyethylene homopolymer.⁸ By taking advantages of both systems studied, both the crosslinking and the breaking of the polymeric chain from the initial organolithium compound can simultaneously be avoided. The method proceeds by reacting TiCl_4 in toluene with an organolithium compound such as



The optimal experimental conditions are obtained for the ratio

$$[\text{Li}]/[\text{Ti}] = 2$$

The ethylene dissolved in the medium adds on the macromolecular organotitanium active centers prepared.

The addition of the first monomeric units takes place in homogeneous phase, but as soon as the polyethylene block reaches the critical length, the precipitation of the copolymer occurs. This precipitation leads to a change in the slope of the curve of ethylene conversions vs. time (Fig. 1).

The separation of the copolymer from the inefficient or disactivated homopolymer is easy because of the insolubility of the copolymer in the reaction medium.

The results on activity and efficiency of the catalytic system are appreciably different, depending on whether high vacuum or inert gas experimental techniques are used (see Table I). The latter is less sophisticated and allows us to obtain much more polymeric material than the former but leads to less reliable results. In particular, a strong decrease in the efficiency, consequently, appears

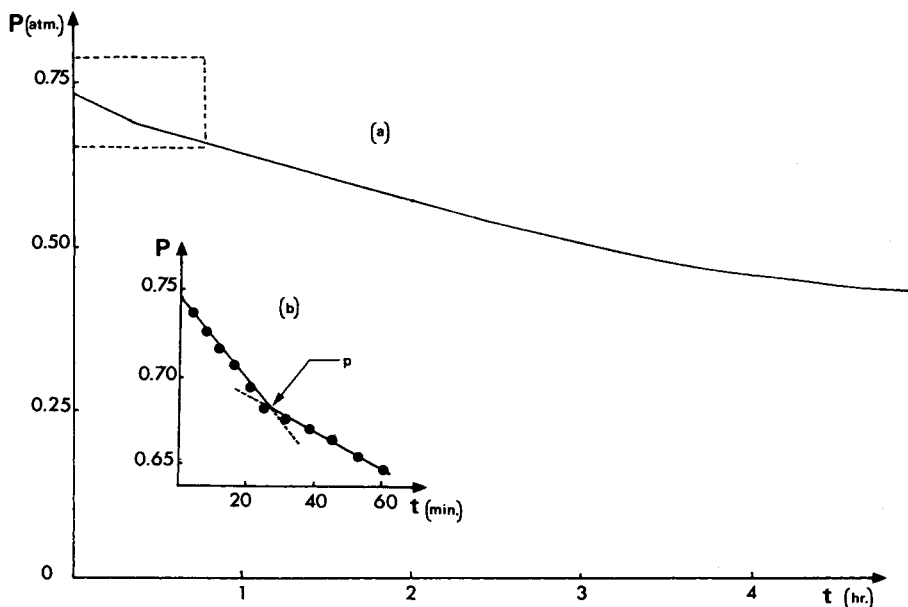


Fig. 1. Polymerization of ethylene initiated by the $pSt_{100}\text{-But}_3\text{-Li/TiCl}_4$ /toluene system ($[pSt_{100}\text{-But}_3\text{-Li}] = 1.3 \text{ mmol}\cdot\text{L}^{-1}$; $r = [\text{Li}]/[\text{Ti}] = 2$; $T = 20^\circ\text{C}$): (a) overall kinetic curve; (b) initial step of the polymerization; (p): Change in the kinetic behavior due to the precipitation of the copolymer $pSt_{100}\text{-But}_3\text{-PE}$ in the reaction medium.

to be followed by a strong decrease of the activity; both can be mainly attributed to the difficulty of purifying the TiCl_4 and the ethylene monomer under inert gas.

Therefore, the most appropriate data are those concerning the polymerizations realized in all-sealed apparatus (under high vacuum).

Copolymer Characterization

The copolymer is recovered from the solution after reaction. The polystyrene soluble in toluene is easily separated from the insoluble copolymer. Thus the

TABLE I
Influence of Organolithium Concentration on Catalytic Behavior of $pSt_x\text{-But}_3\text{-Li/TiCl}_4$ /
Toluene Systems in Polymerization of Ethylene^a

Run	Exptl \overline{M}_n of $pSt_x\text{-But}_3\text{-Li}$	Organolithium concn ($\text{mmol}\cdot\text{L}^{-1}$)	Activity during homogeneous step ($\text{g}\cdot\text{mol}^{-1}\cdot\text{L}\cdot\text{h}^{-1}\cdot\text{atm}^{-1}$)	Efficiency (with respect to C-Ti bond)
1 ^b	7000	20	350	0.16
2 ^b	33,000	10	300	0.10
3 ^c	11,000	1.31	1700	0.88
4 ^c	10,000	0.80	1000	0.82
5 ^c	10,000	0.61	750	0.86
6 ^c	11,000	0.26	350	0.88

^a $0.8 < p < 0.9 \text{ atm}$; $T = 20^\circ\text{C}$; $r = [\text{Li}]/[\text{Ti}] = 2$.

^b Using argon system.

^c Using high vacuum system.

TABLE II
Characterization of Block Copolymers: Molecular Weight of Blocks

Run	Theoretical \overline{M}_n of pSt _x -But ₃ -Li	Exptl \overline{M}_n of Disactivated pSt-But ₃		Theoretical \overline{M}_n of PE block	Exptl \overline{M}_n of PE block	$\overline{M}_w/\overline{M}_n$
		Main peak	Shoulder			
1	6500	7000	13,000	25,000	33,000	2.8
2	30,000	32,000	68,000	40,000	35,000	2.7
3	10,000	11,000	23,000	41,000	63,000	1.4
4	10,000	11,000	23,000	60,000	92,000	1.5
5	10,000	10,000	22,000	95,000	135,000	1.4
6	10,000	10,000	22,000	145,000	210,000	1.4

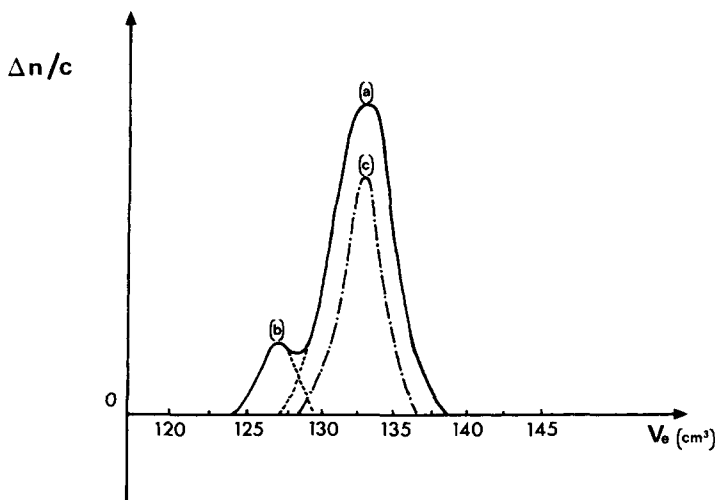


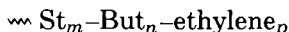
Fig. 2. GPC chromatogram of a deactivated pSt₁₀₀-But₃ "copolymer" extracted from the polymerization filtrate: (—) deactivated "copolymer" [(a) $\overline{M}_n = 11,000$; $\overline{M}_w = 12,000$; (b) $\overline{M}_n = 23,000$; $\overline{M}_w = 24,000$]; (---) initial "copolymer" ($\overline{M}_n = 11,000$; $\overline{M}_w = 11,500$).

homopolymer can be analyzed by GPC. The results are listed in Table II and Figure 2.

The reactional behavior of the pSt_n-But₃ system is the same as p(But)_n⁹: approximately 80% of the organolithium compound is deactivated by disproportionation, and the other part by recombination of the free radicals.

Identification of the Block Structure

If the catalytic system was a living system, the structure of the copolymer would be expected to be:



In order to characterize such a block structure, an ozonolysis of the short polybutadiene sequence was performed. In such a reaction, both homopolymer blocks are released. Nevertheless, the ozonolysis is not sufficiently selective to be limited to the polybutadiene block; the polystyrene block is also partly degraded, and it has not been possible to recover it. On the other hand, the polyethylene block is fully obtained and was analyzed by GPC.

The comparison of the polyethylene GPC chromatogram with that of the copolymer before ozonolysis shows a molecular weight increase due to the copolymerization (Fig. 3). Nevertheless, the lack of copolymer standards for the calibration of the columns precludes any measurements of the molecular weight increase.

The experimental molecular weights of the polyethylene blocks are in agreement to within 30% of the calculated molecular weight, assuming a living system with an efficiency approaching unity (Table II). We should point out that the efficiency of the catalyst can reach 0.88, considering the binuclear structure of the active centers (with regard to C—Ti bond).⁹ This value is very high compared to those of most Ziegler-Natta catalysts.

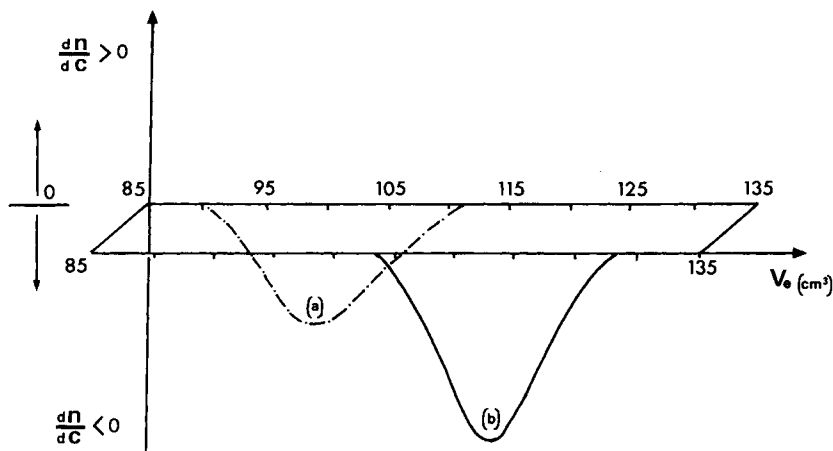


Fig. 3. GPC chromatograms of: (a) pSt₁₀₀-But₃-pEt copolymer (\overline{M}_n theoret = 73,000); (b) pEt block resulting from ozonolysis of (a) (\overline{M}_n theoret = 63,000; \overline{M}_n exptl = 41,000).

Moreover, it is also important to note that the distribution of the molecular weights of the polyethylene block prepared using our method is narrower ($\overline{M}_w/\overline{M}_n = 1.4$) than that obtained from conventional Ziegler-Natta catalysts ($2.5 < \overline{M}_w/\overline{M}_n < 20$).

¹³C NMR Analysis

Due to the low solubility of these copolymers in common solvents, ¹³C NMR spectra showing both aromatic and aliphatic carbons require the use of two solvents. Aromatic carbons can be assigned using decaline, while aliphatic carbon assignments require *o*-dichlorobenzene. One spectrum of the copolymer is represented in Figure 4.

Since the chemical shifts of the β methylene carbons of styrene units are different from those of the methylene carbon of ethylene units, this spectrum demonstrates that there are few alternations. Moreover, the lack of any signal due to



in the 20–30 ppm range confirms the lack of short branches.

These results are consistent with a block structure of the copolymers.

DSC Analysis

The DSC analysis of the copolymer shows a small change of the slope in the polystyrene glass transition area (Fig. 5).

The peak assigned to the melting enthalpy of the polyethylene block appears in a relatively high temperature range. This high melting temperature, in spite of a fairly low molecular weight, indicates a good linearity of the polyethylene blocks.

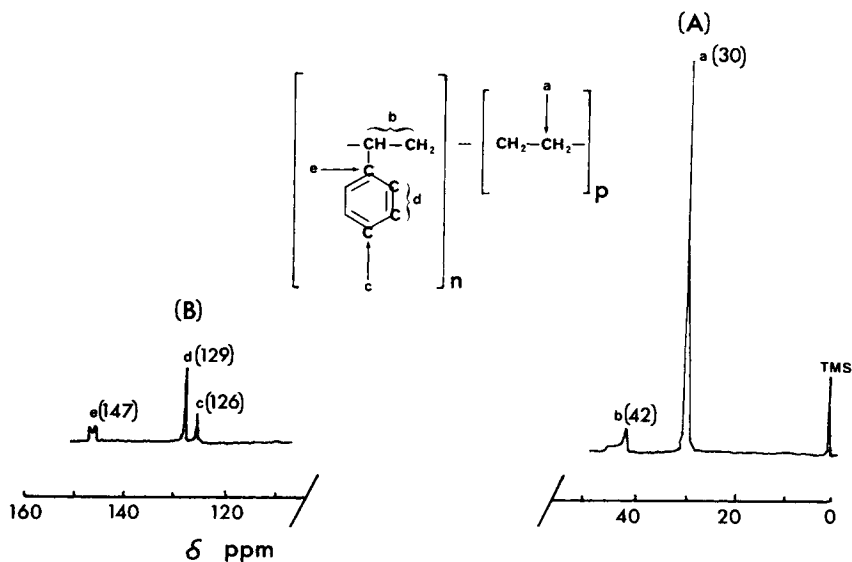


Fig. 4. ^{13}C NMR spectrum of a $\text{pSt}_{100}\text{-But}_3\text{-PE}$ copolymer at 140°C : (A) solvent: *o*-dichlorobenzene; (B) solvent: decaline.

So, all the characterization methods used disclose a relatively well-defined structure of the linear diblock copolymers poly(styrene-*b*-ethylene).

EXPERIMENTAL

High Vacuum System

The general techniques which were used are those of anionic polymerization and have been described previously.¹⁰

Purification of toluene, styrene, butadiene, ethylene, and TiCl_4 were carried out in completely sealed apparatus.

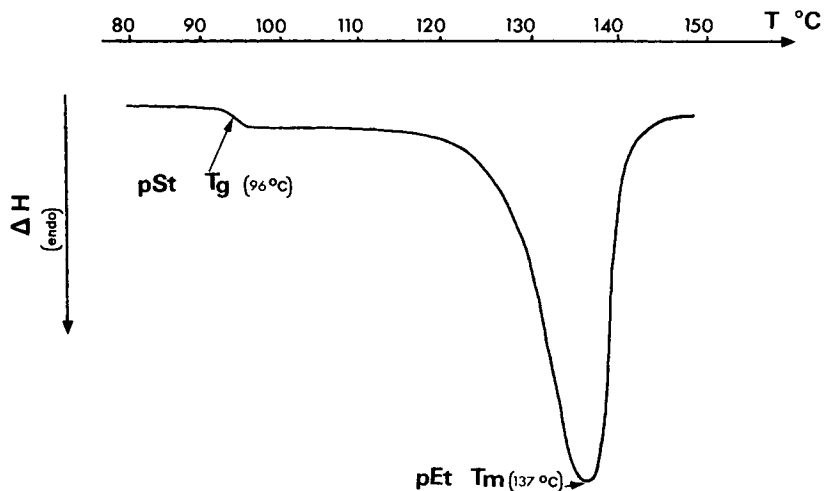


Fig. 5. DSC thermogram of a $\text{pSt}_{100}\text{-But}_3\text{-PE}$ copolymer.

Organolithium compounds were prepared at room temperature according to the methods described by Bywater et al.^{11,12}

Polymerizations of ethylene were performed at low pressures 800–930 mbar, and at room temperature in constant volume apparatus.

The reaction rate was followed by measurements of ethylene pressure by means of a strain gauge.

Argon System

Purification of chemicals and polymerizations were performed inside a glass apparatus built with flasks connected to both a vacuum line and an argon line by means of vacuum stopcocks.

Chemicals were generally distilled under Argon and dried over *n*-butyllithium before use.

Reagents transfers were done either by distilling at low temperature (vacuum line) or by removal using a syringe and a septum system (Argon line).

Copolymer Characterization

The ozonolysis technique of the copolymer has been described previously.⁶

Molecular weight measurements were carried out by GPC at 140°C in 1,2,4-trichlorobenzene with a Waters GPC 200 apparatus.

The ¹³C NMR spectra of copolymers were performed at 140°C in decaline or *o*-dichlorobenzene with a Bruker WP 60 DS (15.09 MHz).

Thermal analyses were carried out on a Perkin-Elmer DSC 2 apparatus.

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