Copolymerization of Styrene and Isoprene: An Insight into the Mechanism of Syndiospecific Styrene Polyinsertion

Claudio Pellecchia, Antonio Proto, and Adolfo Zambelli*

Dipartimento di Fisica, Università di Salerno, I-84081 Baronissi (SA), Italy

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Introduction. As reported in the literature,[1-3] syndiotactic specific polymerization of styrene is promoted by homogeneous catalysts which can be prepared by allowing a titanium compound soluble in aromatic solvents to react with methylalumoxane (MAO). $CpTiX_3$ (where Cp = η^5-cyclopentadienyl, where X = halogen or hydrocarbyl) affords a particularly effective and stereospecific catalyst.[2]

Systematic investigation of the polymerization of styrene as well as of substituted styrenes suggested that the active species are strong electrophiles, possibly organotitanium complex cations.[4] This suggestion was later supported by the finding that syndiotactic polymerization of styrene can also be achieved by preparing the catalyst by reaction of, e.g., $Cp^*Ti(CH_3)_3$ (Cp* = η^5-pentamethylcyclopentadienyl) with $[(C_2H_5)_3NH]^+[B(C_6F_5)_4]^-$ or with $B(C_6F_5)_3$.[5,6] In both cases titanium complex cations would result according to the following reactions:

$$Cp^*Ti(CH_3)_3 + [(C_2H_5)_3NH]^+[B(C_6F_5)_4]^- \rightarrow [Cp^*Ti(CH_3)_2]^+[B(C_6F_5)_4]^- + CH_4 + (C_2H_5)_3N \quad (1)$$

$$Cp^*Ti(CH_3)_3 + B(C_6F_5)_3 \rightarrow [Cp^*Ti(CH_3)_2]^+[B(C_6F_5)_3CH_3]^- \quad (2)$$

The homogeneous catalysts indicated also promote cis-1,4 polymerization of 1,3-butadiene, isoprene, and (*Z*)-1,3-pentadiene[7,8] (in the last case affording a prevalently cis-1,4 isotactic polymer).[9]

In this paper we investigate the copolymerization of styrene and isoprene promoted by $CpTiCl_3$–MAO. The results obtained confirm the close relationship between the mechanisms of syndiotactic polymerization of styrene and cis-1,4 polymerization of conjugated diolefins.

Results and Discussion. Table I reports the results of copolymerizations of styrene with isoprene, as well as two homopolymerizations performed under similar conditions. Due to the low conversions, the compositions of the feed and that of the resulting copolymers can be plotted according to the Fineman–Ross equation (see Figure 1). Accordingly, the reactivity ratios $r_1 = 0.35$ and $r_2 = 6.3$ have been calculated. As usual, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, where the k_{ij} values are the kinetic rate constants for the four copolymerization steps:

$$[Mt(C_8H_8)...]^+ + C_8H_8 \xrightarrow{k_{11}} [Mt(C_8H_8)_2...]^+ \quad (1.1)$$

$$[Mt(C_8H_8)...]^+ + C_5H_8 \xrightarrow{k_{12}} [Mt(C_5H_8)(C_8H_8)...]^+ \quad (1.2)$$

$$[Mt(C_5H_8)...]^+ + C_5H_8 \xrightarrow{k_{22}} [Mt(C_5H_8)_2...]^+ \quad (2.2)$$

$$[Mt(C_5H_8)...]^+ + C_8H_8 \xrightarrow{k_{21}} [Mt(C_8H_8)(C_5H_8)...]^+ \quad (2.1)$$

Table I
Polymerization Conditions[a] and Composition of the Copolymers of Styrene and Isoprene

run	styrene, mmol	isoprene, mmol	time, h	yield, mg	f^b	F^c
1	51		1	425		
2		58	68	70		
3	16	36	68	37	0.44	0.075
4	25	30	68	25	0.83	0.15
5	34	19	68	42	1.8	0.28
6	41	10	68	41	4.1	1.1
7	45	9.5	100	60	4.7	1.2

[a] All the runs have been performed in the presence of $CpTiCl_3$ (1×10^{-5} mol) and MAO (11 mmol) in 3 mL of toluene at 40 °C. [b] Composition of the feed (molar ratio of styrene to isoprene). [c] Composition of the copolymer (molar ratio of styrene to isoprene, determined by ^1H NMR; see the Experimental Section).

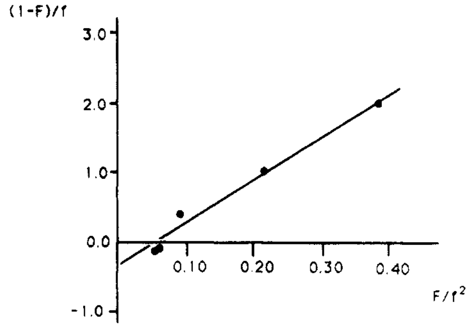


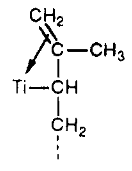
Figure 1. Fineman–Ross plot for the styrene–isoprene copolymers.

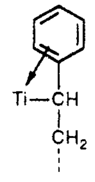
where Mt = titanium of the active complex cation, and (C_8H_8) and (C_5H_8) represent growing polymer chains ending, respectively, either with a styrene or an isoprene unit.

The value of the product of the reactivity ratios $r_1r_2 = 2.3$ is low enough to suggest that the two comonomers react according to closely related mechanisms, although homosequences occur appreciably more frequently than they should in a perfectly random copolymer (for an ideally random copolymer, $r_1r_2 = 1$). Probably the observed deviation from the random distribution of the comonomer units arises from the particularly low reactivity of styrene (eq 2.1) in comparison with isoprene (eq 2.2) in the insertion on growing chains ending with isoprene units. As a matter of fact, insertion of styrene in eq 2.1 leads to a weaker bond with titanium (Ti–benzyl instead of Ti–allyl).

The yields reported in Table I also show that homopolymerization of isoprene is much slower than that of styrene. Thus, $k_{22} \ll k_{11}$, although $k_{12} > k_{11}$ and $k_{22} > k_{21}$. It is also worth noting that addition of even a small amount of isoprene to styrene causes a dramatic decrease of the yield.

η^3 coordination of the growing chain to the titanium of the active cations and preliminary η^4 coordination of the monomer to be incorporated into the chain before insertion have been postulated[10] for both styrene and conjugated diolefins in previous papers.[7,11] Accordingly, one could hypothesize a stronger bond with titanium for π-allyl-type rather than benzyl-type[10] growing chain ends





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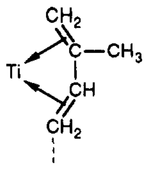
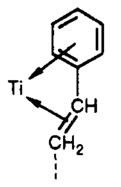
as well as a stronger π-dienyl coordination of isoprene in comparison with styrene:[10]





In fact, a decrease of the resonance energy is expected if the aromatic ring is involved in the coordination of styrene and styrene units to titanium. Thus, coordination of isoprene would be faster and more favored than coordination of styrene, but insertion on the Ti–allyl bond would be slower than insertion on the Ti–benzyl bond.

Possibly, coordination and insertion could both be rate determining. As a consequence, one can justify the apparently conflicting results, i.e., a lower reactivity of isoprene in comparison with styrene in homopolymerization and a higher reactivity of isoprene in copolymerization (i.e., $k_{22} < k_{11}$; $k_{12} > k_{11}$; $k_{22} > k_{21}$), as well as the strong decrease of the yield in the presence of even a small amount of isoprene.

Experimental Section. Toluene was refluxed over sodium–benzophenone for 48 h and distilled before use. Methylalumoxane (MAO) was purchased from Schering in 30% toluene solution: the solvent and excess $Al(CH_3)_3$ were removed by distillation under reduced pressure, and the isolated MAO was stocked as a 5.0 M (based on Al) toluene solution. Monomer-grade styrene and isoprene were distilled over CaH_2 before use. $CpTiCl_3$ was prepared as described in the literature.[12]

Runs 1–7 were carried out by introducing sequentially toluene, MAO, the monomer(s), and $CpTiCl_3$ in stirred 50-mL glass flasks thermostated at 40 °C. Polymerization runs were stopped by pouring the reaction mixtures into acidified methanol, and the obtained solids (samples 1–7) were recovered by filtration, washed with fresh methanol and dried in vacuo. Polymerization conditions and results are reported in Table I.

^1H and ^{13}C NMR analyses were performed on samples dissolved in tetrachloro-1,2-dideuterioethane containing hexamethyldisiloxane (HMDS) as an internal chemical shift reference, by using an AM 250 Bruker spectrometer operating in FT mode at 393 K. The compositions of the copolymer samples reported in Table I as F (moles of styrene per moles of isoprene) have been evaluated from the ^1H NMR spectra by the relationship

$$F = {}^1/_5 A_S/(A_{I(1,4)} + {}^1/_2 A_{I(3,4)})$$

where A_S is the area of the resonances due to the aromatic protons of the styrene units (δ = 6.5–7.5), $A_{I(1,4)}$ is the area of the resonance due to the vinylic protons of the 1,4-isoprene units (δ = 5.1), and $A_{I(3,4)}$ is the area of the resonance due to the terminal methylidene protons of the 3,4-isoprene units (δ = 4.7).

In Figures 2 and 3 are reported as examples the ^1H and ^{13}C NMR spectra of sample 6. The number of ^{13}C resonances observed in the spectrum is larger than that expected for a mixture of *cis*-1,4-polyisoprene and syndiotactic polystyrenes, confirming that actually the two comonomers copolymerize almost at random.

Conclusions. Copolymerization of styrene with isoprene in the presence of homogenous catalysts shows that the mechanism of syndiotactic specific polymerization of styrene and cis-1,4 polymerization of conjugated diolefins are strictly related, as suggested in previous papers.[4,7,11]

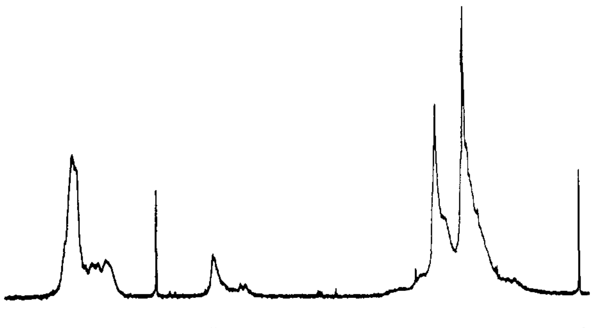


Figure 2. ^1H NMR spectrum of a styrene–isoprene copolymer (sample 6; see the Experimental Section). HMDS scale.

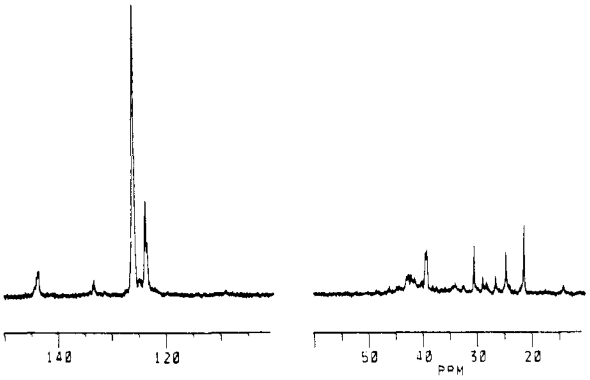


Figure 3. ^{13}C NMR spectrum of a styrene–isoprene copolymer (sample 6; see the Experimental Section). HMDS scale.

As a matter of fact, the distribution of the monomer units in the copolymers is reasonably close to random.

The yields observed for the homopolymerizations in comparison with those observed for copolymerizations of styrene with isoprene, as well as the composition of the obtained copolymers, suggest that incorporation of the monomers occurs through two steps, both rate determining: coordination of the monomer and subsequent insertion.

π-Dienyl coordination of isoprene to the titanium of the active species seems to be faster (or thermodynamically favored) in comparison with coordination of styrene, but insertion of any coordinated monomer seems to be much faster when the last unit of the growing chain end is styrene.

At least in part, the trend of the observed reactivities could arise from the decrease of the resonance energy when the aromatic ring is involved in coordination to titanium.

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(10) η^3 and η^4 nomenclature is strictly applicable to π-allyl type ligands and conjugated diolefins. In this paper, as well as in a previous one,[4] the same nomenclature is used also for a nonsymmetrical benzyl-type ligand and styrene, in order to stress that they behave as ligands isoelectronic with π-allyl and isoprene, i.e., as three- and four-electron ligands, respectively, without any reference to the distance of the ortho aromatic carbons from the metal. As a matter of fact, both η^2 and η^3 coordination have been reported for three-electron benzyl ligands in different transition-metal complexes. See, e.g.: (a) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418.

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Registry No. $CpTiCl_3$, 1270-98-0; styrene, 100-42-5; isoprene, 78-79-5; (styrene)(isoprene) (copolymer), 25038-32-8.