Stereoregularity of Polystyrenes Obtained by Different Ion-Pairs and Mechanism of Polymerization

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ABSTRACT: The stereoregularity of polystyrenes obtained with lithium, sodium, potassium, rubidium, and cesium as counterions in various solvents was determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy, according to new assignments. Polystyrenes produced by tight ion-pairs of polystyryllithium in toluene had the proportions of a 73% *racemic* dyad (P_r), whereas the P_r values decreased to 56% by substituting cesium for lithium. Polystyrene produced by loose ion-pairs, cryptated ion-pairs and free ions had the proportion of a 69—74% *racemic* dyad. Two reaction schemes have been developed in order to explain the results obtained.

KEY WORDS Polystyrene / Carbon-13 NMR / Polymerization /

In the anionic polymerization of styrene with alkali counterions, tight ion-pairs, loose ion-pairs, and free ions are present in equilibrium, depending on the nature of the solvent and on the temperature.^{1,2} Moreover, recent improvement in ^{13}C nuclear magnetic resonance (NMR) spectroscopy has made it possible to detect a small difference in the stereoregularity of polystyrene.³⁻⁵ Therefore the configuration of polystyrenes produced by individual growing species has been investigated.⁶⁻⁹

Matsuzaki *et al.*^{8,9} have reported that polymerization with potassium and cesium as counterions gives isotactic-rich polystyrenes in solvents with low dielectric constants, whereas polymerization with butyllithium and sodium naphthalene as the catalyst gives syndiotactic-rich polystyrenes.

More recently, the spectra of the aromatic C_1 and methylene have been reexamined, and new assignments have been established, based strictly on a one-parameter Bernoullian fit that was in satisfactory agreement with the relative intensities of the peaks

observed.¹⁰

Consequently, in this study, we wish to report the effects of tight and loose ion-pairs, cryptated ion-pairs, and free ions in the anionic polymerization of styrene on the stereoregularity of polymers changing solvents and temperature with lithium, sodium, potassium, rubidium, and cesium cations as counterions.

EXPERIMENTAL

Catalysts

Sodium, potassium, rubidium, and cesium were vacuum-distilled into bulbs provided with break seals. Lithium naphthalene was synthesized by the reaction of lithium metal with naphthalene in tetrahydrofuran (THF) at an ambient temperature under high vacuum. The cation-complexing agent (cryptand [222]) was recrystallized from hexane, dried and sealed off under vacuum.

Solvents and Monomer

The purification and the drying of styrene and

solvents are described in previous papers.¹¹⁻¹²

precision of the measurement was about 1%.

Polymerization

The high reactivity of the growing species requires the use of high vacuum techniques and all glass apparatus. The polymerization is described in a previous paper.¹²

NMR Measurements

¹³C NMR spectra (25.033 MHz) were measured in 10–20% polymer solutions in *o*-dichlorobenzene at 150°C with a JEOL JNM-NMR spectrometer (model PS-100). Polystyrene spectra were accumulated with pulse spacings of 2.1 and 3.5 s. The spectra were ¹H noise-decoupled and obtained after the accumulation of 7–25 thousand transients. Relative intensities were obtained through curve resolution assuming a Lorentzian peak shape. The

RESULTS AND DISCUSSION

Proposal for the Reaction Scheme

In anionic polymerization, the structure of the macromolecules depends strictly on the nature of the active propagating species.¹

Tight ion-pairs, loose ion-pairs, and free ions are present in equilibrium, depending on the nature of the solvent, the complexing agent and on the temperature.

The coordination of the counterion with both the propagating chain-end and the incoming monomer occurs more or less in order to orient the monomer with respect to the growing chain-end and to bring about its stereospecific addition. Different mechanisms have been advanced to explain the usual

Figure 1. Anionic polymerization of styrene. Reaction scheme in a nonpolar medium.

Figure 2. Anionic polymerization of styrene. Reaction scheme in a polar medium.

isotactic placement obtained with anionic catalysts.^{1,13-15}

Two reaction schemes can be proposed. The first one in a nonpolar medium depicts a general situation in which the end of isotactic polymer chain (I) is tight ion-pair (Figure 1). By the addition of a styrene unit, the isotactic (VI) and/or syndiotactic (VII) structures are (is) formed. The counterion is coordinated with both the propagating chain-end and the incoming monomer molecule. The monomer is oriented and "held in position" by the coordination during addition to the polymer chain. The coordination bond between the counterion and the propagating chain is broken simultaneously with the formation of bonds between the chain end and the new monomer unit, and between the counterion and the new monomer unit. Propagation proceeds in the four membered cyclic transition state (II and/or III) by the insertion of the monomer between the counterion and the propagating chain-end. In transition state (II), the two benzene rings each are located above and underneath the four-membered cycle (C_3 , C_4 , C_5 , M). In transition state (III), the two benzene rings are located on the same side of the four-membered cycle. The driving force for syndiotactic placement derives from the attrac-

tive interactions of the counterion with the two benzene rings, and these interactions are highest in transition state (III), and the lowest in transition state (II).

The second reaction scheme (Figure 2) depicts an isomerization from the isotactic configuration (I') to the syndiotactic configuration (II') (and *vice versa*) through free ions (III'). This scheme applies for free ions, loose ion-pairs in polar medium and/or cryptated ion-pairs in polar and nonpolar media.

The type of stereochemical control obtained in the anionic polymerization reactions of styrene probably applies, in general, to either polar monomers or monomers with large substituents. In all such cases, propagation involving a freely-dissociated anionic end group produces a syndiotactic polymer; that is, the syndiotactic form is the thermodynamically most stable configuration for the attainment of minimum steric and polar repulsions.

Influence of the Nature of the Solvent and the Counterion

Polar solvents lead to the formation of loose ion-pairs and free ions.

The proportion of the *racemic* dyad, P_r , obtained

Table I. Polymerization of styrene^a

Initiator	Solvent	Temp of polymerization	mm	mr	rr	P_r	Matsuzaki results ⁹	
		°C					Temp of polymerization/°C	P_r
Li-Naphtalene	THF	-78	0.10	0.32	0.58	0.74		
BuLi	THF	+20	0.12	0.37	0.51	0.69		
BuLi	THF	-20	0.13	0.37	0.50	0.69		
BuLi	THF	-78	0.09	0.40	0.51	0.71		
K film	THF	-78	0.09	0.34	0.57	0.74	-78	0.67
Cs film	THF	-78	0.14	0.35	0.51	0.69	-78	0.63
BuLi	Toluene	+20	0.07	0.41	0.52	0.73		
BuLi	Toluene	-20	0.13	0.42	0.45	0.66	-20	0.71
Na film	Toluene	+10	0.15	0.40	0.45	0.65	+30	0.66
K film	Toluene	+10	0.22	0.37	0.41	0.59	+30	0.46
Rb film	Toluene	+10	0.21	0.44	0.35	0.57		
Cs film	Toluene	+10	0.24	0.41	0.35	0.56	+30	0.45
Na [222]	THF	-78	0.11	0.39	0.50	0.70		
K [222]	THF	-78	0.14	0.34	0.52	0.69		
Rb [222]	THF	-78	0.16	0.34	0.50	0.67		
Na [222]	Benzene	+10	0.11	0.37	0.52	0.71		
K [222]	Benzene	+10	0.10	0.29	0.61	0.75		
Rb [222]	Benzene	+10	0.16	0.28	0.56	0.70		
Cs [222]	Benzene	+10	0.16	0.36	0.48	0.66		
Cs [222]	Dioxane	+10	0.17	0.35	0.48	0.66		

^a Stereoregularity of polystyrene is represented in terms of percentages of triad and racemic dyads.

at -78°C with lithium, potassium and, cesium in THF was 69–74% (Table I). P_r was determined according to the relationships between the dyad-triad: $P_r = (rr) + 1/2 (mr)$.

The polar solvent favors the syndiotactic structure (II) (Figure 2).

These results are close to those observed by Matsuzaki *et al.*⁶ In a nonpolar solvent, the reaction scheme follows the paths, I, II, IV, VI or I, III, V, VII (Figure 1).

For lithium as a counterion, the attractive interactions with the two benzene rings occur most in transition state (III), (Figure 1), leading to a syndiotactic placement ($P_r = 0.66$ in toluene at -20°C).

But, with an increase in the ring of the counterion, the steric hindrance between the cation and the two benzene rings takes on greater importance, favoring more the transition state (II) which leads to an increase in the isotactic placement. Indeed, the proportions of *racemic* dyad, P_r , of the polymer obtained in toluene at +10°C, decrease slightly according to whether lithium or cesium is used.

For a last counterion, P_r equals 56%, indicating the polymer has almost random configuration.

No agreement could be found with the results obtained by Matsuzaki, who reported that polymerization with potassium and cesium as counterions gives isotactic-rich polystyrenes.⁹

Influence of a Complexing Agent: Cryptand [222]: (Table I)

It is well known that cryptands such as,

referred to as [222], complex very strongly with cationic species and hence promote nucleophilic reactions.¹⁶⁻¹⁹

In using benzene and dioxane as solvents, we obtained a complexed ion pair ("cryptate") in which all interactions between the cation and the benzene rings of styrene were annihilated, thus leading to the reaction scheme depicted in Figure 2.

The polymers obtained were mostly syndiotactic and the proportions of racemic dyads (66 to 71%) are roughly independent of the nature of the cation which lost its identity through complexation. However, an exception was found for potassium where P_r is equal to 75%.

In polar media like THF, the presence of cryptated ion-pairs, loose ion-pairs and free ions leads to the same configuration as that observed in the absence of cryptand [222].

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