

Use of Cryptates in Bulk Anionic Polymerization of Styrene

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ABSTRACT: The stereoregularity of polystyrene obtained with lithium, sodium, potassium, rubidium, and cesium naphthalenes in the presence of cryptates without solvent was determined by ^{13}C NMR spectroscopy. The effects of cryptates on the polymerization initiated with organolithium compounds were examined. The influence of polymerization temperature and the nature of the cation on the molecular weight, induction period, and stereoregularity of polystyrenes produced were also studied. The polystyrenes obtained were mostly syndiotactic and obeyed the Bernoullian statistics. Finally block copolymerization with isoprene and methyl methacrylate was studied.

KEY WORDS Polystyrene / Bulk Polymerization / NMR / Cryptand /
Molecular Weight / Copolymerization /

It is well known that in the anionic polymerization of styrene with alkali counterions, tight and loose ion-pairs, and free ions are present in equilibrium depending on the nature of the solvents and temperature. The effects of alkali cation, solvent, and temperature on the rate of polymerization and the stereoregularity of polystyrenes have been investigated in detail.¹⁻¹⁹ More recently, the NMR spectra of the aromatic C_1 and methylene carbon were reexamined, and new assignments made based on Bernoullian statistics.^{16,17}

In this study I wish to report the effects of cryptated ion-pairs on the stereoregularity of polystyrenes produced in bulk anionic polymerization. The block copolymerization of styrene with isoprene or methyl methacrylate was also studied in the presence of a cryptate. The results were compared with those of solution polymerization of styrene in both the presence and absence of cryptates.

EXPERIMENTAL

The purification of styrene was described in previous papers.^{18,19} The purification of cryptates and the preparation of BuLi, MeLi, PhLi, and alkali naphthalene were outlined in the preceding paper.²⁰ Measurement of molecular weights was carried out by GPC using a Waters 200 instrument.

^{13}C NMR spectra (25.033 MHz) were measured on 10–20% polymer solutions in *o*-dichlorobenzene at 150°C with a Bruker spectrometer (model WP 80). The interferograms were accumulated at pulse intervals of 2.1 and 3.5 s. Relative intensities were obtained through the curve resolution assuming a Lorentzian peak shape.

RESULTS AND DISCUSSION

Variation in Induction Period, Molecular Weight, and Stereoregularity with Polymerization Temperature

It is well known that temperature has only a slight effect on the rate of propagation in anionic polymerization of styrene in tetrahydrofuran.²¹ In a solution, containing cryptates, polymerization is instantaneous and it is difficult to determine the rate of propagation.^{22,23} However in the bulk polymerization of styrene initiated by BuLi with the cryptate [211] it was found that the rates of initiation and propagation are measurable and slower (Figure 1) than in the case of the polymerization in solution.^{22,23} Induction periods are observed as in the case of the polymerization of methyl methacrylate under the same conditions.²⁰ Induction periods and the rate of polymerization (Figure 1) are influenced by temperature, but no variation was observed in molecular weight or polydispersity (Table I).

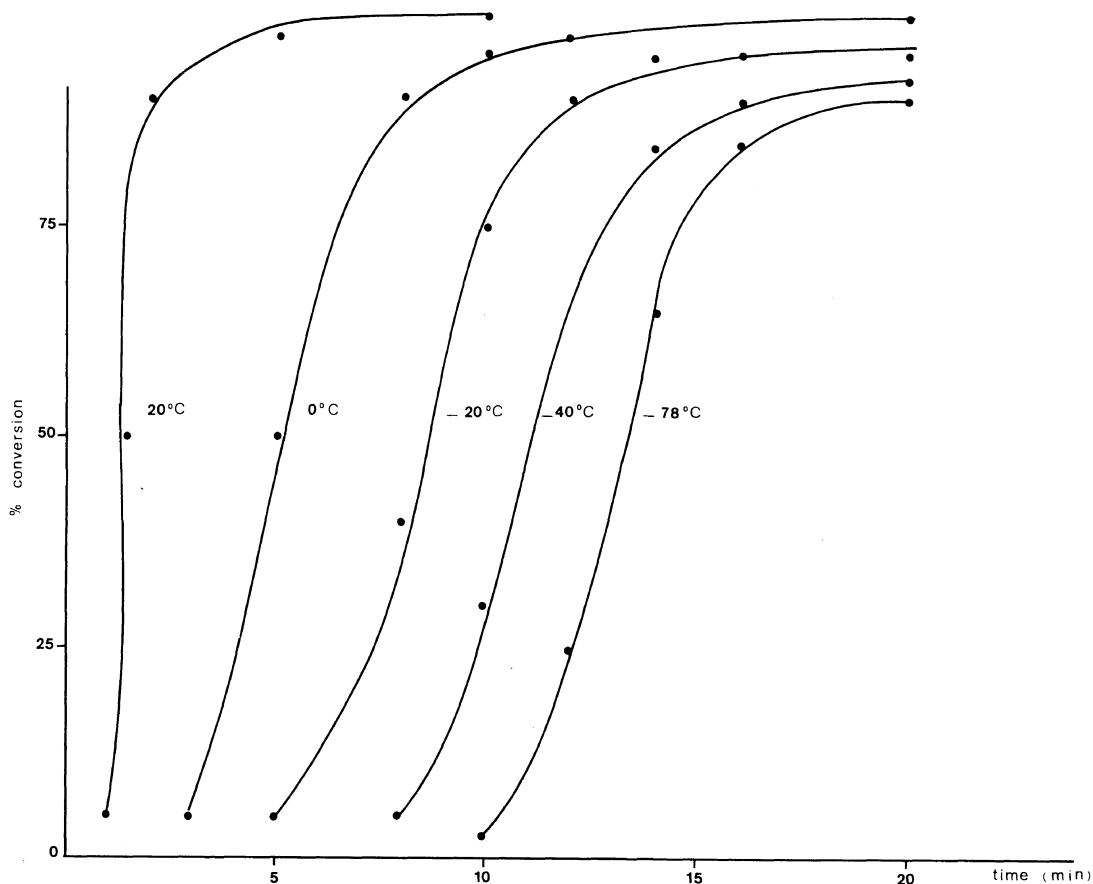
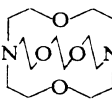


Figure 1. Influence of temperature on the induction period and rate of bulk polymerization BuLi,

2 mmol; Styrene, 100 mmol;  [211], 2 mmol.

Polystyrenes obtained with cryptates in bulk polymerization are mostly syndiotactic and the stereoregularity of the polymer is almost independent of the temperature (Table II). The presence of cryptated ion-pairs does not affect the configuration (Table II).

Variation in Induction Period, Molecular Weight, and Stereoregularity According to the Nature of the Counterion

The results obtained for the bulk polymerization of styrene initiated by lithium, sodium, potassium, rubidium, and cesium naphthalenes cryptated are

summarized in Table III. The nature of the cation had little influence on molecular weight and polydispersity of the polymers produced. In all cases, an induction period was observed which did not vary with the nature of the cation, in contrast to the polymerization of methyl metacrylate and diene monomers under the same conditions.²⁰

The polymers obtained were mostly syndiotactic and the proportion of racemic dyads (0.59 to 0.67) was practically independent of the cation whose properties were lost through complexation (see Table IV).

Table I. Effect of cryptate [211] on the polymerization systems of styrene/RLi

Initiator ^a	Temp	Yield	M_n^b	M_w^b	M_w/M_n^b
	°C	%			
BuLi-[211]	-78	90	125,000	372,500	3.0
BuLi-[211]	-40	92	133,000	359,000	2.7
BuLi-[211]	-20	97	130,000	370,000	2.8
BuLi-[211]	0	100	140,000	387,000	2.8
BuLi-[211]	20	100	137,000	392,500	2.9
MeLi-[211]	20	100	129,500	359,500	2.8
PhLi-[211]	20	100	141,000	380,300	2.7

^a RLi, 2 mmol; styrene, 100 mmol; RLi/[211] molar ratio, 1; polymerization time, 20 min.^b Measured by GPC at 30°C in THF.**Table II.** Stereoregularity of polystyrenes prepared by BuLi, represented in terms of the triad and racemo dyad fractions

Initiator	Solvent	Temp	mm	mr	rr	Pr
		°C				
BuLi	THF ^a	-78	0.09	0.40	0.51	0.71
BuLi	THF	-40	0.11	0.39	0.50	0.69
BuLi	THF	-20	0.13	0.37	0.50	0.68
BuLi	THF	0	0.12	0.37	0.51	0.69
BuLi	THF	20	0.12	0.37	0.51	0.69
BuLi	PhCH ₃	-78	0.14	0.40	0.46	0.66
BuLi	PhCH ₃	-40	0.14	0.39	0.47	0.66
BuLi	PhCH ₃	-20	0.13	0.42	0.45	0.66
BuLi	PhCH ₃	0	0.10	0.40	0.50	0.70
BuLi	PhCH ₃	20	0.07	0.41	0.52	0.72
BuLi-[211]	PhCH ₃	-78	0.10	0.35	0.55	0.72
BuLi-[211]	PhCH ₃	-40	0.11	0.37	0.52	0.70
BuLi-[211]	PhCH ₃	-20	0.11	0.35	0.54	0.71
BuLi-[211]	PhCH ₃	0	0.12	0.38	0.50	0.69
BuLi-[211]	PhCH ₃	20	0.11	0.37	0.52	0.70
BuLi-[211]	—	-78	0.11	0.40	0.49	0.69
BuLi-[211]	—	-40	0.12	0.41	0.47	0.67
BuLi-[211]	—	-20	0.12	0.42	0.46	0.67
BuLi-[211]	—	0	0.12	0.44	0.44	0.66
BuLi-[211]	—	20	0.12	0.44	0.44	0.66

^a THF, tetrahydrofuran.

Chain Statistics

The persistence ratio (ρ) as well as the mean length of the isotactic (μ_i) and syndiotactic (μ_s) sequences are given in Table V. The persistence ratio defined by Coleman and Fox^{24,25} was close to unity in THF, toluene, and bulk polymerization, indicating that stereoregulation in the polymeri-

zation followed Bernoullian statistics. The values of μ_i and μ_s indicate the presence of very short isotactic and syndiotactic sequences.

Block Copolymerization with Methyl Methacrylate and Isoprene

Spectroscopic study of the stability of the prop-

Table III. Effect of cryptates on the polymerization systems of styrene/alkali metal naphthalene

Initiator ^a	Yield	M_n^b	M_w^b	M_w/M_n^b
	%			
Nap Li-[211]	90	157,500	343,000	2.2
Nap Na-[221]	95	163,500	368,000	2.3
Nap K-[222]	90	168,000	370,000	2.2
Nap Rb-[222]	100	187,500	403,000	2.1
Nap Cs-[222]	100	210,000	407,000	2.0

^a Alkali metal naphthalene, 2 mmol; styrene, 100 mmol; alkali naphthalene/cryptate molar ratio = 1; temperature of polymerization, 0°C.

^b Measured by GPC at 30°C in THF.

Table IV. Stereoregularity of polystyrenes prepared by alkali metal naphthalene at 0°C, represented in terms of the triad and racemo dyad fractions

Initiator	Solvent	mm	mr	rr	Pr
Nap Li	THF	0.10	0.40	0.50	0.70
Nap Na	THF	0.15	0.40	0.45	0.75
Nap K	THF	0.15	0.39	0.46	0.65
Nap Rb	THF	0.17	0.40	0.43	0.63
Nap Cs	THF	0.20	0.42	0.38	0.59
Nap Li-[211]	PhCH ₃	0.12	0.38	0.50	0.69
Nap Na-[221]	PhCH ₃	0.11	0.37	0.52	0.70
Nap K-[222]	PhCH ₃	0.10	0.30	0.60	0.75
Nap Rb-[222]	PhCH ₃	0.15	0.29	0.56	0.71
Nap Cs-[222]	PhCH ₃	0.18	0.35	0.47	0.64
Nap Li-[211]	—	0.11	0.44	0.45	0.67
Nap Na-[221]	—	0.12	0.47	0.41	0.64
Nap K-[222]	—	0.14	0.46	0.40	0.63
Nap Rb-[222]	—	0.17	0.49	0.34	0.59
Nap Cs-[222]	—	0.16	0.50	0.34	0.59

agating carbanion end in the polymerization of styrene initiated in the presence of cryptates showed that an absorption at 343 nm due to the benzylic carbanion,²⁶ disappeared very rapidly to give a new absorption at 560 nm corresponding to the inactive benzyl allyl carbanion. Therefore, it is difficult to obtain block copolymers with cryptated ion pairs in solution.

In bulk polymerization in the presence of the cryptate [211] it seems that deactivation of the carbanion end is slower than in solution under the same conditions and much block copolymers of styrene with methyl methacrylate or isoprene

Table V. Persistence ratio (ρ) and mean length of the isotactic (μ_i) and syndiotactic (μ_s) sequence of polystyrenes

Initiator	Solvent	Temp	μ_i	μ_s	ρ
		°C			
BuLi	THF	-78	1.45	3.55	0.97
BuLi	THF	-40	1.56	3.56	0.92
BuLi	THF	-20	1.70	3.70	0.86
BuLi	THF	0	1.65	3.76	0.87
BuLi	THF	20	1.65	3.76	0.87
BuLi	PhCH ₃	-78	1.70	3.30	0.89
BuLi	PhCH ₃	-40	1.97	3.41	0.86
BuLi	PhCH ₃	-20	1.62	3.14	0.94
BuLi	PhCH ₃	0	1.50	3.50	0.95
BuLi	PhCH ₃	20	1.34	3.54	1.03
BuLi-[211]	PhCH ₃	-78	1.57	4.14	0.88
BuLi-[211]	PhCH ₃	-40	1.59	3.81	0.89
BuLi-[211]	PhCH ₃	-20	1.63	4.08	0.86
BuLi-[211]	PhCH ₃	0	1.63	3.63	0.89
BuLi-[211]	PhCH ₃	20	1.59	3.81	0.89
BuLi-[211]	—	-78	1.55	3.45	0.93
BuLi-[211]	—	-40	1.59	3.29	0.93
BuLi-[211]	—	-20	1.57	3.18	0.95
BuLi-[211]	—	0	1.55	3.00	0.98
BuLi-[211]	—	20	1.55	3.00	0.98
Nap Li	THF	0	1.50	3.25	0.97
Nap Na	THF	0	1.75	3.75	0.84
Nap K	THF	0	1.77	3.36	0.86
Nap Rb	THF	0	1.85	3.15	0.86
Nap Cs	THF	0	1.95	2.81	0.87
Nap Li-[211]	PhCH ₃	0	1.63	3.63	0.89
Nap Na-[221]	PhCH ₃	0	1.59	3.81	0.89
Nap K-[222]	PhCH ₃	0	1.66	5.00	0.80
Nap Rb-[222]	PhCH ₃	0	2.03	4.86	0.70
Nap Cs-[222]	PhCH ₃	0	2.02	3.69	0.76
Nap Li-[211]	—	0	1.50	3.05	0.99
Nap Na-[221]	—	0	1.51	2.74	1.03
Nap K-[222]	—	0	1.61	2.74	0.99
Nap Rb-[222]	—	0	1.69	2.39	1.01
Nap Cs-[222]	—	0	1.64	2.36	1.03

were obtained. (see Table VI). The difference observed between the theoretical and experimental M_n 's was due to an incomplete reaction of the sequence of poly(methyl methacrylate) and polyisoprene. However, it is clear that the polymer chains formed from styrene carry active centers capable of initiating the polymerization of other monomers.

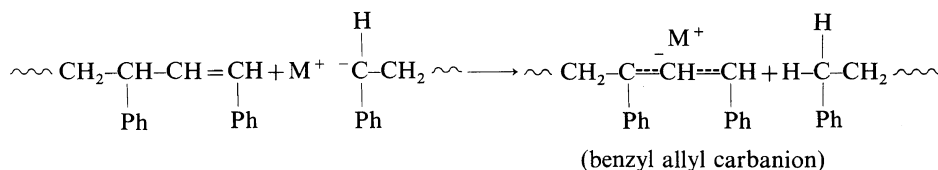
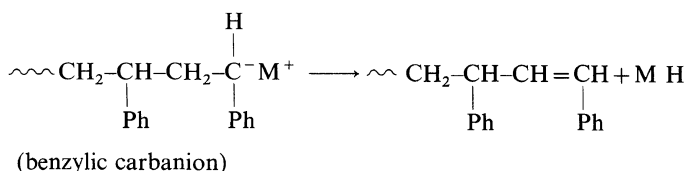


Table VI. Block copolymerization of styrene with methyl methacrylate or isoprene initiated by cryptated BuLi

	M_n (theoretical)	M_n^a (measured)
1 Sequence of polystyrene	2,500	35,000
Sequence of poly(methyl methacrylate)	35,700 ^b	23,500
Copolymer	38,200	68,500
2 Sequence of polystyrene	2,500	38,000
Sequence of polyisoprene	24,600 ^b	21,300
Copolymer	27,100	59,300

Styrene, 48 mmol; methyl methacrylate, 50 mmol; isoprene, 47 mmol; BuLi, 2 mmol; [211], 2 mmol; temperature of polymerization, 0°C.

^a Measured by GPC at 30°C in THF.

^b Estimated from the measured M_n of the polystyrene sequence.

CONCLUSIONS

From the present work it was found that the stereoregularity of polystyrenes produced is mostly syndiotactic and is hardly changed by temperature and the nature of the cation. As in the case of bulk polymerization, in the presence of cryptate [211], with methyl methacrylate and diene monomers, the induction period is slightly modified. The possibility of preparing block copolymers should also warrant interest.

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