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Serge Raynal[a]; Gilberte Ndebeka[b]; Paul Caubere[b]; Satira Suparno[c]; Joseph Sledz[d]; Francois Schue[d]
[a] Centre de Recherches du Bouchet SNPE, Vert-le-Petit, France [b] Laboratoire de Chimie Organique 1, UniversitÉ de Nancy 1, Nancy CEDEX, France [c] Institute of Technology of Bandung, Bandung, Indonesia [d] Laboratoire de Chimie MacromolÉculaire, UniversitÉ des Sciences et Techniques du Languedoc, Montpellier, CEDEX, France

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Steroregularity of Polystyrenes Obtained by New Complex Bases

SERGE RAYNAL

Centre de Recherches du Bouchet
SNPE
91710 Vert-le-Petit, France

GILBERTE NDEBEKA and PAUL CAUBERE

Laboratoire de Chimie Organique 1
Université de Nancy 1
54037 Nancy, CEDEX, France

SATIRA SUPARNO

Institute of Technology of Bandung
Bandung, Indonesia

JOSEPH SLEDZ and FRANCOIS SCHUE

Laboratoire de Chimie Macromoléculaire
Université des Sciences et Techniques du Languedoc
34060 Montpellier, CEDEX, France

ABSTRACT

The stereoregularity of polystyrenes obtained with complex bases and salt complex bases in various solvents was determined by ^{13}C-NMR spectroscopy. Polystyrenes produced by complex bases are mostly syndiotactic and obey Bernoullian statistics.

INTRODUCTION

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 of ^{13}C-NMR spectroscopy has made it possible to detect small difference in the stereoregularity of polystyrene [3-5]. Therefore, the configuration of polystyrenes produced by individual growing species has been investigated [6-9].

The spectra of aromatic C_1 and methylene have recently 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, 11].

In this study we report the effect of new complex bases [12-20] in the anionic polymerization of styrene on the stereoregularity of polymers.

EXPERIMENTAL

Complex Bases Preparation

A solution of the activating alcohol (8.3 mM) in the chosen solvent was added dropwise to a suspension of the alkali amide (25 mM) in the same solvent at room temperature (NH_3 must evolve). The mixture was then heated for 2 h at 45-50°C. In the case of solid complex bases prepared without solvent, the activating agent was added dropwise to the ground alkali amide at room temperature. The mixture was then heated for 2 h at 45-50°C under stirring.

Salt Complex Bases Preparation

The salt (8.3 mM) was added to a suspension of the alkali amide (16.7 mM) in the chosen solvent at room temperature. The mixture was then heated for 2 h at 45-50°C. In the case of solid salt complex bases prepared without solvent, the salt was added to the ground alkali amide at room temperature. The mixture was then heated for 2 h at 45-50°C under stirring.

Polymerization Procedure

In the same reactor used for the preparation of complex bases or salt complex bases, polymerization was carried out under argon. After reaching the polymerization temperature, the monomer was introduced under stirring with a hypodermic syringe. The polymerization was stopped by adding a small amount of methanol. The polymer was precipitated by pouring the reaction mixture into a large excess of methanol. Polymerization was realized with 88 mM of monomers. The polymerization time was 3 h with THF at 30°C and 6 h with $PhCH_3$ at 50°C in 40 mL of solvent.

NMR Measurements

^{13}C-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 ^{1}H noise was decoupled and obtained after accumulation of 7-25 thousand transients. Relative intensities were obtained through curve resolution assuming a Lorentzian peak shape.

RESULTS AND DISCUSSION

Use of conventional anionic initiators on a large scale is restricted by their high cost and difficulty of handling. In order to avoid those inconveniences, Caubere et al. investigated the possibilities offered by a new class of cheap and easily handled potential initiators. They demonstrated [12-14] that the concept of base synergy applied to sodamide and sodium alkoxides led to the preparation of new reagents $NaNH_2$–RONa called complex bases. These bases have properties different from those of $NaNH_2$ and RONa taken separately and may be very powerful bases even in low polar solvents such as tetrahydrofuran (THF), toluene, and benzene.

In several previous notes and articles, Caubere et al. [15-18] showed that not only it was possible to initiate anionic polymerization with complex bases but also that varying the nature of the activating agent led to variations in the nature of the polymers formed.

In the present paper we report a description of the main results obtained in anionic polymerization of styrene using sodamide containing complex bases as initiator agents. We also report some results obtained by using salt complex bases [19, 20] with the same cation (NMH_2–MZ) but also complex bases constituted by an amide and a salt with different cations (MNH_2–M'Z).

Complex Bases $NaNH_2$–RONa as Initiators

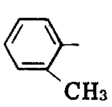
$Et(OCH_2CH_2)_2ONa$, which was the best activating agent [17], was chosen as the activating agent in THF, toluene, and benzene. The microstructures obtained are gathered in Table 1.

The polymers obtained are mostly syndiotactic and the proportions observed are roughly independent from the solvent. It seems that the complexation between the propagating species and the

TABLE 1. Tacticity of Polystyrenes. Influence of the Solvent

	Triads		
Solvent	Iso	Hetero	Syndio
THF	0.13	0.34	0.53
Toluene	0.13	0.37	0.51
Benzene	0.23	0.32	0.45
In bulk	0.15	0.39	0.46

TABLE 2. Tacticity of Polystyrenes in THF. Influence of the Nature of the Activating Agent

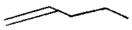
	Triads		
Activating agent (R)	Iso	Hetero	Syndio
nBu–	0.09	0.35	0.56
Et_2CH–	0.08	0.35	0.57
tBu–	0.11	0.39	0.50
$Et(OCH_2CH_2)_2$–	0.13	0.34	0.53
$Et(OCH_2CH_2)_6$–	0.12	0.43	0.45
C_6H_5–	0.09	0.44	0.47
	0.13	0.34	0.43
$C_6H_5-\underset{\vert}{C}=CH_2$	0.14	0.40	0.46

alkoxide prevails over that with the solvent, leading to a complexed ion pair where all the interactions between the cation and the penultimate unit of styrene are annihilated. In these conditions, the syndiotactic placement is favored [11]. By changing the nature of the activating agent R, we obtained the results given in Tables 2 and 3.

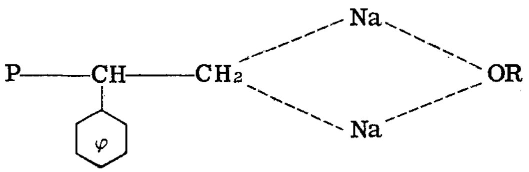
After this change the polymers formed are mostly syndiotactic and roughly independent from the nature of the activating agent. We observe that alkoxides influence the initiation and the propagation rates [17] but do not influence the nature of polymers formed although they must be complexed with the living carbanion.

To reconcile this apparent contradiction we propose the following

TABLE 3. Tacticity of Polystyrenes in Toluene. Influence of the Nature of the Activating Agent

	Triads		
Activating agent (R)	Iso	Hetero	Syndio
$(CH_3)_2CHCH_2$–	0.09	0.33	0.58
Me_2CH–	0.08	0.35	0.57
	0.14	0.38	0.48
tBu–	0.11	0.40	0.49
$Et(OCH_2CH_2)_2$–	0.13	0.37	0.51
$Bu(OCH_2CH_2)_2$–	0.17	0.40	0.43

hypothesis: During the propagation step, the alkoxides, by complexation of the cation (see scheme), maintain a sufficient electron density to propagate the polymerization but they are too far from the active site to have enough steric influence on the pathway of polymerization.



Salt Complex Bases as Initiators [19, 20]

In a preliminary series of experiments, we chose sodamide with a different activating agent in THF and toluene. The tacticities obtained are gathered in Table 4.

Even if the characteristics of these salt complex bases in organic solvents are little known, it is clear that the solvent plays a role on the structure of the polymers obtained. Polar solvents like THF led to the formation of mostly syndiotactic polymers, independent of the nature of the activating agent. In toluene, the syndiotacticity decreases to about 0.35 independent of the nature of the activating agent.

These observations confirm the generality of our concept concerning the reactivity activation of bases and more generally of salts A^-M^+ by another $B^-M'^+$ [14].

TABLE 4. Tacticity of Polystyrene in THF and Toluene. Influence of the Nature of the Activating Agent

		Triads		
Activating agent	Solvent	Iso	Hetero	Syndio
$NaNO_2$	Toluene	0.23	0.37	0.40
NaCN	Toluene	0.34	0.33	0.33
NaSCN	THF	0.14	0.34	0.52
KCN	Toluene	0.26	0.45	0.29
KNO_2	Toluene	0.21	0.44	0.35
KNO_2	THF	0.19	0.29	0.52

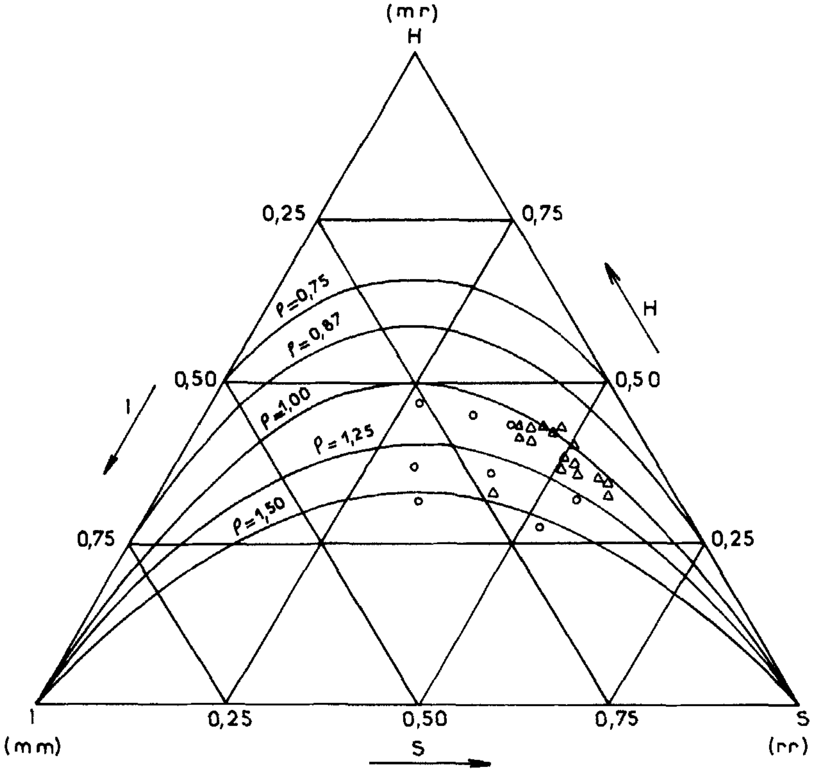


FIG. 1. Geometrical presentation of the observed triads.

Chain Statistics

The combination of triads can be represented geometrically in a reference system constituted by an equilateral triangle as proposed by Bovey and Kato [21, 22]. The three summits H, I, and S in Fig. 1 correspond, respectively, to polymers whose structure is entirely heterotactic, isotactic, and syndiotactic. With each point inside the triangle we can associate a combination of the three triads by drawing three straight lines parallel to the sides of the triangle and passing through this point. Under these conditions we plotted curves relative to different values of the constant ratio ρ defined by Coleman and Fox [23, 24]. If ρ equals unity, the mechanism of polymerization obeys Bernoullian statistics.

In Fig. 1 we see that the values of the triads obtained with the complex bases roughly obey Bernoullian statistics, and this confirms the absence of a penultimate effect. The values obtained with salt complex bases deviate from $\rho = 1$, and roughly obey Markovian statistics.

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