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Salt Complex Bases as New Initiators in the Polymerization of Methyl Methacrylate

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Salt Complex Bases as New Initiators in the Polymerization of Methyl Methacrylate

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ABSTRACT

The stereoregularity of poly(methyl methacrylate)s obtained with salt complex bases (MNH_2-MZ) in various solvents was determined by ^{1}H-NMR spectroscopy. Poly(methyl methacrylate)s produced by salt complex bases are mostly heterotactic and obey Bernoullian statistics.

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INTRODUCTION

Previously we reported the polymerization of methyl methacrylate (MMA), by new complex bases [1]. It was concluded that poly(methyl methacrylate)s produced by these catalysts are mostly hetero and/or syndiotactic and obey Bernoullian statistics. In this paper we report the effect of salt complex bases [2, 3] constituted by an alkali amide and an organic salt with different cations or the same cation (MNH_2-M'Z) in the anionic polymerization of methyl methacrylate in the stereoregularity of the polymer.

EXPERIMENTAL

Degussa broken sodamide was used, washed several times with the solvent of the reaction, and ground in a mortar under the same solvent. Fluka lithium amide was used as such. Potassium amide was prepared from potassium metal and liquid ammonia according to a previous publication [4]. Badisch Anilin reagent grade THF and DMF were distilled from sodium or benzophenone-sodium before use. Toluene, thiophene-free benzene, and hexane were refluxed on sodium metal, then distilled and kept on sodium wire. Salts were either commercial Fluka or Prolabo.

Methyl methacrylate was distilled on calcium hydride under argon or high vacuum.

Salt Complex Bases Preparation

The salt was added to a suspension of the alkali amide 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 grinding alkali amide at room temperature; the mixture was then heated for 2 h at 45-50°C with stirring.

Polymerization Procedure

In the same reactor used for the preparation of salt complex bases, the polymerizations were carried out under nitrogen or argon. After setting the polymerization temperature, the monomer was introduced with 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.

The time of polymerization was 1 h.

TABLE 1. Tacticity of Poly(methyl Methacrylate). Influence of the Ratio (Amide)/(Activating Agent)[a]

(Amide)/(Activating agent)	Microstructure (%)		
	Isotactic	Heterotactic	Syndiotactic
Amide alone	14	47	39
1	15	50	35
2	12	57	31
4	12	53	35
6	15	50	35
10	15	45	40
12	14	47	39

[a] Temperature of polymerization: 30°C. Solvent: THF. Amide: $NaNH_2$. Activating agent: $NaNO_2$.

NMR Measurements

^{1}H-NMR spectra (90 MHz) were measured in 10% polymer solutions in o-dichlorobenzene at 150°C with a Varian spectrometer (Model EM-390).

RESULTS AND DISCUSSION

Several experiments on the polymerization of vinyl monomers showed that salt complex bases might be used as initiators of polymerization in solution and in bulk [2, 3]. The best activating agents are the same as those identified by Caubère [2] and Biehl and coworkers [5, 6]. Indeed, a strong activation of $NaNH_2$ by nitrates and thiocyanates of sodium was observed in THF. The kinetics of polymerization depend on the nature of the activating agent and the polymerization method.

Therefore, to have more information on the mechanism of the polymerization, we wish to report the main results regarding the stereoregularity of the polymers obtained using sodamide, lithium amide, and potassium amide containing salt complex bases. PMMA's were prepared in various solvents and at various temperatures.

TABLE 2. Tacticity of Poly(methyl Methacrylate). Influence of the Solvent[a]

	Microstructure (%)		
Solvent	Isotactic	Heterotactic	Syndiotactic
DMF	10	50	40
THF	12	57	31
$PhCH_3$	36	44	20
Ph	35	43	22
Hexane	37	45	18
-	20	50	30

[a] Temperature of polymerization: 30°C. Amide: $NaNH_2$. Activating agent: $NaNO_2$. (Amide)/(activating agent) = 2.

Tacticity of Poly(methyl Methacrylate)

Influence of the (Amide)/(Activating Agent) Ratio

Preliminary experiments have shown that the best activating agent in the salt complex bases was $NaNO_2$ [3]. We chose this activating agent in THF. The microstructures obtained are gathered in Table 1. As the ratio (amide)/(activating agent) increases, the microstructure, mainly heterotactic, remains constant, tending to the value observed with the amide alone.

Influence of the Solvent (Table 2)

The polymers obtained are mostly heterotactic, but the isotacticity (or the syndiotacticity) increases (or decreases) when the polarity of the solvent decreases. One can suppose that the complexation between the propagating species and the salt prevails more and more as the polarity of the solvent decreases.

Influence of the Concentration of Monomer (Table 3)

Amerik [7] has shown that in toluene the tacticity of PMMA is influenced by the monomer concentration. The polarity of MMA induces solvatation of the cation leading to an increase of syndiotacticity. The polymers obtained with $NaNH_2$-$NaNO_2$ in THF are mostly heterotactic, but the isotacticity (or the syndiotacticity) decreases (or increases) with increasing monomer concentration.

TABLE 3. Tacticity of Poly(methyl Methacrylate). Influence of the Monomer Concentration[a]

(MMA) mol × 10^{-3}	Microstructure (%)		
	Isotactic	Heterotactic	Syndiotactic
50	14	56	30
100	12	57	31
200	10	52	38
300	10	50	40
500	11	47	43

[a] Temperature of polymerization: 30°C. Solvent: THF. Amide: $NaNH_2$. Activating agent: $NaNO_2$. (Amide)/(activating agent) = 2.

TABLE 4. Tacticity of Poly(methyl Methacrylate). Influence of the Temperature[a]

θ (°C)	Microstructure (%)		
	Isotactic	Heterotactic	Syndiotactic
40	14	53	33
30	12	57	31
0	13	55	32
-20	11	54	35
-40	12	55	33
-60	10	56	34
-78	9	53	38

[a] Solvent: THF. Amide: $NaNH_2$. Activating agent: $NaNO_2$. (Amide)/(activating agent) = 2.

Influence of the Temperature (Table 4)

Pascault [8], Inoue [9], and Schulz [10] have shown that in polar media, and also for the same counterion, a decrease in temperature leads to an increase in syndiotacticity. Such a variation, though very small, was observed without initiator.

TABLE 5. Tacticity of Poly(methyl Methacrylate). Influence of the Activating Agent, the Amide, and the Solvent[a]

		Microstructure (%)								
Solvent		THF			$PhCH_3$			Without solvent		
Initiator	Activating agent	Iso-tactic	Hetero-tactic	Syndio-tactic	Iso-tactic	Hetero-tactic	Syndio-tactic	Iso-tactic	Hetero-tactic	Syndio-tactic
$LiNH_2$	-	9	30	61	62	27	11	58	32	10
	$NaNO_2$	16	50	34	35	49	16	29	50	21
	NaSCN	25	53	22	40	47	13	30	49	21
	NaCNO	26	56	18	36	49	15	29	50	21
	NaCN	24	55	21	35	49	16	31	48	21
	KNO_2	12	54	34	26	47	27	20	50	30
	KSCN	17	55	28	30	43	27	21	54	25
	KCNO	18	53	29	34	44	22	24	50	26
	KCN	20	50	30	32	50	18	25	52	23
$NaNH_2$	-	14	47	39	42	41	17	23	53	24
	$NaNO_2$	12	57	31	36	44	20	20	50	30

	NaSCN	21	54	25	39	43	18	32	49	19
	NaCNO	17	55	28	37	38	25	23	50	27
	NaCN	23	55	22	40	42	18	25	50	25
	KNO_2	10	55	35	27	52	21	20	51	29
	KSCN	15	54	31	24	53	23	19	50	31
	KCNO	13	56	31	22	52	26	20	50	30
	KCN	11	58	31	24	50	26	29	50	31
KNH_2	-	16	50	34	36	40	24	29	50	21
	$NaNO_2$	10	55	35	23	47	30	17	52	31
	NaSCN	15	52	33	26	45	29	20	53	27
	NaCNO	14	53	33	22	48	30	15	51	34
	NaCN	12	54	34	22	49	29	18	54	28
	KNO_2	10	48	42	14	50	36	15	49	36
	KSCN	9	44	47	12	53	35	14	45	41
	KCNO	12	45	43	15	47	38	15	48	37
	KCN	10	43	47	13	48	29	14	47	39

[a] Temperature of polymerization: 30° C. (Amide)/(Activating agent) = 2.

TABLE 6. Persistence Ratio ρ and Mean Lengths of the Isotactic (μ_i) and Syndiotactic (μ_s) Sequences[a]

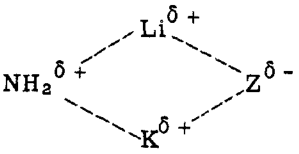
Solvent		THF			$PhCH_3$			Without solvent		
Initiator	Activating agent	ρ	μ_i	μ_s	ρ	μ_i	μ_s	ρ	μ_i	μ_s
$LiNH_2$	-	1.22	1.600	5.067	1.37	5.592	1.815	1.20	4.625	1.625
	$NaNO_2$	0.97	1.640	2.360	0.98	2.428	1.653	0.99	2.160	1.840
	NaSCN	0.94	1.943	1.830	0.99	2.702	1.553	1.01	2.224	1.857
	NaCNO	0.89	1.929	1.643	0.98	2.469	1.612	0.99	2.160	1.840
	NaCN	0.92	1.873	1.764	0.98	2.429	1.653	1.03	2.292	1.875
	KNO_2	0.88	1.444	2.259	1.06	2.106	2.149	0.99	1.800	2.200
	KSCN	0.90	1.618	2.018	1.16	2.395	2.256	0.93	1.778	1.926
	KCNO	0.93	1.679	2.094	1.12	2.545	2.000	1.00	1.960	2.040
	KCN	0.99	1.800	2.200	0.98	2.280	1.720	1.01	1.962	2.077
$NaNH_2$	-	1.00	1.596	2.660	1.14	3.049	1.829	0.94	1.868	1.906
	$NaNO_2$	0.85	1.421	2.088	1.10	2.636	1.909	0.99	1.800	2.200
	NaSCN	0.92	1.778	1.926	1.11	2.814	1.837	1.00	2.306	1.775
	NaCNO	0.90	1.618	2.018	1.29	2.947	2.316	1.00	1.920	2.080
	NaCN	0.91	1.836	1.800	1.13	2.905	1.857	1.00	2.000	2.000

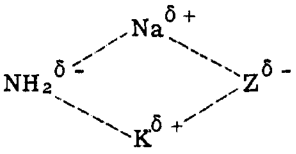
	KNO_2	0.85	1.364	2.273	0.96	2.038	1.807	0.97	1.784	2.137
	KSCN	0.90	1.556	2.148	0.94	1.906	1.868	0.99	1.760	2.240
	KCNO	0.86	1.464	2.107	0.96	1.846	2.000	0.99	1.800	2.200
	KCN	0.83	1.379	2.069	1.00	1.960	2.040	0.99	1.760	2.240
KNH_2	-	0.97	1.640	2.360	1.23	2.800	2.200	0.99	2.160	1.840
	$NaNO_2$	0.85	1.364	2.273	1.06	1.979	2.277	0.94	1.654	2.192
	NaSCN	0.93	1.577	2.260	1.10	2.155	2.289	0.94	1.755	2.019
	NaCNO	0.91	1.528	2.245	1.03	1.917	2.250	0.94	1.588	2.333
	NaCN	0.88	1.444	2.259	1.02	1.898	2.184	0.92	1.667	2.037
	KNO_2	0.94	1.417	2.750	0.95	1.560	2.440	0.98	1.612	2.469
	KSCN	0.97	1.409	3.136	0.90	1.453	2.321	1.03	1.622	2.822
	KCNO	1.00	1.533	2.911	1.01	1.638	2.617	0.99	1.625	2.542
	KCN	1.00	1.465	3.186	0.91	1.542	2.208	1.00	1.596	2.660

[a] Temperature of polymerization: 30° C. (Amide)/(activating agent) = 2.

Influence of the Activating Agent, the Amide, and the Solvent Table 5)

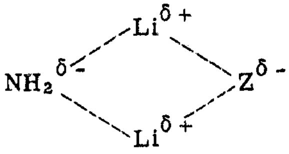
We have associated lithium, sodium, and potassium amides with different salts. The polymers obtained have a microstructure which is mainly heterotactic. Moreover, the association of an amide and salts with different cations leads us to believe that we have mixed aggregates [2]:

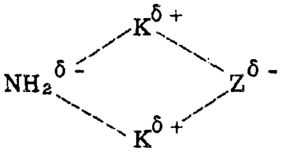




Similar cases have been observed when alkali alkoxides are added to living polymer [11-13].

We can also think of another possibility by forming two complexes, each possessing a different cation:





Chain Statistics (Table 6)

The persistence ratio ρ as well as the mean lengths of the isostatic (μ_i) and syndiotactic (μ_s) sequences are gathered in Table 6.

The persistence ratio is near unity in THF, in toluene, and in the absence of solvent, indicating that the mechanism of polymerization obeys Bernoullian statistics.

The values of μ_i and μ_s indicate the presence of very short isotactic and syndiotactic sequences.

CONCLUSIONS

We note that polymethyl methacrylates produced by salt complex bases are mostly hetero and/or syndiotactic, and generally independent of the nature of the reaction parameters. We observe that activating agents influence the initiation and the propagation rates [3] but do not influence the nature of the polymers formed.

During the propagation step, the salt, by complexation of the cation maintains a sufficient electron density to propagate polymerization but are too far from the active site to have a steric influence on the pathway of polymerization. Moreover, we note that the influence of salt in salt complex bases is less important than that of alkoxides in complex bases.

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