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# Stereoregularity of Poly(methyl Methacrylate) Obtained by New Complex Bases

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## ABSTRACT

The stereoregularity of poly(methyl methacrylate) obtained with complex bases in various solvents was determined by $^1$H-NMR spectroscopy. Polymethyl methacrylates produced by complex bases are mostly hetero and/or syndiotactic and obey Bernoullian statistics.

## INTRODUCTION

Fox et al. [1] first reported on the stereospecific polymerization of methyl methacrylate (MMA) using organometallic catalysts. The conditions for obtaining isotactic and syndiotactic fractions with highly steric purity have become well known through several articles [2-11]. Fox et al. obtained two types of poly(methyl methacrylate) (PMMA) from lithium-derivatives-initiated polymerization, i.e., syndiotactic PMMA in 1,2-dimethoxyethane at -60°C and isotactic PMMA in toluene at -60°C. They believe that the propagating species are free ions in 1,2-dimethoxyethane and ion pairs in toluene.

An aim of this paper is to report the effect of new complex bases [12-21] in the anionic polymerization of methyl methacrylate on the stereoregularity of the polymers.

## EXPERIMENTAL

### Complex Bases Preparation

A solution of the activating alcohol (8.3 mmol) in the chosen solvent was added dropwise to a suspension of the alkali amide (25 mmol) in the same solvent at room temperature ($NH_3$ must evolve). The mixture was then heated for 2 h at 45-50°C.

### Polymerization Procedure

Polymerization was carried out under argon in the same reactor used for the preparation of the complex bases. After establishing the polymerization temperature, the monomers were introduced under stirring with a hypodermic syringe. 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 polymerization was realized with 100 mmol of monomer. The polymerization time was 1 h.

### 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

Use of conventional anionic initiators on a large scale is restricted by their high cost and difficulty of handling. In order to avoid these inconveniences, Caubere et al. have investigated the possibilities offered by a new class of cheap and easily handled potential initiators. They have demonstrated [12-14] that the concept of 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 tetrahydrofurane (THF), toluene, and benzene.

In several notes and articles, Caubere et al. [15-18] showed that not only was it 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 the main results obtained in the anionic polymerization of methyl methacrylate using sodamide, lithium amide, and potassium amide containing complex bases as initiator agents. PMMA's were prepared in various solvents and at various temperatures between -78 and 40°C.

## COMPLEX BASES $NaNH_2$–RONa AS INITIATORS

Different activating agents were used in both THF and toluene. The microstructures obtained are listed in Tables 1 and 2.

Each component of the complex bases as well as the complex bases themselves are good initiators for the polymerization of MMA.

We note that the complex bases gave microstructures different from the ones obtained when each component was taken separately in toluene. They are similar to $NaNH_2$ in THF.

The polymers obtained are mostly heterotactic, and the proportions observed are roughly independent from the solvent and the nature of the activating agent. It seems that the complexation between the propagating species and the 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 MMA are annihilated.

The following hypotheses is proposed: During the propagation step the alkoxides complex the cation (see p. 317) but are too far from the active site to have a significant steric influence on the polymerization pathway.

Similar schemes have been proposed for polystyrene [21].

### Influence of the Nature of the Cation (Table 3)

It is well known that in nonpolar solvents the isotacticity of PMMA decreases as the size of the counterion increases. In order to explain

TABLE 1. Tacticity of Poly(methyl Methacrylate): Influence of the Activating Agent and the Solvent[a]

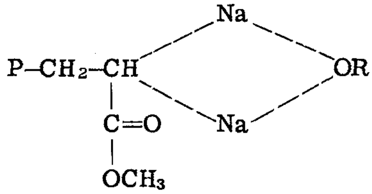
| | Microstructure (%) | | | | | |
|---|---|---|---|---|---|---|
| Solvent: | THF | | | $PhCH_3$ | | |
| Initiator | i | h | s | i | h | s |
| $NaNH_2$ | 14 | 47 | 39 | 42 | 41 | 17 |
| n-BuONa | 26 | 36 | 38 | 28 | 33 | 39 |
| $NaNH_2$-n-BuONa | 16 | 50 | 34 | 18 | 52 | 30 |
| $CH_2{=}CH{-}CH_2ONa$ | 21 | 36 | 43 | 23 | 36 | 41 |
| $NaNH_2{-}CH_2{=}CH{-}CH_2ONa$ | 15 | 49 | 36 | 19 | 51 | 30 |
| i-PrONa | 25 | 36 | 39 | 27 | 37 | 36 |
| $NaNH_2$-i-PrONa | 18 | 51 | 31 | 19 | 50 | 31 |
| t-BuONa | 22 | 36 | 42 | 20 | 35 | 45 |
| $NaNH_2$-t-BuONa | 13 | 50 | 37 | 16 | 52 | 32 |
| $MeOCH_2CH_2ONa$ | 22 | 38 | 40 | 23 | 38 | 39 |
| $NaNH_2{-}MeOCH_2CH_2ONa$ | 18 | 52 | 30 | 16 | 53 | 31 |
| $Et(OCH_2CH_2)_2ONa$ | 20 | 38 | 42 | 25 | 36 | 39 |
| $NaNH_2{-}Et(OCH_2CH_2)_2ONa$ | 12 | 50 | 38 | 14 | 50 | 36 |
| $Et(OCH_2CH_2)_6ONa$ | 22 | 36 | 42 | 23 | 35 | 42 |
| $NaNH_2{-}Et(OCH_2CH_2)_6ONa$ | 16 | 52 | 32 | 15 | 52 | 33 |

[a] Temperature of polymerization: 20° C.

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

| | Microstructure % | | |
|---|---|---|---|
| Solvent | i | h | s |
| DMF | 11 | 52 | 37 |
| THF | 12 | 50 | 38 |
| $PhCH_3$ | 14 | 50 | 36 |
| Ph | 14 | 52 | 34 |
| Hexane | 14 | 54 | 32 |

[a] Initiator: $NaNH_2{-}Et(OCH_2CH_2)_2ONa$. Temperature of polymerization: 20° C.



this variation, Bovey et al. [22] believe that the increased solvation of the cation as its size decreases is due to the carbonyl groups of the monomer units at the end of the polymer chain.

The polymers obtained with $LiNH_2$-$Et(OCH_2CH_2)_2OLi$, $NaNH_2$-$Et(OCH_2CH_2)_2ONa$, and $KNH_2$-$Et(OCH_2CH_2)_2OK$ are mostly heterotactic and the proportions observed are roughly independent of the counterion. This confirms the hypothesis that the species of the propagating end are complexed.

### Influence of the Concentration of Monomer (Table 4)

Amerik [23] has shown that the tacticity of PMMA in toluene was influenced by the monomer concentration. The polarity of MMA induces solvation of the cation, leading to an increase of the syndiotacticity.

The polymers obtained with $NaNH_2$-$Et(OCH_2CH_2)_2ONa$ in toluene are mostly heterotactic and the proportions observed are independent of the monomer concentration, confirming the hypothesis of complexed ion pairs.

### Influence of the Temperature (Table 5)

Pascault [24], Inoue [6], and Schulz [25] have shown that in polar media, and for the same counterion, a decrease in temperature leads to an increase in syndiotacticity.

No variation was observed with our initiator. These observations confirm the generality of our concept concerning the propagating end species.

### Influence of the Ratio (Amide)/(Activating Agent) (Table 6)

As the ratio (amide)/(activating agent) increases, the heterotacticity remains constant but the syndiotacticity decreases, tending to the value observed with the amide alone.

TABLE 3. Tacticity of Poly(methyl Methacrylate): Influence of the Cation[a]

| | Microstructure (%) | | | | | |
|---|---|---|---|---|---|---|
| Solvent: | THF | | | $PhCH_3$ | | |
| Initiator | i | h | s | i | h | s |
| $LiNH_2$ | 9 | 30 | 61 | 62 | 27 | 11 |
| $Et(OCH_2CH_2)_2OLi$ | 16 | 34 | 50 | 50 | 26 | 24 |
| $LiNH_2$-$Et(OCH_2CH_2)_2OLi$ | 12 | 50 | 38 | 27 | 50 | 23 |
| $NaNH_2$ | 14 | 47 | 39 | 42 | 41 | 17 |
| $Et(OCH_2CH_2)_2ONa$ | 20 | 38 | 42 | 25 | 36 | 39 |
| $NaNH_2$-$Et(OCH_2CH_2)_2ONa$ | 12 | 50 | 38 | 14 | 50 | 36 |
| $KNH_2$ | 16 | 50 | 34 | 36 | 40 | 24 |
| $Et(OCH_2CH_2)_2OK$ | 27 | 34 | 39 | 22 | 45 | 33 |
| $NaNH_2$-$Et(OCH_2CH_2)_2OK$ | 10 | 49 | 41 | 12 | 50 | 38 |

[a] Temperature of polymerization: 20° C.

TABLE 4. Tacticity of Poly(methyl Methacrylate): Influence of the Monomer Concentration[a]

| [MMA] mol × $10^{-3}$ | Microstructure (%) i | h | s |
|---|---|---|---|
| 50 | 15 | 52 | 33 |
| 100 | 14 | 50 | 36 |
| 200 | 13 | 52 | 35 |
| 300 | 15 | 51 | 34 |
| 500 | 18 | 49 | 33 |

[a] Initiator: $NaNH_2$-$Et(OCH_2CH_2)_2ONa$. Solvent: toluene. Temperature of polymerization: 20° C.

TABLE 5. Tacticity of Poly(methyl Methacrylate): Influence of the Temperature[a]

| $\theta$ (°C) | Microstructure (%) i | h | s |
|---|---|---|---|
| 40 | 15 | 50 | 35 |
| 20 | 14 | 50 | 36 |
| 0 | 10 | 49 | 41 |
| -20 | 10 | 49 | 41 |
| -40 | 10 | 50 | 40 |
| -60 | 9 | 51 | 41 |
| -78 | 9 | 52 | 39 |

[a] Initiator: $NaNH_2$-$Et(OCH_2CH_2)_2ONa$. Solvent: toluene.

TABLE 6. Tacticity of Poly(methyl Methacrylate): Influence of the Ratio (Amide)/(Activating Agent)[a]

| (amide)/(activating agent) | Microstructure (%) i | h | s |
|---|---|---|---|
| 1 | 18 | 50 | 32 |
| 2 | 14 | 50 | 36 |
| 4 | 16 | 53 | 31 |
| 6 | 20 | 50 | 30 |
| 10 | 24 | 50 | 26 |
| 12 | 30 | 51 | 19 |

[a] Initiator: $NaNH_2$-$Et(OCH_2CH_2)_2ONa$. Solvent: toluene. Temperature of polymerization: 20° C.

TABLE 7. Persistance Ratio $\rho$ and Mean Lengths of the Isotactic ($\mu$i) and Syndiotactic ($\mu$s) Sequences[a]

| Solvent: | THF | | | PhCH$_3$ | | |
|---|---|---|---|---|---|---|
| Initiator | $\rho$ | $\mu$i | $\mu$s | $\rho$ | $\mu$i | $\mu$s |
| NaNH$_2$-n-BuONa | 0.97 | 1.640 | 2.236 | 0.95 | 1.692 | 2.153 |
| NaNH$_2$-CH$_2$=CH–CH$_2$ONa | 0.97 | 1.588 | 2.469 | 0.97 | 1.748 | 2.150 |
| NaNH$_2$-i-PrONa | 0.96 | 1.705 | 2.216 | 0.99 | 1.760 | 2.240 |
| NaNH$_2$-t-BuONa | 0.94 | 1.520 | 2.480 | 0.94 | 1.615 | 2.231 |
| NaNH$_2$-MeOCH$_2$CH$_2$ONa | 0.95 | 1.692 | 2.154 | 0.92 | 1.602 | 2.169 |
| NaNH$_2$-Et(OCH$_2$CH$_2$)$_2$ONa | 0.93 | 1.480 | 2.520 | 0.95 | 1.560 | 2.440 |
| NaNH$_2$-Et(OCH$_2$CH$_2$)$_6$ONa | 0.94 | 1.615 | 2.230 | 0.93 | 1.577 | 2.269 |
| LiNH$_2$-Et(OCH$_2$CH$_2$)$_2$OLi | 0.93 | 1.480 | 2.520 | 1.00 | 2.080 | 1.920 |
| KNH$_2$-Et(OCH$_2$CH$_2$)$_2$OK | 0.92 | 1.408 | 2.673 | 0.93 | 1.480 | 2.525 |

[a] Temperature of polymerization: 20° C.

### Chain Statistics (Table 7)

The persistance ratio $\rho$ as well as the mean lengths of the isotactic ($\mu$i) and syndiotactic ($\mu$s) sequences are collected in Table 7.

The persistance ratio is close to unity in THF and in toluene, indicating that the mechanism of polymerization obeys the Bernoullian statistic.

The values of $\mu$i and $\mu$s indicate the presence of very short isotactic and syndiotactic sequences.

## CONCLUSIONS

We note that polymethyl methacrylates produced by complex bases are mostly hetero and/or syndiotactic, and roughly independent of the nature of the activating agent. We observe that activating agents influence the initiation and propagation rates [17, 18] but do not influence the nature of the polymers formed.

During the propagation step the alkoxides, by complexation of the cation, maintain a sufficient electron density to propagate polymerization, but they are too far from the active site to have a significant steric influence on the pathway of the polymerizations.

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