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Homogeneous Polymerization of Methyl Methacrylate Initiated by Potassium Salts of Methanol and *t*-Butyl Alcohol in the Presence of Cryptand [222]

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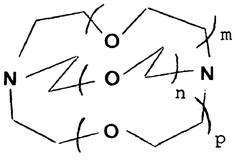
ABSTRACT: Homogeneous polymerization of methyl methacrylate initiated by potassium salts of methanol and *t*-butyl alcohol was studied in toluene in the presence of cryptand [222]. The polymers prepared were predominantly syndiotactic. The isotacticities increased slightly with an increase in temperature. The propagation steps follow Bernoullian statistics within experimental errors.

KEY WORDS Anionic activation / Poly(methyl methacrylate) / Potassium methoxide / Potassium *t*-Butoxide / Cryptand [222] /

More than thirty years ago, it was claimed that alkali metal salts of primary alcohols could not initiate the polymerization of methyl methacrylate (MMA) in ether.[1] More recently, the oligomerization of MMA by CH_3O^-/CH_3OH solutions has been studied.[2,3] Oligomers having a degree of polymerization up to six were isolated and characterized. Initiation proceeded by the addition of CH_3O^- to the double bond, and termination by protonation from the methanol.

t-Alkoxides, *n*-butoxides, derivatives of poly(ethylene oxide) of alkali metals as well as ethylmagnesium alkoxides for the initiation of the homogeneous polymerization of methacrylic acid esters have been described in previous papers.[4-10]

It has also been shown that the polymerization of MMA by alkali metal salts of 2-methoxyethanol and like compounds can be carried out in aprotic dipolar solvents such as hexamethylphosphoramide, dimethyl sulfoxide, and dimethylacetamide.[11] Polymerization was greatly promoted by these solvents, even when in small quantities. It is also well known that cryptands such as (I) complex cationic species very strongly and hence promote nucleophilic reactions.[12] Several studies on the polymerization using such complexing agents have been reported.[13-16]



(I)

$m=n=p=2$ called [222]

In this paper, we report on the homogeneous polymerization of MMA in toluene by potassium salts of methanol and *t*-butyl alcohol in the presence of cryptand (I). It was accepted, according to our previous communication,[17] that such complexing agents increase the reactivity of the alkoxide. (Potassium methoxide and *t*-butoxide are noted respectively MeOK and *t*-BuOK.)

EXPERIMENTAL

Materials

The purification of toluene and MMA as well as the experimental techniques are described elsewhere.[17] Potassium salts of the alcohols were prepared by the reaction of potassium metal with an excess of alcohol in toluene followed by removing solvent and alcohol under vacuum at 100°C during at least 15 hours. This gave the alkoxides as snowwhite powders. The elementary analysis of the isolated compounds are given in Table I.

Table I. Elementary analysis of the alkoxide compounds[a]

Alkoxide compound	C (%)	H (%)	K (%)
Potassium methoxide			
Calculated %	17.12	4.31	55.75
Found %	16.63	4.33	55.19
Potassium *t*-butoxide			
Calculated %	42.81	8.08	34.84
Found %	42.20		31.85

(Column header: Calculated found, %)

[a] CNRS, Service Central d'analyse, Vernaison, France.

The small differences observed in the elemental analysis can be explained as owing either to a lack of accuracy, or/and traces of alcohol.

This matter is now being studied and will be published soon along with a paper on the NMR of metal alkoxides.

Cryptand [222] was recrystallized in hexane. (mp, 69°C).

Polymerization Procedure

The polymerization (carried out under high vacuum) was initiated by introducing MMA (0.5 to 1 M) in 30 ml of toluene containing the cryptand and the alkoxide in a ratio 1 : 1. After a given time, the polymerization mixture was poured into methanol. The precipitated polymer was collected by filtration, washed with methanol, and dried in vacuum.

Measurements

The NMR spectra of the polymer solutions in *o*-dichlorobenzene were measured at 120°C by a Varian HA 100 and a Varian EM 390 spectrometers. The tacticity was deduced from the proton resonance of the α-methyl group.

The molecular weights were measured by gel-permeation chromatography using a WATERS ASSOCIATES 6000 A Spectrometer and are expressed in polystyrene equivalent.

RESULTS AND DISCUSSION

Solubilities of the Metal Alkoxides in the Absence and Presence of Cryptand [222]

The solubilities of the alkoxides in the absence and presence of cryptand [222] are given in Table II. They were determined by acid-base titration. Our results disagree with those noted by Pearson and Buehler.[18]

We succeeded in dissolving MeOK in toluene in the presence of [222], thus making possible a homogeneous initiation in the field of anionic polymerization.

This dissolution can be tentatively explained by partial or total rupture of the aggregate of alkoxides through complexation of the cation by the cryptand.

Table II. Solubilities of MeOK[a] and *t*-BuOK in toluene at 20°C in the absence and presence of cryptand [222]

Alkoxide	Solubility of the alkoxide/mol l^{-1}	
	Without [222]	Alkoxide/[222] > 1
MeOK	Insoluble	1.3×10^{-2}
t-BuOK	9.1×10^{-2} 0.176 (18)	Large increase[b]

[a] MeOK, potassium methoxide and *t*-BuOK, *t*-butoxide.

[b] At least two to three times the value obtained without [222].

Table III. Results of MeOK [222]-initiated polymerization of methyl methacrylate in toluene[a]

Temperature °C	Time h	Yield %	M_n	M_w	M_w/M_n
−78	0.5	100	88,200	123,300	1.4
−40	1	95	35,000	56,000	1.6
−20	0.5	100	52,800	112,500	2.13
0	1	90	43,200	58,600	1.36
20	0.5	85	33,300	48,800	1.46

[a] Conditions of the polymerization: [Initiator], 2.10^{-4} to 2.10^{-3} mol l^{-1}; [Monomer], 0.3 to 0.4 mol l^{-1}; solvent, 30 ml.

Polymerization in the Presence of MeOK [222]

Table III shows the results of polymerizations initiated with MeOK complexed by cryptand [222] in toluene at various temperatures between −78 and 20°C. The potassium salt, complexed by cryptand [222] could initiate the polymerization even in toluene. These results indicate that cryptand [222] is the most effective in increasing the reactivity of the alkoxide.

Polymerization in the Presence of t-BuOK [222]

Table IV shows the results of the polymerization initiated with *t*-BuOK complexed and uncomplexed by cryptand [222] in toluene at various temperatures between −78°C and 20°C. As noted before, the reactivity of the alkoxide highly increased in the presence of [222]. Thus, the yield of the polymers obtained at −40°C increased from 4% to 98% in the presence of the complexing agent.

Microtacticity of PMMA

The propagation mechanism can be studied by examining the dyad and triad information about the polymers obtained.

The polymers prepared were predominantly syndiotactic, except for the one obtained without a complexing agent.

The isotacticities increased slightly with an increase in temperature.

If the propagation steps obey Bernoullian statistics, the following equations should hold,[19,20]

Table IV. Results of *t*-BuOK [222]-initiated polymerization of methyl methacrylate in toluene[a]

Temperature °C	Yield %	M_n	M_w	M_w/M_n
−78	100	19,700	37,000	1.88
−40	98	37,750	66,400	1.76
−40[b]	4	48,400	146,600	3.03
−20	99	34,100	47,000	1.38
0	99	37,900	119,900	3.16
20	87	42,000	102,800	2.45

[a] Conditions of the polymerization [Initiator], 3 to 4 10^{-3} mol l^{-1}; [Monomer], 0.5 to 1 mol l^{-1}; solvent, 30 ml; time of polymerization, 0.5 h.

[b] Without [222]. The other conditions are the same as previously indicated.

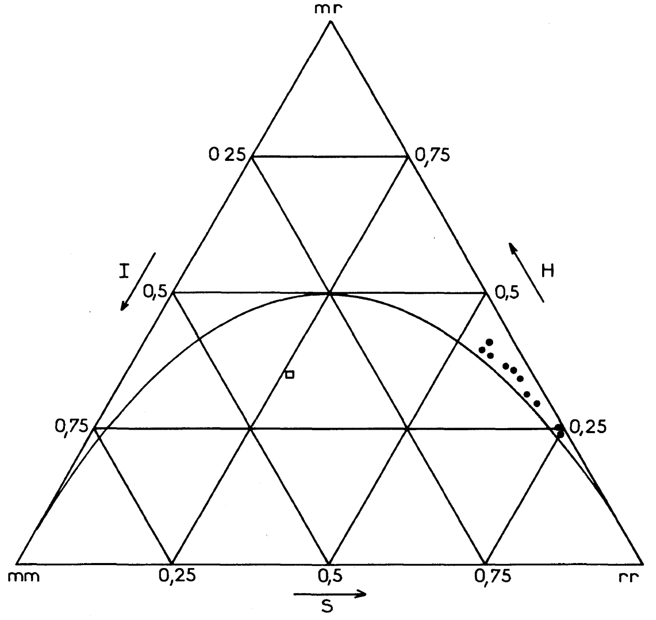


Figure 1. Stereoregularity of poly(methyl methacrylate) represented by a triangular coordinate. Poly(MMA) initiated with metal alkoxide: ●, complexed with [222]; □, without [222].

Table V. Stereoregularity of poly(methyl methacrylate)[a]

Temperature	Initiator	Triads × 10^2			Dyads × 10^2		ρ^c
°C		mm	mr	rr	m	r	
−78	MeOK	0.8	25	74.2	13.3	86.7	0.92
	t-BuOK	1	24	75	13	87	0.94
−40	MeOK	2.5	31	66	18	81.5	0.95
	t-BuOK	2	30	68	17	83	0.94
	t-BuOK[b]	39	35	26	56.5	43.5	1.4
−20	MeOK	2.5	36	61.5	20.5	79.5	0.91
	t-BuOK	2.3	34.4	63.3	19.5	80.5	0.91
0	MeOK	3.4	36.7	59.9	21.65	78.35	0.92
	t-BuOK	4	41	55	24.5	75.5	0.90
20	MeOK	5.1	38.3	56.6	24.25	75.75	0.96
	t-BuOK	6	39.5	54.5	25.75	74.25	0.97

[a] The conditions of the polymerization are given on Tables III and IV.

[b] Without [222].

[c] ρ = persistence ratio.

$$\rho=\frac{2(\mathrm{m})(\mathrm{r})}{(\mathrm{mr})} \text{ for a Bernoullian statistic } \rho=1\,.$$

$$\begin{aligned}\text{Dyad:}\quad & (\mathrm{m})=P_\mathrm{m},\ (\mathrm{r})=1-P_\mathrm{m}\\ \text{Triad:}\quad & (\mathrm{mm})=P_\mathrm{m}{}^2\\ & (\mathrm{mr})=2P_\mathrm{m}(1-P_\mathrm{m})\\ & (\mathrm{rr})=(1-P_\mathrm{m})^2\end{aligned}$$

where P_m represents the probability of a meso (isotactic) placement during propagation.

As Figure 1 and Table V show, the propagation steps to yield the polymers follow Bernoullian statistics within experimental error, except for the uncomplexed species.

We can, as Furukawa[21] did, devise an expression which evaluates the magnitude of ultimate unit effects in stereospecific polymerization as follows,

$$\Delta G^*=-RT\ln(\mathrm{m}/\mathrm{r})$$

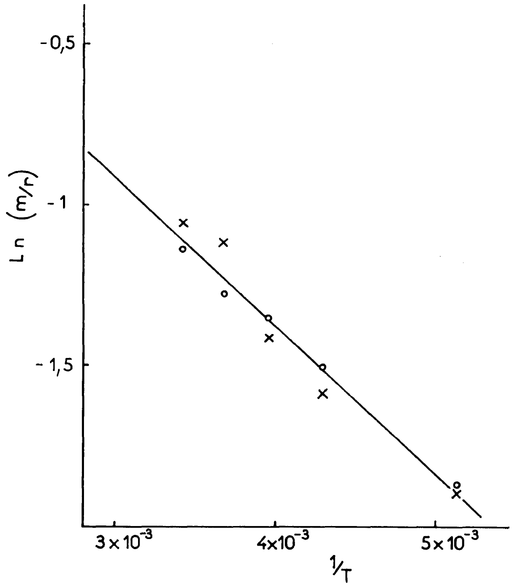


Figure 2. The plot of ln(m/r) *vs.* $1/T$ for PMMA. Symbols show the polymerization series as follows: ○, MeOK [222]; ×, t-BuOK [222].

Where ΔG^* is the difference in activated free energy between isotactic and syndiotactic placements. ln(m/r) is plotted against $1/T$ in Figure 2. From this plot, it is shown that ΔG^* is linearly dependent on temperature. This indicates that there was little penultimate unit effect and thus, the propagation mechanism could be specified roughly by Bernoulli trial as described before. Under these conditions, there is only one propagation mechanism due to one kind of ion pair, the complexed one. These species lead to a preference for syndiotactic placement.

ΔS^* and ΔH^*, being the difference, respectively, in the entropy and the enthalpy between isotactic and syndiotactic placements, can be readily calculated from the usual realtion:

$$\ln(\mathrm{m/r}) = -\frac{\Delta G^*}{RT} = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

The values of 0.92 kcal $\mathrm{mol^{-1}\ l^{-1}}$ for ΔH^* and 0.942 e.u. for ΔS^* were obtained. Thus, in this system, syndiotactic placement appears to be favored by the additional enthalpy of activation required for isotactic placement, which itself is favored by entropy.

Very similar results were obtained by Pascault, Kawak, Gole, and Pham,[22] for the anionic polymerization of MMA and by Elias, Goeldi, and Kamar[23] for the radical polymerization.

The complexation of the potassium cation by cryptand [222] allows for the dissolution of primary alkoxide (methoxide) which is known to be insoluble in non polar solvents, and activates the alkoxides for initiating the polymerization of MMA in the homogeneous phase.

The enhanced basicity of the cryptated MeOK makes possible the polymerization of MMA in toluene with high yields. The microstructures resemble those obtained in polar solvents; thus it may be concluded that cryptated ions pairs are very similar to loose ions pairs in polar solvents.

The thermodynamic parameters obtained (ΔH^* and ΔS^*) support this view.

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