

AMBIENT TEMPERATURE ANIONIC POLYMERIZATION OF METHYLMETHACRYLATE BY USING ALKYL LITHIUM/DIMETHYLSULFOXIDE INITIATOR SYSTEM

N.Nugay¹, T.Nugay¹, R.Jérôme² and Ph.Teyssié²

¹Dept. of Chemistry/Polymer Research Center, Bogazici University, 80815 Bebek, Istanbul, Turkey

²Center for Education and Research on Macromolecules (CERM), University of Liege, B6, Sart-Tilman, 4000 Liege, Belgium

Introduction

It has been already shown that methylsulfynylmethylsodium (dimethylsodium) in dimethylsulfoxide (DMSO) solution initiates the polymerisation of vinyl monomers with electron-attracting substituents and the results were consistent with an anionic initiation¹. In these studies, some evidences of termination by chain transfer to DMSO were observed. Very similar results were later reported by other authors². Prioala et. al. studied the anionic polymerisation of styrene by using DMSO free solutions of dimethylsodium in hexamethylenephosphoramide and fast as well as quantitative polymerisation of styrene was reported³. In this study polymerisation of methyl methacrylate (MMA) was conducted by using alkyl lithium/DMSO system as initiator in toluene as solvent. Special attention was focused on using some lithium polyether alkoxides as polymerisation promoters at moderate temperatures.

Experimental

The purification of chemicals, the preparation of various polydentate alkoxides (Table 1), initiators and anionic polymerisation of MMA have been well described in previous publication⁴. Compositions are given in Table 2.

Table 1. Polyether alkoxides (LiOEnM) used

LiOEM	Lithium methoxyethoxide
LiOEEM	Lithium methoxyethoxyethoxide

Table 2. Anionic polymerization conditions of MMA in toluene in the presence of DMSO

Code	Temp. (°C)	LiOEM (mole*10 ⁴)	HOEM (mole*10 ⁴)	Alkyl Li (mole*10 ⁴)	DMSO (mole*10 ⁴)
1	0	-	32.0	n-BuLi 35.2	3.2
2	20	-	32.0	n-BuLi 35.2	3.2

Size Exclusion Chromatography (SEC) analysis was carried out by using Hewlett Packard 1090 equipped with HP 1037 refractive index detector. Polystyrene standards were used for calibration in THF at 40 °C. Microstructure of samples was determined by ¹H-NMR using Bruker AM 400 spectrometer operating at room temperature.

Results and Discussion

Anionic polymerization of MMA in toluene in the presence of DMSO-polyether alcohol (HOEM) and 2 equivalents excess of n-butyllithium (n-BuLi) per mole of alcohol at ambient temperatures was conducted successfully in high yields (Table 3).

Table 3. Data related with anionic polymerization of MMA in toluene in the presence of DMSO

Code	Yield (%)	M _n (SEC)	HI	Tacticity		
				s	h	i
1	88.0	101300	1.52	74	23	1
2	97.2	84200	1.62	76	25	1

It has to be noted here that coloration of the solution in terms of metallation of toluene was not observed during reaction. It has been previously reported that in the absence of DMSO, the same reaction causes the appearance of red color due to metallation of toluene⁵. On the other hand, when MMA monomer was added to DMSO free solution no polymer was obtained in one-hour reaction period, due to the excess amount of n-BuLi reacting preferentially with carbonyl group of MMA monomer preventing the

polymerization of MMA⁶. As a solution to this problem, it was proposed that whenever a well delocalized and crowded initiator, instead of n-BuLi, is used together with a polyetheralkoxide in the absence of DMSO, it is possible to obtain PMMA in high yields⁶.

In order to understand the effect of the amount of DMSO in detail, on both initiator efficiency (f) and tacticity, a series of experiments were conducted by using more reactive sec-butyllithium (sec-BuLi) (Table 4).

Table 4. Anionic polymerization conditions of MMA in toluene in the presence of DMSO^a and sec-BuLi

Code	DMSO (x10 ⁴)	Yield (%)	M _n (x10 ⁻³)	HI	f	Tacticity		
						s	h	i
4A ^b	2.5	100	121.7	1.5	0.16	80	19	1
4B ^b	25	100	132.9	1.3	0.15	79	21	0
4C ^b	130	100	102.1	1.4	0.20	74	25	1
4D ^b	250	100	77.4	1.3	0.26	78	21	1
4E ^b	452	100	81.7	1.2	0.24	72	25	3
4F ^b	904	100	75.9	1.2	0.26	70	26	1
4G ^b	1510	100	81.3	1.2	0.24	66	31	3
4H ^b	452	100	50300	1.3	0.20	76	22	2
4I ^b	452	100	39900	1.3	0.13	73	26	1
4J ^{b,c}	452	100	17000	5.2	0.18	76	23	1

^a polymerization time: 1 hour, polymerization temperature: 0°C^b in the presence of LiOEEM (25*10⁻⁴ mole)^c monomer resumption experiment

Here, all the samples up to 4 H have the same concentration of sec-BuLi which is 2.5x10⁻⁴ mole whereas 4 H and 4 I both contain 5.0x10⁻⁴ moles and 10.0x10⁻⁴ moles, respectively.

As it is clearly seen from Table 4 that molecular weight and heterogeneity index values decrease (Figure 1) by the increase in amount of DMSO in the polymerization solution.

RI response

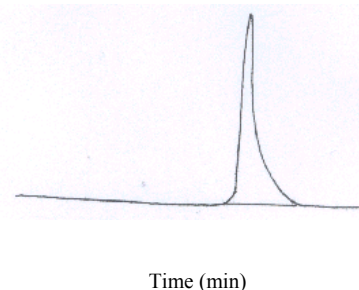
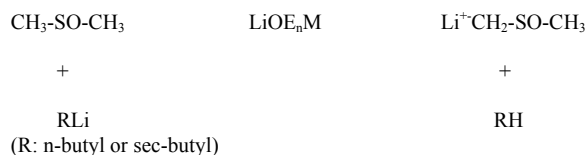


Figure 1. SEC chromatogram of PMMA sample 4G.

These results are proving that the product of reaction between alkyl lithium (RLi) and DMSO acts as an active specie in the polymerization of MMA as a complex initiator system.



Here active participation of DMSO in initiation mechanism as a complexed initiator is also obvious.

Heterogeneity index (HI) values, moreover, are lower than that of PMMA samples synthesized almost in the absence of DMSO (ca 2.5) which indicates again the importance of DMSO in initiation of MMA polymerization at relatively moderate temperature - 0°C.

On the other hand, when the amount of sec-BuLi was increased by keeping the concentrations of DMSO and LiOEEM constant, the reflection of this to the molecular weight has also a linear character showing cocontribution of DMSO and sec-BuLi as complexed initiator system. The existence of a decrease in initiation efficiency from 0.24 to 0.13 may be attributed to possible termination reaction via chain transfer to DMSO as reported before².

All these results at the same time indicate that any alkyllithium- n-BuLi, or sec-BuLi -can give a complexation with DMSO especially in the presence of promoters -lithium polyether alkoxides and acts as active initiator system in the polymerization of methylmethacrylates.

In order to determine the life time of the active centers on growing chain, a monomer resumption experiment was conducted for PMMA sample (4 J). Result is given in Figure 2.

RI response

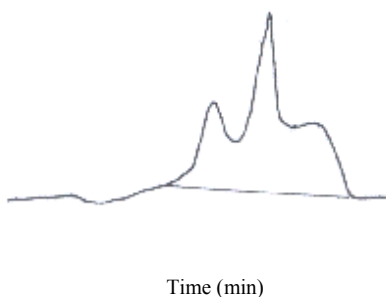


Figure 2. SEC chromatogram of PMMA sample 4 J

A multimodal molecular weight distribution shows that the produced active chain end complexed with DMSO, and/or LiOEEM is not stable for a long time which then give rise to polymer formation with different molecular weights.

Besides, as in the case of LiOEEM-DMSO-alkyllithium initiator system, high syndiotactic character of PMMA samples does not change deeply up to 10% DMSO.

Conclusions

It can be safely stated that alkyllithium/DMSO/LiOEEM initiator system is an efficient initiator for the anionic polymerization of MMA in nonpolar solvents at 0°C. Yields are quantitative and molecular weight distributions are relatively narrow. An increase in DMSO content of initiator system causes to increase in initiator efficiency which is not higher than ca 0.34 as a drawback for this initiator system. In all cases, triad compositions are ca. 78% syndiotactic (s), 20% heterotactic (h) and 2% isotactic (i).

Acknowledgement. The authors gratefully acknowledge the financial support given by ATOCHEM.

References

- (1) Trossarelli, L.; Guaita, M. and Priola, A. *J. Polym. Sci.*, **1967**, B5, 535.
- (2) Mulvaney, J.E and Markam, R.L., *J. Polym. Sci.*, **1965**, B4, 343.
- (3) Priola, A.; Trossarelli, L., *Makromol. Chem.* **1970**, 139, 281.
- (4) Nugay, N.; Nugay, T.; Jerome, R. and Teyssie, Ph. *J. Polym. Sci.*, *Polym. Chem. Ed.*, **1997**, 35, 361.
- (5) Nugay, N.; Nugay, T.; Jerome, R. and Teyssie, Ph., *J. Molec. Cat. A: Chem.*, **2002**, 179, 59.

- (8) Hatada, K.; Kitayana, T.; Fumikana, K.; Onta, K. and Yuki, H. Anionic Polymerisation: Kinetics, Mechanisms and Synthesis (edited by J.E. McGrath), *ACS Symposium Series*, **1981**, 166, 327.
- (9) Allen, R.D.; Smith, S.D.; Long, L.E. and McGrath, J.E., *ACS Polym. Prepr.* **1985**, 26, 247.
- (10) Ph. Bayard, R. Jerome, Ph. Teyssie, S.K. Varshney and J.S. Wang, *Polym. Bull.*, **1994**, 32, 381.