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Notes

Photopolymerization of Methyl Methacrylate Induced by Methylaluminoxane: Evidence for Unusual Radical Behavior[1]

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Introduction

Photopolymerization of methyl methacrylate induced by triethylaluminum (TEA) was extensively studied by Allen and co-workers[2]. Photoinduced polymerization of methyl methacrylate (MMA) by a 1:1 (molar ratio) TEA/MMA complex was found to proceed via a free-radical mechanism. Low molecular weight polymers were formed ($\bar{M}_n \sim 10^4$ at 20% conversion) at -15 °C at MMA/Al = 5 in toluene as solvent. A photoexcited state of the carbonyl complex of the Wittig "ate" type was proposed as the active initiator. More recently, Inoue and co-workers have studied the light-induced polymerization of methyl methacrylate using aluminum tetraphenylporphyrin as initiator.[3] The reaction was shown to proceed by a concerted mechanism involving the enol ester of MMA bound to aluminum as the active species. The polymerization exhibits the characteristics of a living polymerization such as controlled and predictable molecular weight and narrow molecular weight distribution.

Methylaluminoxane (MAO) is a product of controlled hydrolysis of trimethylaluminum (TMA) and is believed to be a mixture of linear and cyclic oligomers bearing the $[-Al(CH_3)O]_n-$ linkages and free TMA. MAO has achieved significance in recent years as a component of a high-activity homogeneous catalyst for olefin polymerizations.[4]

We have found that, similar to triethylaluminum, MAO also forms a weak complex with MMA. When irradiated with UV or diffused light, the MMA/MAO complex undergoes polymerization to high molecular weight polymers. The features of MAO-induced photopolymerization of MMA differ significantly from the TEA-induced photopolymerization described earlier in the literature. This paper reports some preliminary results of this study.

Experimental Section

Materials. All manipulations and operations were done using bench-top inert atmosphere techniques using dry argon. MMA (Loba Chemie, Bombay) was passed through a column of neutral alumina and then stirred over calcium hydride for 24 h and distilled under argon prior to use. Toluene (Loba Chemie, AR) was dried over sodium wire and distilled under argon. TMA and MAO (Schering AG, Germany) were used as received. MAO (5.5 wt % Al, average molecular weight = 850) in toluene had a methyl/aluminum ratio of 1.22. The content of free TMA in MAO was also estimated by NMR in toluene-d_8 and was found to be 12 (±1) mol %.[5] Hexaisobutyltetraaluminoxane (HIBTAO, 4.3 wt % Al) and tetraisobutyldialuminoxane (TIBDAO, 3.6 wt % Al) (Schering AG) were used as received.

Polymerization. Polymerizations were conducted in sealed glass tubes by illuminating the mixture of MMA and MAO/TMA/HIBTAO/TIBDAO with UV radiation (350 nm) at 30 °C in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co.) for the desired time. Reactions were terminated by adding acidified methanol. The coagulated polymers were dried to constant weight.

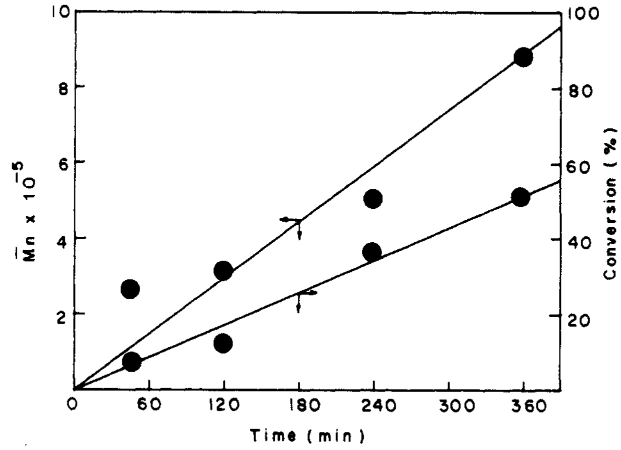

Figure 1. Plot of $\bar{M}_n$ and conversion with time for the photopolymerization of methyl methacrylate with MAO.

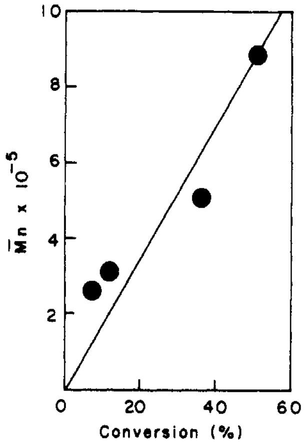

Figure 2. Plot of $\bar{M}_n$ vs conversion for the photopolymerization of methyl methacrylate with MAO.

Analysis. Aluminum was estimated by EDTA titration. Methyl content in MAO was estimated by gas volume measurement of methane gas obtained on hydrolysis. Intrinsic viscosity of polymer was measured using an Ubbelhode viscometer using toluene as solvent at 30 °C. NMR analysis of MAO and poly(methyl methacrylate) was performed in toluene-d_8 and $CDCl_3$, respectively, using a Bruker AC-200 spectrometer. UV analyses were performed on a Hitachi Model 220 UV-visible spectrophotometer in toluene as solvent. The molecular weight distribution for the polymers (0.3% w/v in THF) was determined by using a Waters GPC-II equipped with a refractive index detector. The measurements were carried out using Waters μ-Styragel columns (10^5, 10^4, 10^3, and 500 Å) at ambient temperature (27 °C) and THF as eluent at a flow rate of 1.0 mL/min. Monodisperse PMMA was used to calibrate the columns.

Results and Discussion

A 4:1 (mole ratio) mixture of MMA/MAO at room temperature shows a λ_{max} = 284 nm with a molar extinction coefficient of $\epsilon = 0.435\ M^{-1}\ cm^{-1}$. The photopolymerization experiments were therefore conducted at 350 nm at 30 °C.

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Table I
Photopolymerization of MMA Using Organoaluminum Compounds as Initiators[a]

sample no.	organoaluminum	[Al] × 10^2 mol/L	[MMA]/[Al]	time, min	conv, %	[η],[b] dL g^{-1}	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	% triads *mr*	% triads *rr*	% triads *mm*
1	MAO	13.4	70	45	7	0.83	4.26	2.63	1.62	39	55	6
2	MAO	13.4	70	120	12	0.94	4.84	3.14	1.54			
3	MAO	13.4	70	240	36	1.66	8.33	5.00	1.68	33	63	4
4	MAO	13.4	70	360	51	2.20	13.20	8.77	1.50	35	58	7
5	MAO	8.8	106	240	24	1.32						
6	MAO	4.4	212	240	20	1.22						
7	HIBTAO	8.8	106	240	20	1.29						
8	TIBDAO	8.8	106	240	20	1.30						
9	TMA	13.4	70	45	30	0.27				37	51	12
10	TMA	13.4	70	70	62	0.34						
11	TMA	13.4	70	120	80	0.37						
12	TMA	13.4	70	180	85	0.36				34	48	18

[a] Polymerization conditions: MMA = 4.68 g; temperature = 30 °C. [b] In toluene at 30 °C.

For purposes of comparison, neat TMA was also studied. The results are shown in Table I. Photopolymerizations were conducted in bulk with MMA/Al ratios of 70, 106, and 212. Conversions and molecular weight were found to be higher at lower MMA/Al ratios. Consequently, further studies were performed at MMA/Al ratios of 70. It was confirmed that in the absence of light MAO caused no polymerization of MMA. Photopolymerization of MMA induced by MAO and TMA was studied as function of time. A plot of conversion and number-average molecular weight as a function of time is shown in Figure 1. With MAO both conversion and molecular weight increased linearly with time. The plot of number-average molecular weight vs conversion was also linear (Figure 2). This behavior is reminiscent of the "living" radical polymerization of MMA observed with thermal iniferters and photoiniferters.[6] However, compared to thermal iniferter induced and photoiniferter-initiated polymerizations, higher conversions were obtained in shorter reaction times. The molecular weights of poly(methyl methacrylate)s were also substantially higher. Molecular weights acheived in the case of MAO-induced photopolymerization of MMA were much higher than those obtained through TMA-induced photopolymerization. Conversions and molecular weights achieved with both HIBTAO and TIBDAO were similar to those of MAO.

PMMA obtained from MAO-induced photopolymerization was examined by NMR for tacticity. The fraction of the *mr*, *rr*, and *mm* triads observed (Table I) were indicative of a chain-end free radical as the propagating species. The molecular weight distribution of poly(methyl methacrylate)s was in the range 1.5–1.7, indicating that the predominant chain-breaking event was termination by coupling. No broadening of the distribution was observed with conversion.

We presume that the true initiating species in the photoinitiated polymerization is the complex of MMA with MAO or with TMA (in the case of MAO) and triisobutylaluminum (in the case of HIBTAO and TIBDAO). However, the features of MAO-induced photopolymerization of MMA differ significantly from that of pure trialkylaluminum. Although the precise mechanism is far from clear at the present time, it appears as though the unique structure of oligomeric MAO offers a substantially higher degree of stability to the growing free radical. Additional kinetic and spectroscopic studies to elucidate the characteristics of this unusual reaction are in progress.

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