Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ali, Güneri Akov , Demierel, Günay and Özkar, Saim(1983) 'Some Studies on the Plasma-Initiated Polymerization of Methyl Methacrylate in the Liquid State', Journal of Macromolecular Science, Part A, 20: 8, 887 — 894
To link to this Article: DOI: 10.1080/00222338308061406
URL: http://dx.doi.org/10.1080/00222338308061406

J. MACROMOL. SCI.–CHEM., A20(8), pp. 887-894 (1983)

Some Studies on the Plasma-Initiated Polymerization of Methyl Methacrylate in the Liquid State

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ABSTRACT

Previous results obtained for the free radical polymerization of methyl methacrylate were used to predict the mechanism of plasma-initiated polymerization of this monomer in the liquid state. The data obtained by use of high resolution NMR spectra strongly predict a free radical mechanism for the plasma-initiated polymerization of methyl methacrylate.

INTRODUCTION

High resolution nuclear magnetic resonance (NMR) spectra of polymer solutions have been widely used to determine the stereochemical structure of certain vinyl polymers [1]. Bovey [2] employed this technique to investigate the dependence of stereoregularity on temperature for polymethyl methacrylate (PMMA), prepared by free radical polymerization. By considering the polymerization to consist of two indepen-

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0022-233X/83/2008-0887$3.50/0

dent competing reactions producing iso- and syndiotactic stereochemical placements of nearest neighbors in the chain, respectively, Bovey found that the syndiotactic addition was favored by an activation energy lower by 3.2 kJ, with no appreciable difference in the frequency factors, while Fox and Schnecko [3] carried out similar studies with PMMA prepared via free radical mechanism and concluded that the tacticity parameter α obeys Bernoulli trial statistics, increasing slightly (from 0.64 to 0.86) as the temperature decreases (from 250 to -40°C). Consequently, the isotactic placement reaction occurs with an Arrhenius factor 1.65-fold greater and an activation energy 4.5 kJ larger than for the competing syndiotactic addition, which is somewhat different from the pioneering investigations of Bovey.

In this work, both results were used as available evidence in predicting the mechanism of plasma-initiated polymerization of MMA in the liquid state for which a free radical mechanism has been suggested by Shen [4]. For this purpose, plasma-initiated polymers of MMA were prepared at four different postpolymerization temperatures ranging from 4 to 70°C with conversions between 3 and 29%. Their stereostructural characterization was made by ^{1}H-NMR spectroscopy from which the difference in activation enthalpies and entropies between the syndio- and isotactic propagation step was conveniently calculated.

EXPERIMENTAL PART

Plasma-Initiated Polymerizations in the Liquid State

The monomer, MMA (Rohm and Haas) was destabilized with 10% NaOH solution, washed with water, and twice vacuum distilled. It was degassed at 10^{-1} to 10^{-2} torr and the ampule was sealed in liquid nitrogen. The frozen ampule was then inserted between a pair of parallel electrodes connected to a rf generator operating at 13.56 MHz and delivering up to 100 W [5]. It was permitted to warm up until droplets of liquid monomer had appeared. A glow was then generated for a certain period of time. After initiation, the ampule was immediately immersed in a water bath where it was left standing at constant temperatures for prescribed periods of time, at the end of which the seal was broken and the contents were dissolved in chloroform, precipitated with ethanol, and dried under vacuum at 30°C up to constant weight.

The ^{1}H-NMR Spectra

The ^{1}H-NMR spectra were recorded on a Bruker WP-200 PFT Spectrometer at 54°C from the solution of PMMA in chloroform-d. The chemical shifts were determined relative to the TMS signal used as internal reference. The protons of the α-CH_3 groups give three lines in the spectrum due to syndio-, hetero-, and isotactic triads appearing at 0.87, 1.02, and 1.2 ppm, respectively. From the ratio of intensities of these lines, it was possible to calculate the fraction of these triads in the integral mode (by use of the computer system ASPECT 2000). The positions of the peaks were determined by comparison of the ^{1}H-NMR spectra of PMMA prepared via plasma-initiation with those of reference PMMA [6] samples prepared in ionic fashion to produce almost pure syndiotactic, isotactic, and heterotactic polymers.

RESULTS

In Table 1 the microtacticity results of four PMMA samples prepared by plasma-initiated polymerization in the liquid state over a temperature range of 4 to 70°C are presented. The quantity α represents the probability that a polymer chain will add a monomer unit to give the same configuration as that of the last unit at its growing end. As can be clearly seen from the table, the tendency to form syndiotactic sequences increases with decreasing postpolymerization temperature and propagation tends toward randomness as the polymerization temperature is increased, as in the case for the free radical polymerization of MMA.

The characteristic ^{1}H-NMR spectra of PMMA taken with the WP-200-PFT spectrometer are shown in Figs. 1a and 1b. In addition to the spectra of syndiotactic polymers prepared by plasma initiation, the spectrum of highly stereoregular polymers of PMMA prepared via an ionic mechanism is also included for comparison purposes in Fig. 2.

In order to evaluate the amount of stereoregularity from the α-CH_3 peaks, the ratio P_{het}/P_{syn} of the larger areas for the polymer of interest is used from which the tacticity parameter α for isotactic placement is easily calculated by the relation [3]

$$\alpha/(1 - \alpha) = 0.5(P_{het}/P_{syn}) \tag{1}$$

assuming that Bernoulli trial statistics are obeyed by α.

Also,

$$\alpha(1 - \alpha) = (k_{iso}/k_{syn}) = \exp\{(\Delta S^{\ddagger}_{iso} - \Delta S^{\ddagger}_{syn})/R - (\Delta H^{\ddagger}_{iso} - \Delta H^{\ddagger}_{syn})/RT\} \tag{2}$$

TABLE 1. Plasma-Initiated Polymerization Conditions of MMA and Tacticities Obtained (sealing pressure, 0.4 mmHg; power, 20 W)

Sample	t (°C)	Discharge period (s)	Postpolymerization period (h)	Percent conversion	Percent Triad Tacticity			
					Syndiotactic	Heterotactic	Isotactic	α
1	4	30	96	4.51	68	31	< 1	0.1856
2	30	42.5	24	16.58	63	36	< 1	0.2222
3	50	30	24	24.50	62	37	< 1	0.2298
4	70	46	24	29.40	60	39	< 1	0.2453

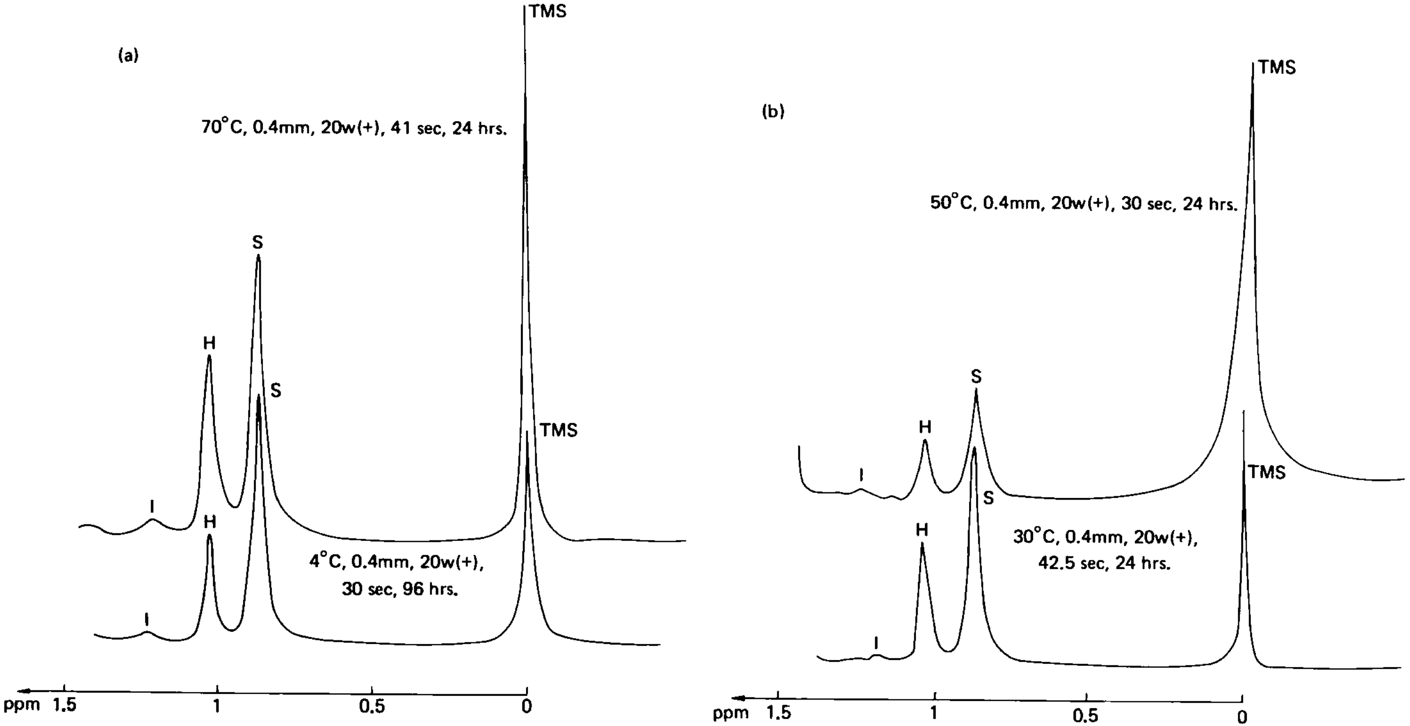

FIG. 1. The ^{1}H-NMR spectra of plasma-initiated polymer MMA. (a) Postpolymerization temperatures (4 and 70°C) at two different postpolymerization times (96 and 24 h), respectively. (b) Postpolymerization temperatures (30 and 50°C) for 24 h postpolymerization time. Other details are shown in the figure.

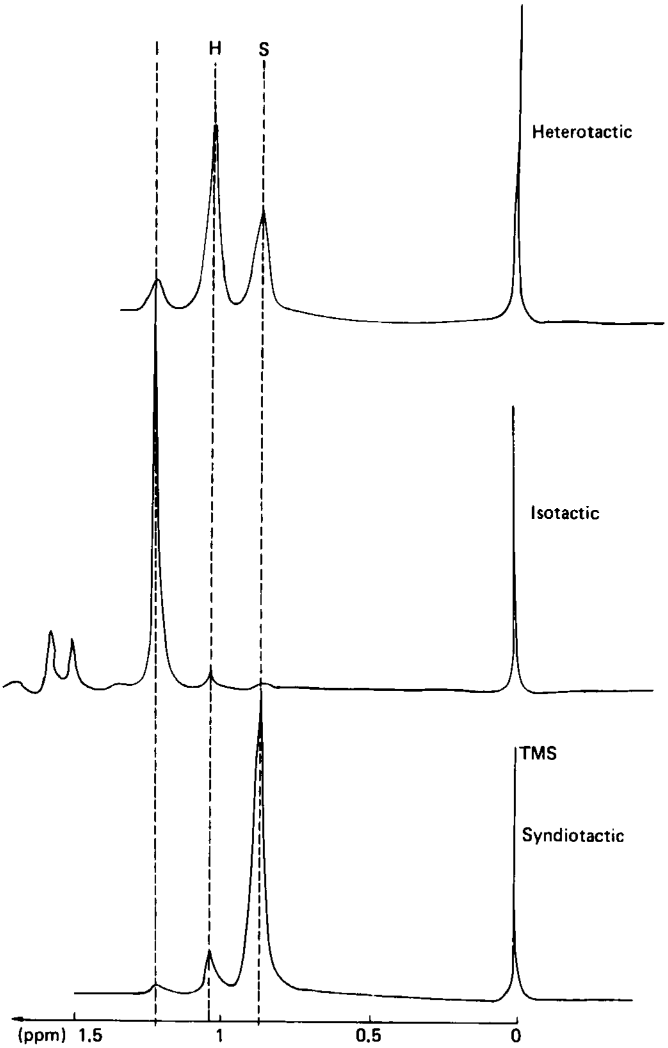

FIG. 2. The ^{1}H-NMR spectra of highly stereoregular polymers of PMMA prepared via an ionic mechanism (sample donated by Prof K. Hatada).

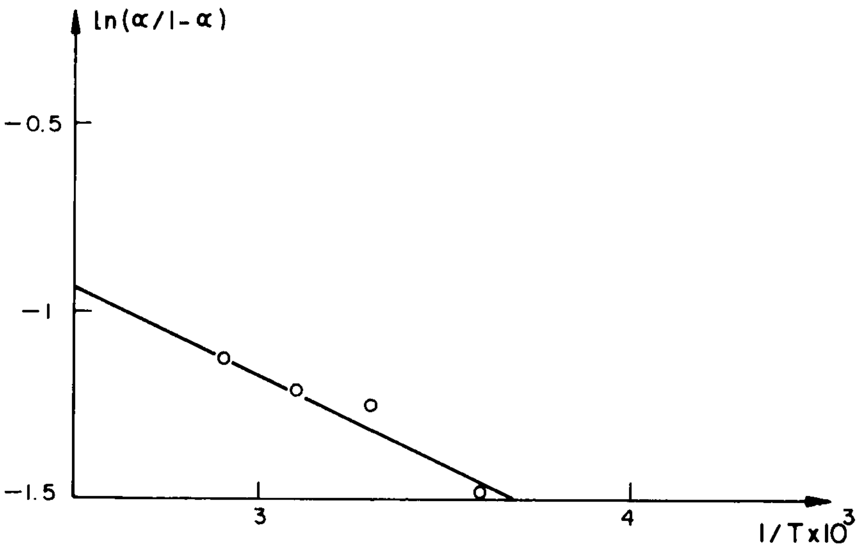

FIG. 3. Arrhenius plot of ln α/(1 - α) versus 1/T for the plasma-initiated PMMA samples.

From the Arrhenius plot of ln α/(1 - α) versus 1/T (Fig. 3), for which the ln α(1 - α) term is readily derived by Eq. (1), the difference in activation enthalpies and entropies between the syndio- and isotactic propagation steps was calculated as

$$(\Delta H^{\ddagger}_{iso} - \Delta H^{\ddagger}_{syn}) = \Delta(\Delta H_p^{\ddagger}) = 4.05 \text{ kJ/mol}$$

$$(\Delta S^{\ddagger}_{iso} - \Delta S^{\ddagger}_{syn}) = \Delta(\Delta S_p^{\ddagger}) = 2.3 \text{ J/mol·K}$$

both of which are in quite good agreement with the corresponding values reported for the free radical polymerization of MMA [2, 3]. In addition, the microtacticity results obtained from high resolution NMR spectroscopy greatly resemble those obtained from PMMA prepared via a free radical mechanism [1].

All of these are solid evidence which lets one strongly predict that plasma-initiated polymerization of MMA in the liquid state does proceed via a free radical mechanism.

ACKNOWLEDGMENTS

We are grateful to Professor Koichi Hatada of Osaka University, Japan, for his generous supply of the reference stereoregular polymers of PMMA together with their ^{1}H-NMR spectra. This work was supported by TBTAK (Turkish National Scientific Research Council), through its TUMKA unit.

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Accepted by editor March 15, 1983
Received for publication April 23, 1983.