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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 Yamashita, Natsuki , Tanaka, Hiroyuki , Deguchi, Satoru , Maeshima, Toshihisa and Wei, Lun-Shin(1987) 'Polymerization of Methyl Methacrylate in the Presence of Imidazole Derivatives. Kinetics and Polymer Structure', *Journal of Macromolecular Science, Part A*, 24: 9, 1121 – 1134

To link to this Article: DOI: 10.1080/00222338708078147

URL: <http://dx.doi.org/10.1080/00222338708078147>

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POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF IMIDAZOLE DERIVATIVES. KINETICS AND POLYMER STRUCTURE

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ABSTRACT

The kinetics of the polymerization of methyl methacrylate (MMA) in the presence of imidazole (Im), 2-methylimidazole (2MIm), or benzimidazole (BIm) in tetrahydrofuran (THF) at 15-40°C was investigated by dilatometry. The rate of polymerization, R_p , was expressed by $R_p = k[\text{Im}][\text{MMA}]^2$, where $k = 3.0 \times 10^{-6} \text{ L}^2/(\text{mol}^2 \cdot \text{s})$ in THF at 30°C. The overall activation energy, E_a , was 6.9 kcal/mol for the Im system and 7.3 kcal/mol for the 2MIm system. The relation between $\log R_p$ and $1/T$ was not linear for the BIm system. The polymers obtained were soluble in acetone, chloroform, benzene, and THF. The melting points of the polymers were in the range of 258-280°C. The $^1\text{H-NMR}$ spectra indicated that the polymers were made up of about 58-72% of syndiotactic structure. The polymerization mechanism is discussed on the basis of these results.

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INTRODUCTION

We reported in earlier articles [1-7] that several polar vinyl monomers such as acrolein, methyl vinyl ketone, acrylamide, and methyl methacrylate (MMA) could be homo- and copolymerized readily by imidazole (Im) at room temperature. Kinetic investigations revealed that polymerization could be initiated by the Im-monomer adduct anion formed in the thermodynamic equilibrium between the Im and Im-monomer adduct. The polymerization of MMA in the presence of Im was carried out in tetrahydrofuran at 20-30°C under nitrogen [2]. The rate of polymerization R_p was expressed by the equation $R_p = k[\text{Im}][\text{MMA}]^2$. The polymers obtained were soluble in acetone, chloroform, benzene, and tetrahydrofuran. The melting points were found to be in the range of 238-242°C. Interestingly, the ¹H-NMR data indicated that these poly-MMA products have an abundance of syndiotactic structures. The kinetic results were obtained quantitatively from time-conversion curves. However, the existence of an induction period, based on the production of an initial adduct (Im-MMA adduct), was recently observed in our experiments.

This investigation was performed to reveal further details of the polymerization mechanisms and the structure of the resulting polymer.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was purified in the usual way (bp 46-47°C torr). Imidazole (Im) and 2-methylimidazole (2MIm) were purified by recrystallization from pure benzene. Benzimidazole (BIm) was recrystallized from pure water. Tetrahydrofuran (THF) was prepared as described in an earlier article [1].

Polymerization Method

The polymerization of MMA was carried out homogeneously in THF at 15-40°C in a nitrogen atmosphere by the use of a dilatometer. The required amounts of Im, THF, and MMA were placed in a dilatometer. The dilatometer was placed in a thermostat kept at 30-50°C to start the polymerization reaction. After the reaction, the polymerization was stopped in a large amount of ether containing hydrochloride, and the precipitate was filtered, vacuum dried, and weighed to determine the yield.

Kinetics

The initial polymerization rate R_p by dilatometry was estimated from the relationship between the volume decrease, the polymerization time, and the polymer conversion.

Polymer Characterization

The viscosity-average molecular weights \bar{M}_v of the polymers were determined in benzene at 30°C with an Ostwald viscometer. M_v was calculated from the Mark-Houwink-Sakurada equation [8]:

$$[\eta] = K \cdot \bar{M}_v^\alpha$$

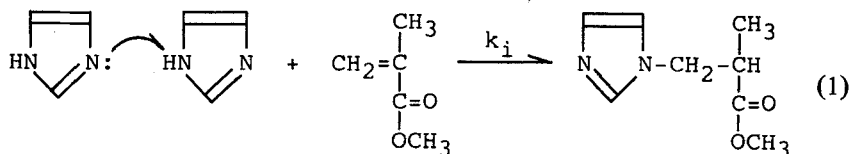
with $K = 5.2 \times 10^{-3}$ and $\alpha = 0.76$.

The $^1\text{H-NMR}$ spectra of the polymers in CDCl_3 were measured at 26°C by a Nihon Denshi JEOL-FX 200 MHz. The syndiotacticity of the polymers was determined from the $^1\text{H-NMR}$ spectra by the method of Bovey et al. [9] and Otsu et al. [10].

RESULTS AND DISCUSSION

Kinetic Results

The polymerization of MMA by Im as anionic catalyst was carried out in THF at 30-50°C. The relationship between the volume decrease and the polymerization time is shown in Fig. 1. MMA showed slight polymerizability without the catalyst, but the presence of Im facilitated polymerization of MMA. The rate of polymerization increased during the course of the polymerization reaction. Polymerization in the presence of 2MIm and BIm also showed the same trend (Figs. 2 and 3). Moreover, the polymerizability was found to be influenced by the structure of Im derivatives. The changes of slope seem to reflect the polymerization mechanism reported in an earlier paper [2]. The polymerization could be initiated by the Im-MMA adduct anion formed in thermodynamic equilibrium between the Im and the Im-MMA adduct. It is assumed to proceed as shown in Eqs. (1)-(3):



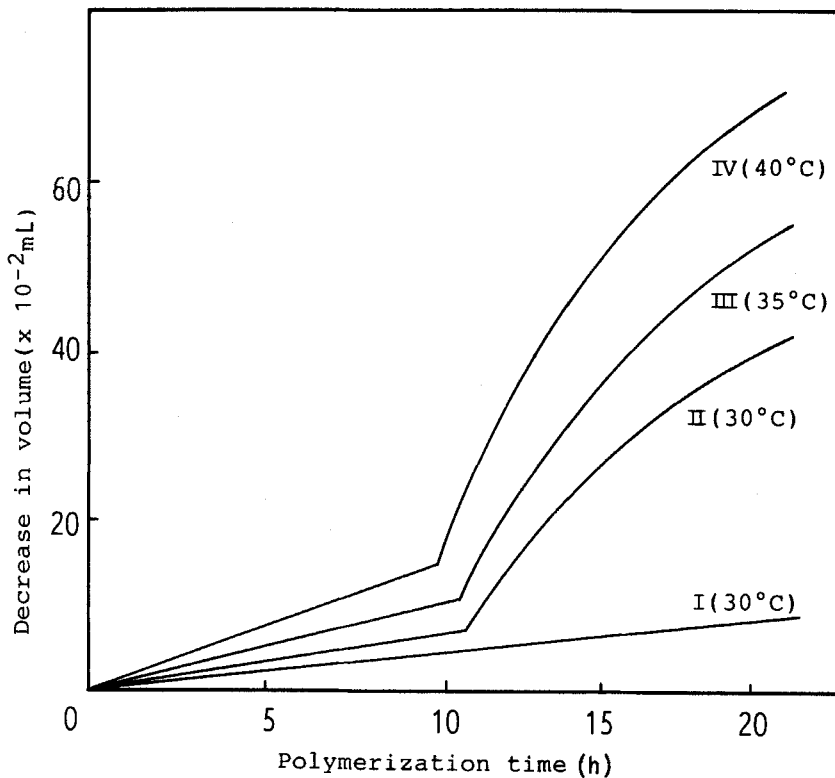
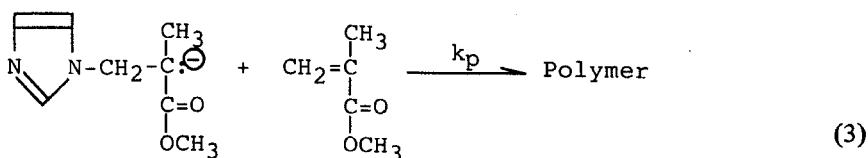
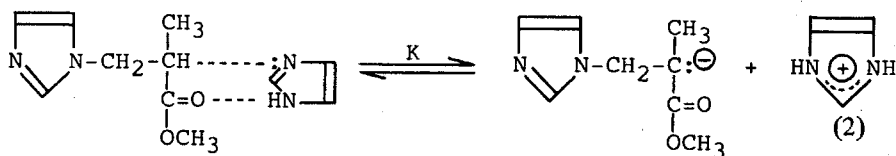


FIG. 1. Relationships between volume decrease and polymerization time at various temperatures; $[Im] = 2.0 \text{ mol/L}$; $[MMA] = 4.0 \text{ mol/L}$; solvent, THF. I: Noncatalyzed polymerization. II-IV: Initiated by Im at the indicated temperature.



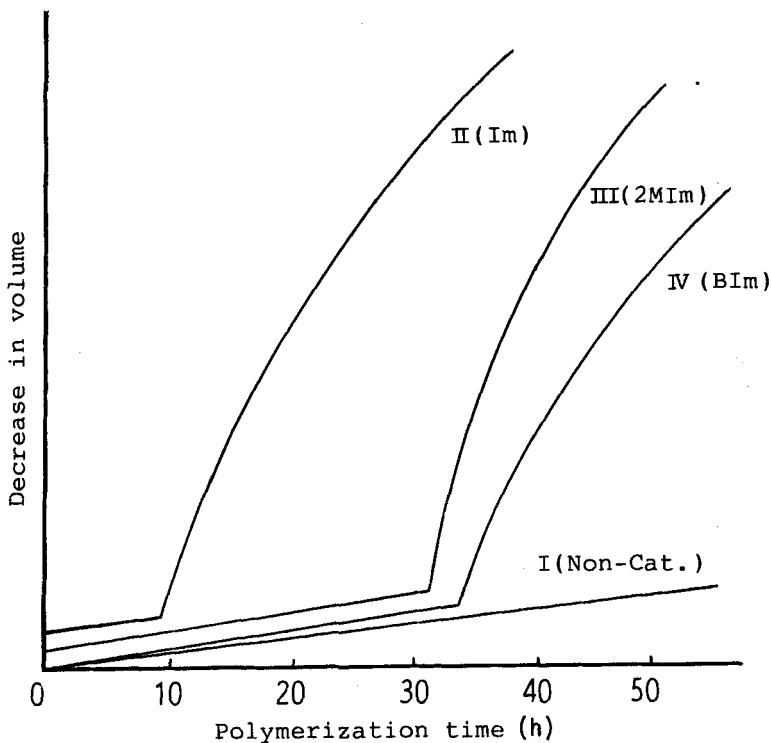


FIG. 2. Relationships between volume decrease and polymerization time at 30°C with various catalysts; [Im] = 0.4 mol/L; [MMA] = 1.6 mol/l; solvent, THF.

Two distinct slopes of the plots in Figs. 1, 2, and 3 may be explained by the presence of two reaction steps, with the first step depending on the formation of Im-MMA adduct (initial adduct) and the second step depending on the polymerization (propagation) reaction.

In the first step the adduct might be formed by the catalyst and the monomer to reach a thermodynamic equilibrium. Little polymer would be obtained at this stage. The existence of the Im-MMA adduct was previously confirmed in the initiation step by $^1\text{H-NMR}$ data in a preceding paper [2]. In the second step the volume of the dilatometer decreases more rapidly as the polymerization reaction proceeds.

The rate of polymerization R_p was determined from the slope of the

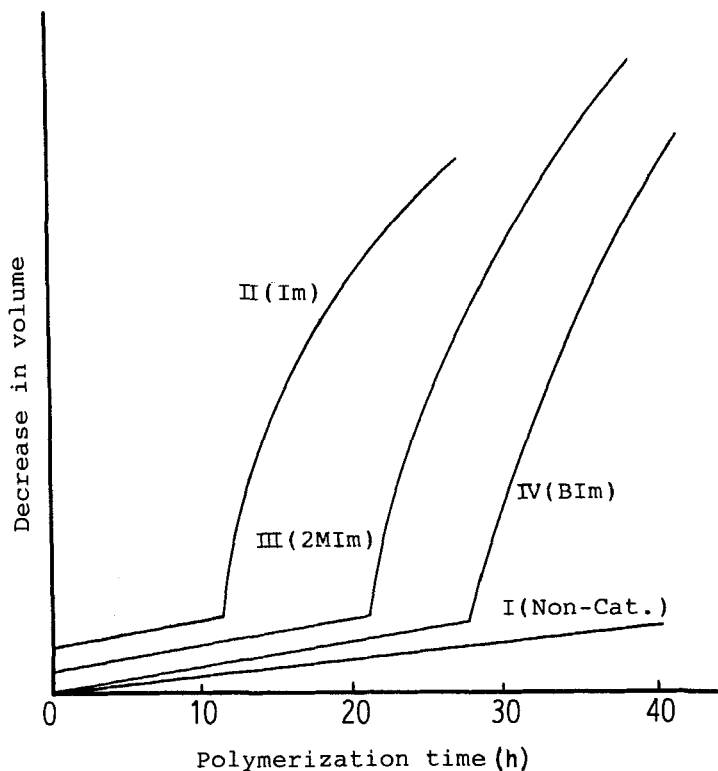


FIG. 3. Relationships between volume decrease and polymerization time at 50°C with various catalysts; [Im] = 0.4 mol/L; [MMA] = 1.6 mol/L; solvent, THF.

second reaction step and the polymer yields. The results were determined from

$$R_p = k[\text{Im}][\text{MMA}]^2$$

where [Im] stands for the concentration of the imidazole derivative. The slopes in Figs. 4 and 5 give $k = 3.0 \times 10^{-6} \text{ L}^2/(\text{mol}^2 \cdot \text{s})$ for imidazole in THF at 30°C. This polymerization equation coincides with our previous results [2]. Table 1 shows the kinetic results for the three imidazoles.

The activation energy, E_a , obtained by Arrhenius plots was 6.9 kcal/mol

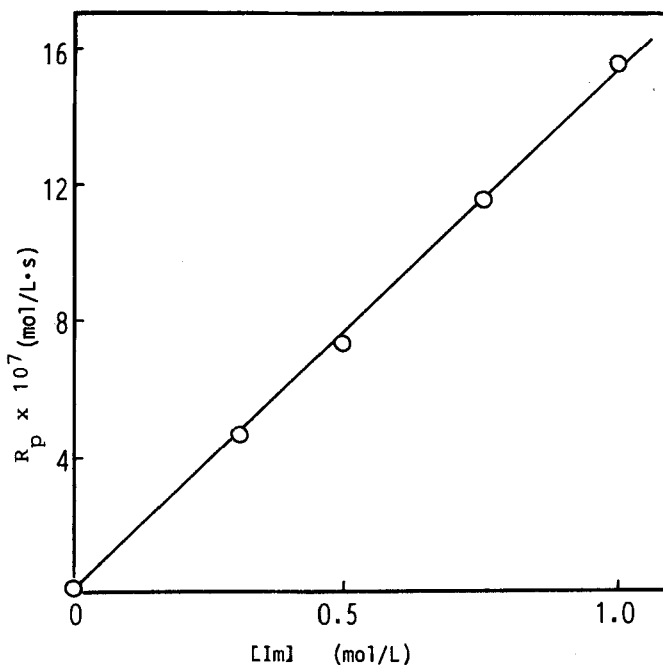


FIG. 4. Relationships between the polymerization rate R_p and Im concentration at 30°C; $[\text{MMA}] = 1.0 \text{ mol/l}$; solvent, THF.

for the Im system and 7.3 kcal/mol for the 2MIm system (Fig. 6). That the E_a of the 2MIm system was higher than that of the Im system may also suggest the presence of a mechanism involving the formation of the complex during the propagation step. Moreover, it suggests that the association of 2MIm is less strong than Im. This was also observed by $^1\text{H-NMR}$.

In Fig. 7, the signal of the proton on 2MIm appeared stronger than that on Im, because the methyl group in the 2-position on 2MIm is an electron-donating group, i.e., the initial adduct (2MIm-MMA adduct) is formed more slowly, while in the polymerization step (the step with the steeper slope), the R_p for 2MIm was higher than for Im. This may be explained as follow: the $\text{p}K_a$ of 2MIm ($\text{p}K_a = 7.9$) is higher than that of Im ($\text{p}K_a = 7.0$), and as the distance between the propagating anion and the counterion becomes greater, it becomes more like a free ion:

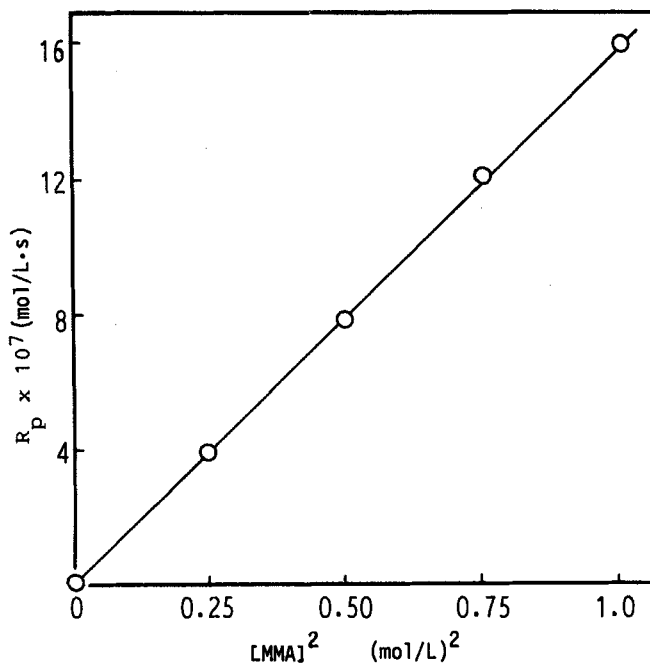
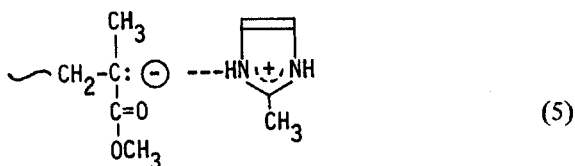
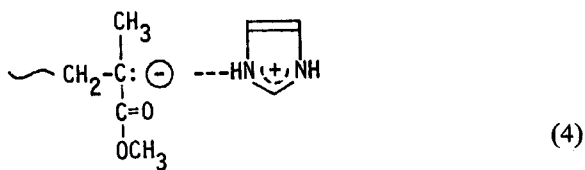


FIG. 5. The relationships between the polymerization rate R_p and MMA concentration at 30°C ; $[\text{Im}] = 1.0 \text{ mol/L}$; solvent, THF.



In the case of the BIm system, the plot of $\log R_p$ and $1/T$ was not linear. It may be assumed that BIm is associated to form molecular aggregates as

TABLE 1. Polymerization Rate R_p in the Presence of Imidazole Derivatives^a

Catalyst	Polymerization temperature, °C	Initiation time, h	$R_p \times 10^6$, mol/L·s	$-\log R_p$
Im	30	10	2.74	5.62
	35	11	3.45	5.45
	40	9	3.86	5.43
	45	9	4.80	5.32
	50	9	5.63	5.25
2MIm	30	31	3.41	5.47
	35	29	4.70	5.33
	40	26	5.99	5.22
	45	19	7.25	5.32
	50	19	8.77	5.06
BIm	30	34	2.07	5.68
	35	38	2.84	5.55
	40	27	5.82	5.23
	45	26	4.81	5.42
	50	23	4.30	5.37

^aPolymerization conditions: [Im] = 0.4 mol/L; [MMA] = 1.6 mol/L; solvent, THF.

steric intermolecular combinations and suggests variation of polymerization mechanisms with polymerization temperature. Hence, this polymerization mechanism must be investigated kinetically and will be the subject for a future study.

Polymer Structure

All of the polymers obtained were easily soluble in acetone, chloroform, benzene, and THF. Their IR spectra revealed adsorption bands characteristic

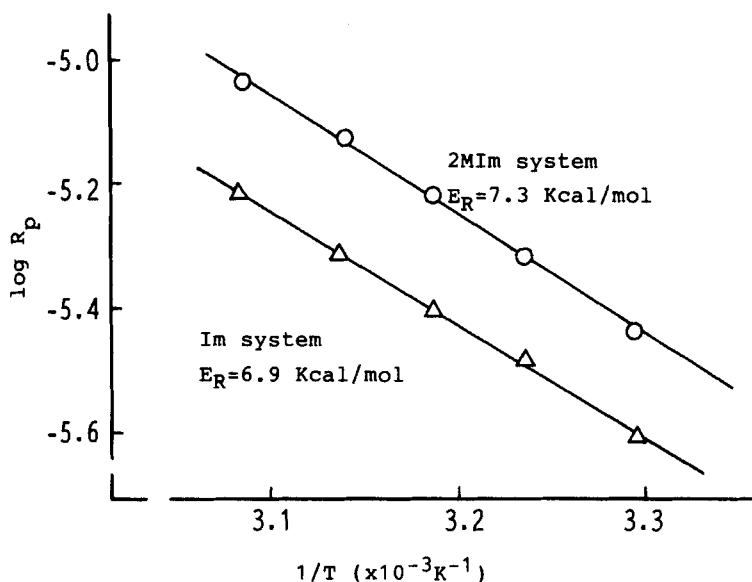


FIG. 6. Arrhenius plots of Im and 2MI systems.

for Im and MMA (2950 and 1160 cm^{-1}) and suggest the same structure as for the free-radical polymers, in agreement with the previous observations. The $^1\text{H-NMR}$ spectra of the polymers was also measured in CDCl_3 at 26°C (e.g., Fig. 8). The spectrum has several signals representing the α -methyl group (0.5-1.5 ppm), the methylene chain (1.5-2.3 ppm), and the methyl ester group (3.7 ppm). The syndiotacticity of these polymers was calculated from the ratios of integrated curves of two peaks obtained from the methylene chain (1.5-2.3 ppm) by the method of Bovey et al. [4] (see Table 2).

The viscosity-average molecular weight \bar{M}_v , and the melting range of the polymers are shown in Table 3. The results of Table 2 indicate that these polymers have an abundance of syndiotactic structure and the melting points support this. However, polymerization temperature has no effect on \bar{M}_v or melting points of the polymers.

In general, the poly-MMA obtained from free-radical polymerization at 60°C has 58% syndiotacticity [10]. Anionic polymerizations of MMA

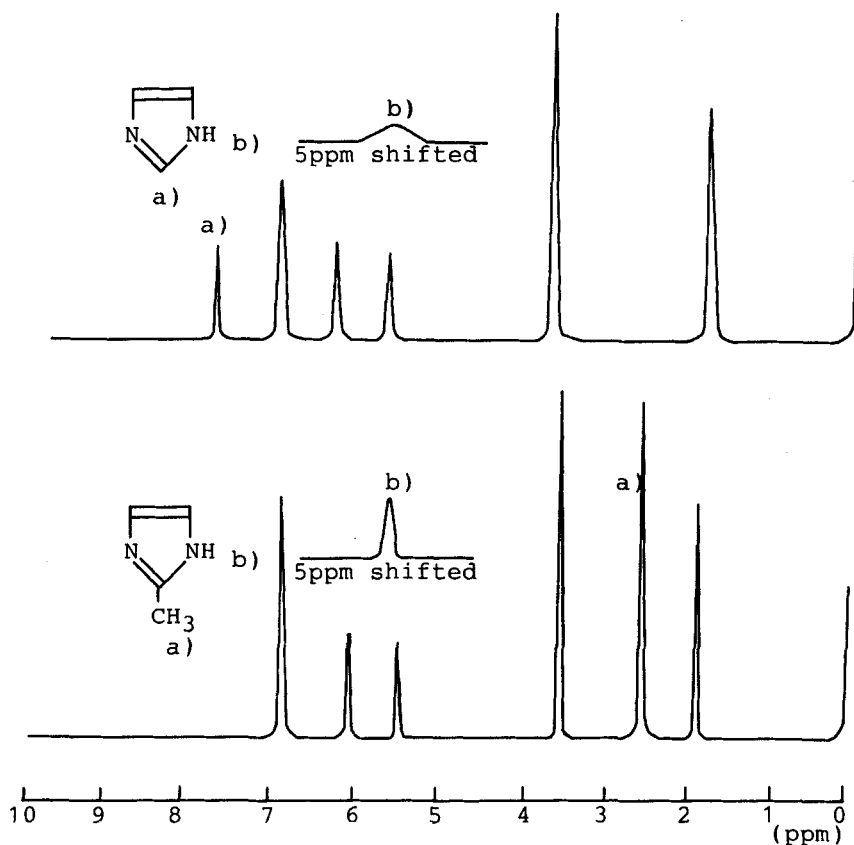


FIG. 7. $^1\text{H-NMR}$ spectra of Im and 2Mim systems in $\text{THF-}d_8$.

in the presence of Grignard reagent or butyllithium in a nonpolar solvent, such as toluene (isotacticity, maximum 79.8%), [11]. However, in a polar solvent such as THF, syndiotactic poly-MMA (syndiotacticity, maximum 54.8%) is produced because of the formation of the free ion [11].

In this study the syndiotacticity of these polymers was high, about 66-72%. Therefore, it is also thought that, in the propagation step, the carbanion of the propagating chain and the counterion (Im cation) are relatively far apart (free ionic propagation). Alternatively, it suggests the presence of one or more controlled reactions by the Im catalyst.

TABLE 2. Syndiotacticity Based on Integrated Peak Ratios of $^1\text{H-NMR}$ Spectra and Melting Point Range of Polymers

Catalyst	Polymerization temperature, $^{\circ}\text{C}$	mp range, $^{\circ}\text{C}$	Syndiotacticity based on integrated ratio, %
Im	30	265-270	69.9
	35	271-276	69.4
	40	264-269	69.5
	45	275-280	65.5
	50	243-258	67.4
2MIm	30	260-265	71.5
	35	269-70.5	70.5
	40	258-263	71.8
	45	264-269	70.5
	50	275-280	68.6
BIm	30	275-280	70.1
	35	271-276	70.9
	40	250-256	69.4
	45	273-278	68.4
	50	265-270	69.8

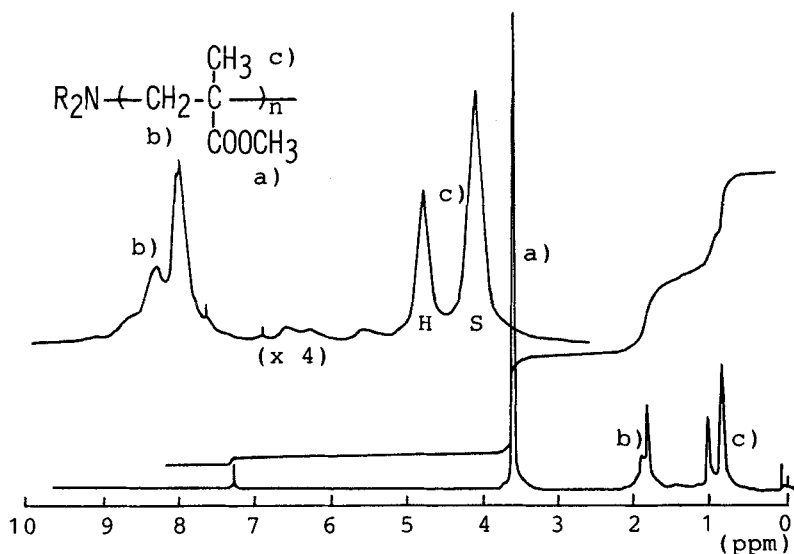


FIG. 8. $^1\text{H-NMR}$ spectrum of poly(methyl methacrylate) in CDCl_3 . This polymer was obtained in THF at 30°C in 720 h (conversion, 16.5%; $\bar{M}_v = 277\,000$; melting point range, $265\text{--}270^\circ\text{C}$).

TABLE 3. Syndiotacticity Based on Integrated Peak Ratios of $^1\text{H-NMR}$ Spectra, Melting Point Range, and Viscosity-Average Molecular Weight of Polymers

Polymerization temperature, $^\circ\text{C}$	Conversion, %	\bar{M}_v	mp range, $^\circ\text{C}$	Syndiotacticity based on integrated ratio, %
15	8.9	148 000	240-280	69.1
20	15.7	—	286-293	64.3
25	18.2	145 000	210-280	63.8
30	16.5	277 000	230-260	58.2
35	21.1	673 000	230-280	67.4
40	17.5	222 000	286-294	66.7

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Received November 12, 1986

Revision received December 29, 1986