End-Group Analysis of Poly(methyl methacrylate) Prepared with Benzoyl Peroxide by 750 MHz High-Resolution ^{1}H NMR Spectroscopy

Koichi Hatada,* Tatsuki Kitayama, Koichi Ute, Yoshio Terawaki, and Takatsune Yanagida

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received May 13, 1997; Revised Manuscript Received August 19, 1997[⊗]

ABSTRACT: ^{1}H NMR spectra of poly(methyl methacrylate) prepared with benzoyl peroxide in toluene at 100 °C were measured on a 750 MHz high-resolution NMR spectrometer. End groups resulting from initiation, chain transfer, and termination reactions were assigned, and the numbers of end groups per polymer molecule were estimated. End-group signals showed splittings due to stereochemical sequences near the chain ends, the analysis of which indicated that the racemo diad at the chain end attached with C_6H_5- was higher than that with C_6H_5COO-.

Introduction

Like many scientific fields, polymer chemistry has benefited from NMR spectroscopy, and the NMR technique is now widely used in areas such as tacticity determination, analysis of end groups and irregular linkages, comonomer-sequence determination in copolymers, and chain-dynamics studies. Analysis of end groups or irregular linkages in polymer chains[1] is a powerful method for studying the mechanism of polymerization as reviewed by Bevington *et al.*[2] and Axelson and Russell.[3] In radical polymerization the ^{14}C-labeling technique has long been used to study initiation and termination mechanisms, in which determination of the number of initiator fragments in a polymer molecule is the key procedure. Later, labeling with NMR accessible nuclei such as ^{13}C,[4−10] ^{2}H,[10,11] ^{19}F,[12] or ^{15}N[9] has been increasingly used to examine the end groups of a polymer chain. The NMR methods have enabled us to determine not only the amount but also the structure of initiator fragments. As an alternative approach, totally deuterated monomers such as methyl methacrylate-d_8 (MMA-d_8)[13,14] and styrene-d_8[15] were polymerized with undeuterated α,α′-azobisisobutyronitrile (AIBN), and the resultant polymers were analyzed for the initiator fragment by ^{1}H NMR spectroscopy.

The progress in NMR technique, particularly the introduction of superconducting magnets with high field strengths makes it much easier to detect very small signals due to end groups and/or irregular linkages. For example, the olefinic proton signals due to the unsaturated chain end of radically prepared poly(methyl methacrylate) (PMMA), which was formed through a disproportionation reaction, could be analyzed by ^{1}H NMR.[13,16] In this article, PMMA prepared with benzoyl peroxide (BPO) in toluene at 100 °C was analyzed by 750 MHz high-resolution ^{1}H NMR spectroscopy. The polymerization conditions intentionally followed those described in Bovey's first report on tacticity determination of PMMA by ^{1}H NMR published in 1960.[17] Structures of end groups resulting from initiation, chain-transfer, and termination reactions were clearly identified. The number of each group was determined, and the chain-transfer constant could be roughly estimated. Moreover, signals of end groups showed splittings due to tacticity at the chain ends, allowing us to discuss stereoregularity in the initiation process.

Experimental Section

Materials. MMA-d_8 was a kind gift from Mitsubishi Rayon Co., Ltd. MMA and MMA-d_8 were purified by distillation under reduced nitrogen pressure and distilled again over CaH_2 under high vacuum just before use. BPO and AIBN were purified by recrystallization from benzene and ethanol, respectively. C_6H_5MgBr was prepared in diethyl ether from bromobenzene and magnesium metal. $C_6H_5CH_2Li$ was prepared from the reaction of toluene and *n*-butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[18] *t*-C_4H_9Li, $(C_2H_5)_3Al$ and (5,10,15,20-tetraphenylporphyrinato)cobalt(II) (CoTPP) were obtained commercially. Toluene, treated with sulfuric acid, aqueous sodium hydroxide, and water, successively, was dried over calcium chloride, distilled, and stored over sodium. The purified toluene was mixed with butyllithium and then distilled under high vacuum before use. Tetrahydrofuran (THF) was refluxed over CaH_2 and then over $LiAlH_4$, stored with $LiAlH_4$, and distilled under high vacuum before use.

Polymerization. Polymerization of MMA with BPO was carried out in a sealed glass ampoule under nitrogen at 100 °C for 4 h. After being cooled to 0 °C to terminate the reaction, the reaction mixture was precipitated into a large amount of methanol. The precipitate was collected by filtration, washed several times with methanol, and dried under high vacuum at 60 °C. The polymerization with C_6H_5MgBr or $C_6H_5CH_2Li$ was initiated by adding monomer to the corresponding initiator solution cooled to the polymerization temperature. The polymerization was terminated by adding methanol containing a small amount of HCl (aq) at the polymerization temperature. The polymer obtained was recovered similarly to the polymerization with BPO. Polymerization conditions, M_n, and tacticity for all the polymer samples are shown in Table 1.

Measurement. ^{1}H NMR spectra of the polymer were taken in $CDCl_3$ at 55 °C on a Varian UNITY INOVA 750 FT NMR spectrometer (750 MHz for ^{1}H nuclei) using remaining chloroform as an internal standard (7.258 ppm) (pulse width 4.1 μs (45° pulse), pulse duration 18.0 s, number of accumulations was 512). Chemical shifts of ^{1}H NMR signals of PMMA depended on the concentration of polymer samples: a downfield shift of 0.009 ppm was observed with 1% decrease of the polymer concentration. Therefore, the chemical shift was calibrated on the basis of the spectrum of sample 1. ^{1}H spin-decoupled NMR spectra were taken on a JEOL GX500 FT NMR spectrometer (500 MHz for ^{1}H nuclei) in $CDCl_3$ at 55 °C. The signal-to-noise ratio of the spectra obtained with the 750 MHz spectrometer is 4 times higher than that with the

---

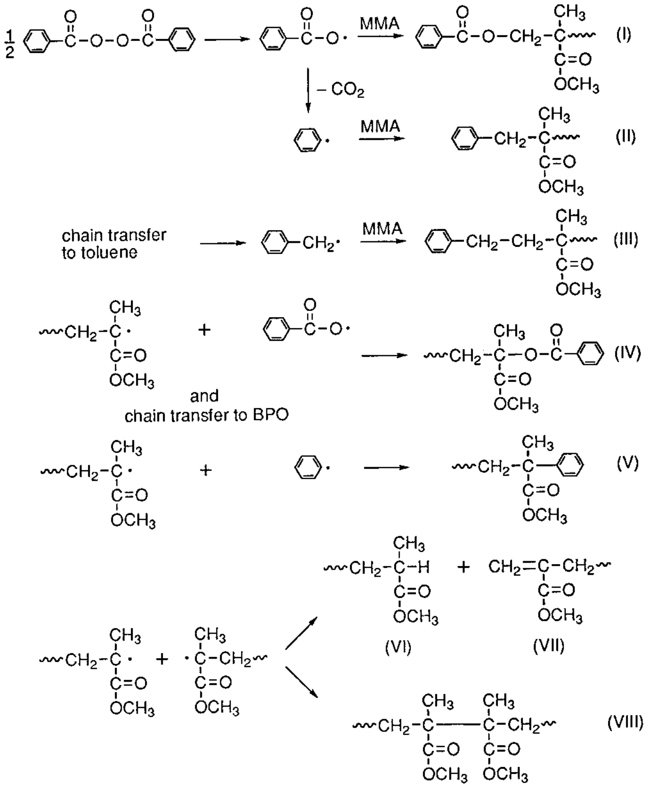
[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

Table 1. NMR Samples of PMMA Prepared with Several Initiators

sample no.	initiator	solvent	temp (°C)	M_n[a]	tacticity(%)[b] mm	mr	rr
1[c]	BPO	toluene	100	17700	5	39	56
2[d]	C_6H_5MgBr	THF	−78	33520	0	13	87
3[d]	C_6H_5MgBr	toluene	40	57660	95	4	1
4[d]	$C_6H_5CH_2Li$[g]	toluene	−78	24400	36	25	39
5[d]	t-$C_4H_9Li/(C_2H_5)_3Al$	toluene	−78	9350	0	10	90
6[e]	AIBN	none	60	4490	3	35	62
7[d,f]	$C_6H_5CH_2Li$[g]	toluene	−78	31350	38	15	47

[a] Determined by ^1H NMR or GPC. [b] Determined by ^1H NMR. [c] MMA 30 mmol, BPO 0.15 mmol, and toluene 30 mL. [d] Fractionated from the formed polymer. [e] In the presence of (5,10,15,20-tetraphenylporphyrinato)cobalt(II). [f] Poly(MMA-d_8). [g] In the presence of N,N,N',N'-tetramethylethylenediamine.

Scheme 1. Elementary Reactions and Possible Terminal Structures in the Polymerization of MMA with BPO in Toluene



500 MHz one under the same conditions, indicating a higher potentiality of the 750 MHz spectrometer for observation of weaker signals to allow us a more detailed analysis.

Molecular weights and their distributions were determined on a JASCO 880-PU chromatograph equipped with two GPC columns (Shodex KF-806L (8 × 300 mm), maximum porosity 2×10^7) at 40 °C using THF as an eluent. The GPC chromatogram was calibrated against standard polystyrene samples.

Results and Discussion

The main objective of this article is to analyze the structure of end groups in PMMA prepared with BPO in toluene at 100 °C by ^1H NMR spectroscopy. In Scheme 1 are shown possible terminal structures and the relating elementary reactions in the polymerization. Initiation reaction with BPO gives structures **I** and **II**. Chain transfer to toluene forms benzyl radicals which initiate the polymerization of MMA leading to the formation of structure **III**. Termination with primary radicals of BPO gives structures **IV** and **V**. Chain transfer to BPO also forms structure **IV**. Termination of the propagating radicals through disproportionation gives end groups **VI** and **VII**, and that through combination forms structure **VIII** in the middle of the polymer chain. On the basis of these considerations the NMR spectra of the radically prepared PMMA were analyzed in detail in the following way.

Aromatic Region. Figure 1 shows the ^1H NMR spectrum of the PMMA (sample **1** in Table 1). Signals at 7.95, 7.52 and 7.41 ppm were assigned to the benzoyloxy group (Figure 1A) and residual signals at 6.95−7.25 ppm to the phenyl group (Figure 1B) as reported previously.[13] Assignments for ortho, meta, and para protons of the benzoyloxy group were determined on the basis of their intensities and splitting patterns of the peaks. Signals at 4.10−4.45 ppm were assigned to methylene groups adjacent to the benzoyloxy group (Figure 1D). Two protons of the methylene group may be nonequivalent due to the existence of the adjacent asymmetric carbon and also may be sensitive to tacticity of the first diad of the polymer chain (meso and racemo). As a result the signals consist of two sets of AB quartets with different intensities. The intensity ratio of benzoyloxy proton signals at 7.41−7.95 ppm (corresponding to five protons) to methylene proton signals at 4.10−4.45 ppm (corresponding to two protons) was determined to be 2.91, slightly larger than the expected value of 2.5. This result indicates that some of the benzoyloxy groups attach to other terminal units such as structure **IV**. The number of structure **I** moieties per chain was determined to be 0.08_6 from the M_n and intensities of the methylene proton signals at 4.10−4.45 ppm and methoxy proton signals of the main chain (Table 2). The number of benzoyloxy groups per chain was calculated from the signal intensity at 7.41−7.95 ppm to be 0.10_0. Thus the number of structure **IV** units per polymer molecule was calculated to be 0.01_4 (Table 2).

Structure **IV** might be formed through combination termination of the propagating radical with the benzoyloxy radical and chain-transfer of the propagating radical with BPO (Scheme 1). The chain-transfer constant to BPO at 60 °C is reported to be 0.02 in one reference[19] and negligibly small in another.[20] If we take the constant of 0.02, the number of structure **IV** units per chain formed by chain transfer to BPO could be estimated to be 0.018, even though the temperature of polymerization is different from that for sample 1. The estimated value is rather close to the observed value, suggesting that chain transfer to BPO is not negligible.

Moad *et al.* suggested from radical trapping experiments that 7% of primary radicals of BPO underwent the head addition to MMA at 60 °C (Scheme 2).[21] The head addition of the primary radical to MMA may be another source of structure **IV** which is located at the initiating chain-end instead of at the terminating end.

There is the possibility that sample 1 contains structure **V**, which may be formed through combination termination of the propagating radical with the phenyl radical and the head addition of phenyl radical to MMA. However, signals due to structure **V** could not be identified.

As mentioned above, sample 1 may contain both structures **II** and **III**. To assign phenyl signals at 6.95−7.25 ppm, PMMAs (samples **2**, **3**, and **4** in Table 1) having phenyl and benzyl end groups were prepared by anionic polymerizations. Samples **2** and **3**, which were syndiotactic and isotactic respectively, were prepared with C_6H_5MgBr and thus contain end groups of struc-

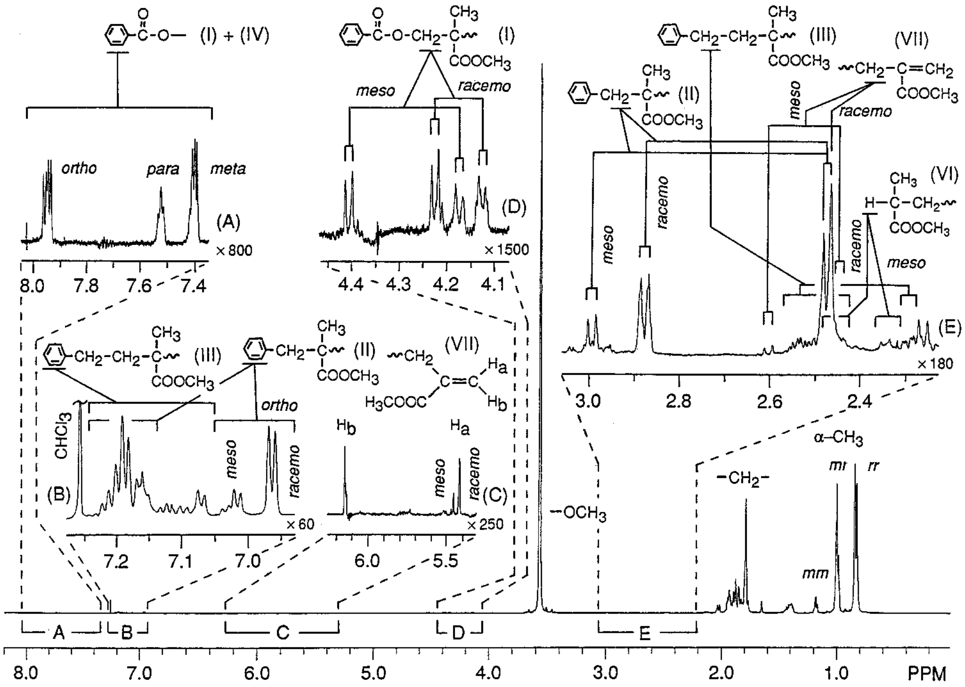


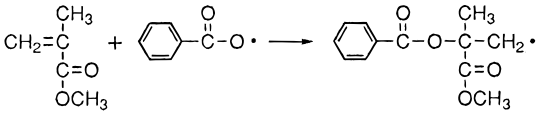
Figure 1. 750 MHz ^{1}H NMR spectrum of PMMA prepared with BPO in toluene at 100 °C (sample 1).

Table 2. Numbers of End Groups per Chain in Sample 1[a]

end group	no. of end groups per chain
I	0.08$_6$
II	0.86$_1$[b]
III	0.29$_5$[b]
(**I** + **II** + **III**)	1.24$_2$
IV	0.01$_4$
VI	0.40$_4$
VII	0.19$_3$
total	1.85$_3$

[a] Calculated from intensities of each signal and the methoxy proton signal and the molecular weight of sample **1**. [b] Determined from the intensity of the corresponding phenyl proton signals and the ratio of structures **II** to **III** (74/26).

Scheme 2



ture **II** but not structure **III**. On the other hand, sample **4** was prepared with $C_6H_5CH_2Li$ and has end groups of structure **III**. Figure 2 shows aromatic proton and benzylic methylene proton regions of samples **1**, **2**, **3**, and **4**. In the aromatic proton region, samples **2** and **3** show characteristic signals at 6.95–7.05 ppm while sample **4** shows signals at 7.05–7.15 ppm, where samples **2** and **3** do not. Sample **1** exhibits signals at both regions and thus contains end groups of both structures **II** and **III**. In spectra B and C, the signals at 6.95–7.05 ppm are assignable to two *ortho* protons in structure **II** based on their splitting pattern (doublets) and the relative peak intensities. In spectrum A, therefore, the signal intensity at 6.95–7.05 ppm corresponds to two protons of structure **II** and that of the region 7.05–7.24 ppm to the sum of three protons of structure **II** and all five protons of structure **III**. From the relative peak intensities of these two regions, the fractions of structures **II** and **III** were found to be 75 and 25%, respectively.

In addition, it is very clear that *ortho* protons and benzylic methylene protons of structure **II** show splittings due to tacticity of the first diad at the chain end (Figure 2B,C). Smaller signals of the *ortho* protons assignable to the meso diad apparently show splittings due to higher order tacticity.

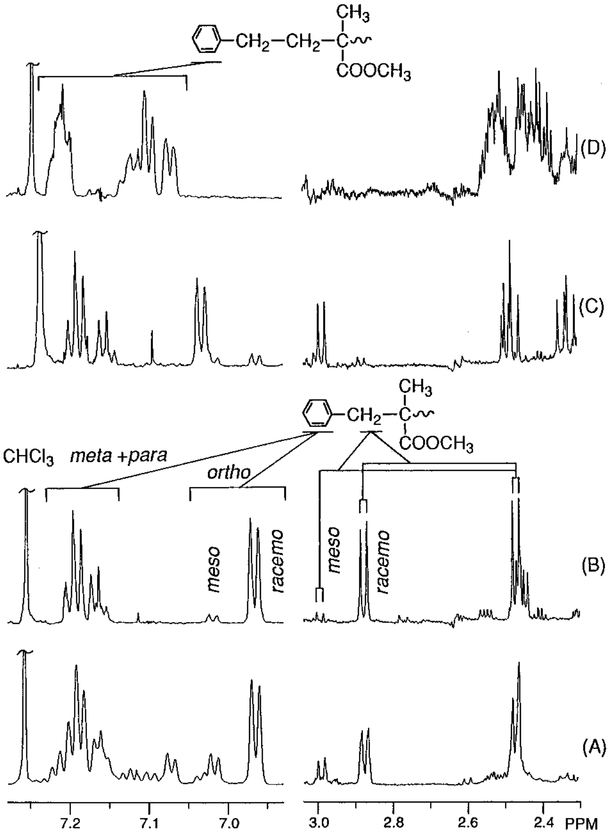


Figure 2. 750 MHz ^{1}H NMR spectra of PMMA prepared with BPO in toluene at 100 °C (sample 1) (A), that with C_6H_5MgBr in THF at −78 °C (sample 2) (B), that with C_6H_5MgBr in toluene at 40 °C (sample 3) (C), and that with $C_6H_5CH_2Li$ in toluene at −78 °C (sample 4) (D).

Methylene and Methine Regions. It is known that the termination of propagating radicals in the polymerization of MMA occurs predominantly through dis-

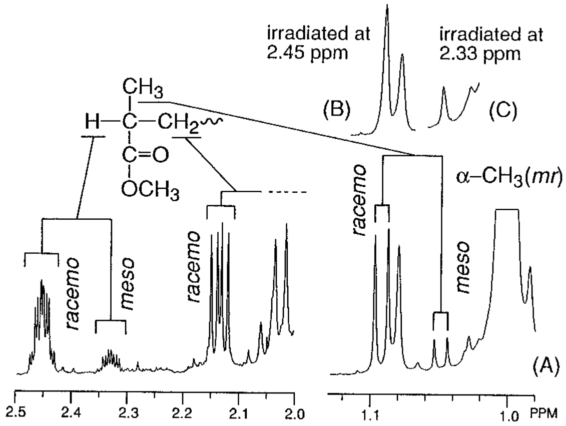
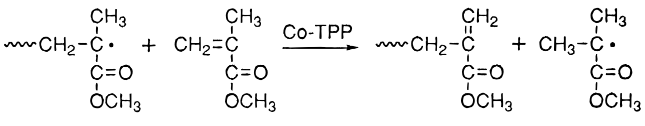


Figure 3. 750 MHz ^1H NMR spectrum (A) and 500 MHz ^1H NMR spin-decoupled spectra (B, C) of PMMA prepared with t-$C_4H_9Li/(C_2H_5)_3Al$ (1/3 mol/mol) in toluene at −78 °C (sample 5).

Scheme 3



$$\sim\!CH_2-\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}\cdot + CH_2=\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}} \xrightarrow{\text{Co-TPP}} \sim\!CH_2-\underset{\underset{OCH_3}{C=O}}{\overset{CH_2}{\overset{\|}{C}}} + CH_3-\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}\cdot$$

(VII)

proportionation,[13] which should give two types of chain-end structures: saturated (structure **VI**) and unsaturated (structure **VII**) terminals. Signals of the vinylidene group at the chain end (structure **VII**) are observed at 5.42 and 6.15 ppm as reported previously[13] (Figure 1C). The signal at 5.42 ppm splits into two peaks due to the tacticity of the terminal diad. The relative intensities indicate the ratio racemo/meso = 74/26.

To facilitate the assignment of the terminal methine proton signal (structure **VI**), a syndiotactic PMMA was prepared with t-$C_4H_9Li/(C_2H_5)_3Al$ (1/3 mol/mol) in toluene at −78 °C (sample **5**) and was subjected to ^1H NMR measurement. The methine proton shows two multiplets at 2.33 and 2.45 ppm as shown in Figure 3A. The splitting into two multiplets is due to the tacticity of the terminal diad, indicating the racemo/meso ratio to be 82/18. Signals due to α-methyl and methylene protons in the terminal monomeric unit were assigned as indicated in Figure 3A. The assignments were made by spin-decoupling measurement of the methine protons as shown in Figure 3B,C. The α-methyl proton signal split into two doublets, again due to the diad tacticity. The diad tacticity obtained from the α-methyl signal (83/17) agreed well with that from the methine signal. The singlet at 1.075 ppm could not be assigned yet. The double doublet of the methylene proton signal at 2.13 ppm was assigned to one of the methylene protons in the racemo diad. Signals of another racemo methylene proton and meso methylene protons may be hidden by the strong signals of the main-chain methylene protons.

The methine proton region of ^1H NMR spectrum of sample **1** is shown in Figure 1E. The methine proton signal of the meso diad appears at 2.31−2.36 ppm but that of the racemo diad overlaps the signals of the methylene protons of structures **II**, **III**, and **VII**. The peak assignments of the latter signals were made in the following way. The assignment of signals due to structure **VII** was made by using the polymer with terminal vinylidene groups (sample **6**) prepared by catalytic chain-transfer polymerization[22,23] initiated with AIBN in bulk in the presence of CoTPP at 60 °C (Scheme 3).[24]

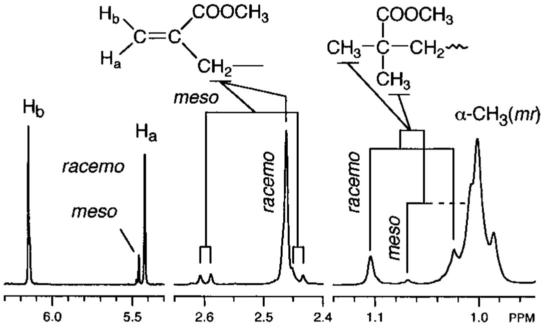


Figure 4. 750 MHz ^1H NMR spectrum of PMMA prepared with AIBN in the presence of CoTPP in bulk at 60 °C (sample 6).

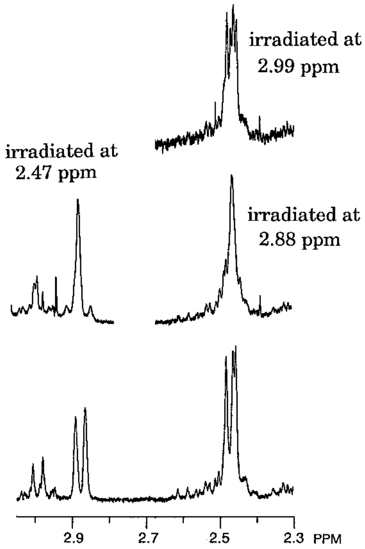
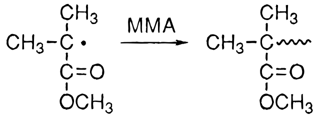


Figure 5. 500 MHz ^1H NMR spectrum of PMMA prepared with BPO in toluene at 100 °C (sample 1).

Scheme 4



$$CH_3-\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}\cdot \xrightarrow{\text{MMA}} CH_3-\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}\!\sim$$

(IX)

Figure 4 displays the partial spectrum of the polymer, showing signals for the unsaturated end. The olefinic region of the spectrum clearly shows the vinylidene proton signals at 5.42 and 6.14 ppm as described above. The allylic methylene proton signals are observed at 2.43−2.62 ppm with the expected intensity, consisting of a singlet peak at 2.47 ppm due to the racemo diad and an AB-type quartet due to the meso diad. The singlet signal had already been assigned for PMMA with an unsaturated end obtained by radical polymerization in the presence of (α-bromomethyl)acrylates.[25] In the spectrum of sample **1** the singlet signal overlaps with methylene proton signals due to structure **II** as described later. In a 500 MHz ^1H NMR spectrum, however, these signals are observed separately (Figure 5), indicating that a stronger magnetic field is not always the best method to separate the signal.

The monomer radicals formed through the chain-transfer reaction (Scheme 3) initiate the polymerization again to form structure **IX** at the chain end (Scheme 4). One of the two methyl groups of structure **IX** showed the signals at 1.07 and 1.10 ppm (due to the existence of the adjacent asymmetric carbon atom). The splitting

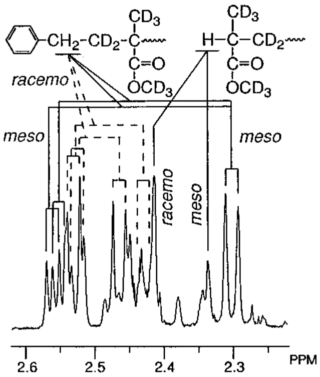


Figure 6. 750 MHz ^{1}H NMR spectrum of poly(MMA-d_8) prepared with $C_6H_5CH_2Li$ in toluene at −78 °C (sample 7).

is due to the chain end tacticity. Other methyl proton signals are hidden under the strong $\alpha-CH_3$ (*mr*) signal.

Methylene proton signals of structure II which consist of two AB quartets were assigned by using the anionically prepared PMMAs (samples **2** and **3**). The two upfield doublets overlap with each other at 2.47 ppm (Figure 2). The downfield doublets at 2.88 and 2.99 ppm turned into singlets when the signal at 2.47 ppm was irradiated. Conversely, the doublet at 2.47 ppm became a singlet when irradiated at 2.88 or 2.99 ppm (Figure 5). The nonequivalency of these methylene protons arises from the existence of the neighboring asymmetric carbon atom. The methylene protons show two AB quartets because of the diad tacticity at the initiating chain end. The intensity of the doublet at 2.88 ppm is stronger than that at 2.99 ppm in the spectrum of the syndiotactic PMMA prepared with C_6H_5MgBr in THF at −78 °C (sample 2) and *vice versa* in the spectrum of the isotactic PMMA prepared in toluene (sample 3) (Figure 2), which indicates the doublet at 2.88 ppm is due to the racemo diad and that at 2.99 ppm is due to the meso diad. The racemo/meso ratio was determined to be 74/26 from the intensities of these two doublets, which is consistent with the value obtained from the *ortho* proton signal of the phenyl group (71/29).

Finally, signals arising from the methylene group adjacent to the phenyl ring in structure **III** were assigned. To clarify the chemical shifts of those signals, poly(MMA-d_8) was prepared with $C_6H_5CH_2Li$ in toluene and its spectrum was measured (Figure 6). The spectrum shows four sets of AB quartets due to the methylene protons at 2.31 and 2.42−2.57 ppm, which were assigned by spin-decoupling experiments, and the terminal methine proton signals at 2.34 and 2.42 ppm. These signals are sensitive to the diad tacticities at the chain ends. Moreover, methylene proton signals due to structure **III** seem to show splittings due to higher order tacticity.

Consequently, the terminal methine proton signal of the racemo diad of sample **1** overlaps the methylene signal of structures **II** and **III** and cannot be observed clearly (Figure 1E). However, the intensity of the terminal methine signal could be calculated from that of the signals at 2.28−2.62 ppm and that of the overlapping groups (structures **II**, **III**, and **VII**) as described later.

The major termination reaction in radical polymerization of MMA is the disproportionation reaction, but the combination reaction also occurs to some extent. The latter gives a head-to-head linkage (structure **VIII**) in the polymer formed. It is reported that the head-to-head linkage is the least stable bond in radically prepared PMMA, being the starting point of thermal degradation occurring around 160 °C under nitrogen.[26] To detect the characteristic signal of the head-to-head linkage, the ^{1}H NMR spectra of the radically prepared PMMA (sample **1**) were measured before and after heating at 200 °C under vacuum for 20 min and compared with each other. However, the spectra did not show appreciable change due to the loss of the head-to-head linkage after heat treatment. Thus the signals due to the head-to-head linkage could not be assigned by ^{1}H NMR spectroscopy. To obtain the information on the head-to-head linkage, ^{13}C NMR analysis of sample **1** is now under way.

Number of End Groups per Chain and Tacticity at Chain End. All the characteristic ^{1}H NMR signals of the end groups of the radically prepared PMMA (sample **1**) were assigned as depicted in Figure 1 and numbers of the end groups per chain were determined from the intensities relative to the methoxy proton signal and the M_n. The results are shown in Table 2. The polymer molecules with terminal methine protons form through termination by disproportionation and chain transfer to toluene. Thus the number of the terminal methine proton should correspond to the sum total of those of structures **III** and **VII**, if all the benzyl radicals formed through the chain-transfer reaction initiate the polymerization of MMA. The obtained value of 0.48_8 ($=0.29_5 + 0.19_3$) roughly agrees with the value of 0.40_4 calculated by subtracting the intensity of overlapping methylene signals due to structures **II**, **III**, and **VII** from that of all the signals in the methine proton region (2.28−2.62 ppm).

The ratio of the number of structures **I** to **II** per chain was 9/91. Bevington *et al.* reported relative numbers of benzoyloxy and phenyl radical fragments per chain for PMMAs prepared at 60 °C by using ^{14}C-labeled BPO; the ratio of benzoyloxy to phenyl fragments decreases with decreasing monomer concentration.[27] The relative number of structures **I** and **II** at the same monomer concentration as that for the preparation of sample **1**, $[M]_0 = 0.90$ mol·L^{-1}, could be estimated to be 26/74. Hatada *et al.* reported that the relative number of benzoyloxy and phenyl groups per chain was 18/82 by ^{1}H NMR end-group analysis of poly(MMA-d_8) prepared with BPO in benzene at 60 °C.[13] The ratio of structures **I** and **II** (9/91) for sample **1** prepared at 100 °C is apparently lower than those reported for PMMAs prepared at 60 °C. The results indicate that the higher the polymerization temperature, the more decomposition to phenyl radical takes place before benzoyloxy radical adds MMA to initiate the polymerization.

From the number of structure **III**, the chain transfer constant to toluene, C_S, can be estimated by the following equation:

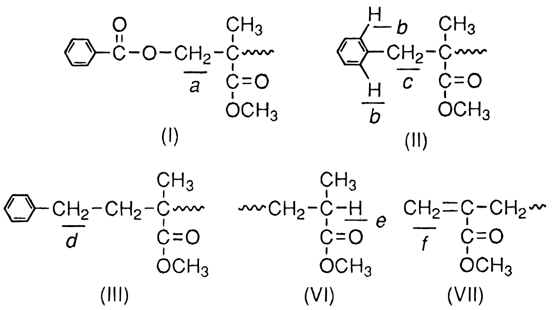
$$C_S = \frac{\text{number of toluene fragment/polymer chain}}{\text{DP of the sample } \mathbf{1}} \times \frac{[M]}{[S]} \quad (1)$$

[M] and [S] are the molar concentrations of MMA and toluene, respectively. The estimated value was 1.8×10^{-4}. The averaged C_S values from several reported values[28] for the polymerization of MMA at 20, 60, and 80 °C are 0.04×10^{-4}, 0.27×10^{-4}, and 0.51×10^{-4}, respectively. From the plots of these values against the temperature, the chain transfer constant at 100 °C was evaluated to be 1.5×10^{-4}, which roughly agrees with the C_S value estimated from eq 1.

Table 3. Diad Tacticities of End Groups of Sample 1

end group (proton in Scheme 5)	racemo diad
I (*a*)	0.59
II (*b*)	0.71
II (*c*)	0.74
III (*d*)	
VI (*e*)	0.71
VII (*f*)	0.74
[in-chain]	0.75

Scheme 5



The total number of structures **I**, **II**, and **III** (1.24_2) indicates that the fraction of polymer molecules having head-to-head linkages is estimated to be 0.24_2. The estimated value does not include the portion of the polymer which contains the head-to-head linkage and structure **IV** formed through the head addition of benzoyloxy radical to MMA. If all of structure **IV** arises through the head addition of benzoyloxy radical to MMA, the fraction of head-to-head structures per chain is estimated to be 0.25_6 ($=0.24_2 + 0.01_4$).

The sum total of the end groups in sample **1** amounts to 1.85_3, which is close to 2.0. The discrepancy between 2.0 and 1.85_3 is probably due to the existence of unidentified end groups.

As already mentioned, most of signals due to the terminal groups, except for structure **III**, are sensitive to the tacticity of the diad at the chain end. Chain-end tacticity of structure **III** could not be determined because of overlapping with other signals. The chain-end tacticities obtained from these signals are shown in Table 3. The racemo diad of structure **II** was higher than that of structure **I** and slightly lower than the in-chain tacticity ($r = 0.75$). The results indicate that the stereospecificity in radical polymerization depends on the bulkiness or steric factor of the radicals.

The chain-end tacticity of structure **VII** was similar to the in-chain tacticity. This is reasonable because the abstraction of a hydrogen atom from the chain-end methyl group does not alter the tacticity of the neighboring diad. The diad tacticity of the chain-end structure **VI** is fixed after the hydrogen abstraction occurs through disproportionation. The fact that the diad tacticity is syndiotactic means that the hydrogen abstraction is not completely nonstereospecific but is predominantly syndiotactic, similar to the propagation.

References and Notes

(1) Solomon, D. H. *J. Macromol. Sci.-Chem.* **1982**, *A17*, 337.
(2) Bevington, J. C.; Ebdon, J. R.; Huckerby, T. N. *Eur. Polym. J.* **1985**, *21*, 685.
(3) Axelson, D. E.; Russell, K. E. *Prog. Polym. Sci.* **1985**, *11*, 221.
(4) Bevington, J. C.; Ebdon, J. R.; Huckerby, T. N.; Hutton, N. W. E. *Polymer* **1982**, *23*, 163.
(5) Bevington, J. C.; Huckerby, T. N.; Hutton, N. W. E. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2655.
(6) Ayrey, G.; Jumangat, K.; Bevington, J. C.; Huckerby, T. N. *Polym. Commun.* **1983**, *24*, 275.
(7) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1984**, *17*, 1094.
(8) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 1188.
(9) Bevington, J. C.; Huckerby, T. N. *J. Macromol. Sci.-Chem.* **1983**, *A20*, 753.
(10) Bevington, J. C.; Huckerby, T. N.; Hutton, N. W. E. *Eur. Polym. J.* **1984**, *20*, 525.
(11) Bevington, J. C.; Huckerby, T. N.; Hutton, N. W. E. *Eur. Polym. J.* **1982**, *18*, 963.
(12) Bevington, J. C.; Huckerby, T. N.; Vickerstaff, N. *Makromol. Chem. Rapid. Commun.* **1983**, *4*, 349.
(13) Hatada, K.; Kitayama, T.; Masuda, E. *Polym. J.* **1986**, *18*, 395.
(14) Hatada, K.; Kitayama, T.; Yuki, H. *Makromol. Chem. Rapid Commun.* **1980**, *1*, 51.
(15) Hatada, K.; Kitayama, T.; Masuda, E. *Polym. J.* **1985**, *17*, 985.
(16) Bevington, J. C. *Fortschr. Hochpolym. Forsch.* **1960**, *2*, 1.
(17) Bovey, F. A.; Tiers, G. V. D. *J. Polymer Sci.* **1960**, *44*, 173.
(18) Cao, J.; Okamoto, Y.; Honda, S.; Hatada, K. *Chem. J. Chin. Univ.* **1989**, *10*, 1246.
(19) Henrici-Olive, G.; Olive, S. *Fortschr. Hochpolym. Forsch.* **1961**, *2*, 496.
(20) Baysal, B.; Tobolsky, A. V. *J. Polym. Sci.* **1952**, *8*, 529.
(21) Moad, G.; Rizzardo, E.; Solomon, D. H. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 533.
(22) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365.
(23) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243.
(24) Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 879.
(25) Yamada, B.; Kobatake, S.; Otsu, T. *Polym. J.* **1992**, *24*, 281.
(26) Kashiwagi, T.; Inaba, A.; Brown, J. E.; Hatada, K.; Kitayama, T.; Masuda, E. *Macromolecules* **1986**, *19*, 2160.
(27) Bevington, J. C. *Trans. Faraday Soc.* **1957**, *53*, 997.
(28) Brandrup, J.; Immergut, E. H. *Polymer handbook*, 3rd ed.; John Wiley & Sons, Inc.: New York, 1989.

MA970672I