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End-group analysis of polymacromonomer formed in the radical polymerization of styrene-type PMMA macromonomers by using ^{2}H NMR spectroscopy

Tatsuki Kitayama, Shigeki Kishiro, Eiji Masuda, and Koichi Hatada*

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

Summary

Isotactic (*iso*-) and syndiotactic (*syn*-) poly(methyl methacrylate) (PMMA) macromonomers having styrene group as a polymerizable function were polymerized with perdeuterated 2,2'-azobisisobutyronitrile in toluene at 60°C. The resultant polymacromonomers were analyzed by ^{2}H NMR spectroscopy to determine the number of initiator fragment in a polymacromonomer chain (N) and initiator efficiency (f). The N values were less than unity (0.50~0.72), indicating the chain transfer reaction to occur in the radical polymerization of macromonomer. The f values were 0.18~0.28 and much smaller than that for styrene polymerization (0.5~0.7). *Iso*-macromonomer gave larger N and f values than *syn*- one, suggesting that the tacticity of macromonomer affects the reaction pathway probably owing to the difference in chain mobility between *iso*- and *syn*-PMMA chains.

Introduction

Macromonomer has become an important source for the preparation of graft copolymer having well-defined structure. Thus, many papers have been published on the syntheses of macromonomers and their polymerization. However, little is known about the feature or mechanism of the radical polymerization of macromonomers. Tsukahara and his coworkers observed the ESR signals of the propagating radicals of a methacrylate-type polystyrene macromonomer, and determined the propagation rate constant (k_p) and termination rate constant (k_t) at 60°C from rate of polymerization (R_p), the steady state concentration of the propagating radical ([M·]), and the degree of polymerization (DP)[1]. In the calculation they assumed that termination reaction proceeded dominantly through disproportionation reaction, and the DP was the same as the kinetic chain length (ν).

Recently we prepared highly isotactic (*iso*-) and syndiotactic (*syn*-) poly(methyl methacrylate) (PMMA) macromonomers having styrene end-group and studied their radical polymerizations[2]. The k_t values for these polymerizations could be directly determined from the decay of ESR signals for the propagating radicals[3]. Then, the k_p value can be estimated from the observed R_p and k_t by using the following equation, if the initiator efficiency, f, is determined experimentally:

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*To whom offprint requests should be sent

$$k_p=R_p/(f\cdot k_d/k_t)^{0.5}[I]^{0.5}[M], \qquad (1)$$

where k_d, [I], and [M] represent the rate constant for decomposition of initiator, initiator concentration, and monomer concentration.

In this work, *iso*- and *syn*-PMMA macromonomers were polymerized with perdeuterated 2,2'-azobisisobutyronitrile (AIBN-d_{12}), and the amounts of initiator fragment incorporated into polymacromonomer chains were determined by ^{2}H NMR spectroscopy to estimate f values in the polymerizations of the macromonomers. The number of initiator fragment per molecule (N) thus obtained was found to be less than unity, indicating that chain transfer reaction is very important in the deactivation process of propagating radicals in the polymerization of macromonomer.

Experimental

Highly *iso*- and *syn*-PMMA macromonomers were prepared through the end-capping reaction of the corresponding living PMMAs with p-vinylbenzyl bromide according to the procedure described in the previous communication[2]. The characteristics of the macromonomer used in this work are summarized in Table 1. AIBN-d_{12} was prepared from acetone-d_6 by the method of Overberger et al.[4] and purified by recrystallization from ethanol. Toluene, purified in a usual manner, was mixed with a small amount of butyllithium and then vacuum-distilled. Polymerization was carried out in a glass ampoule under nitrogen. The reaction mixture was poured into a large amount of hexane to precipitate the reaction mixture. The unchanged macromonomer was removed from the mixture by repeated reprecipitation from toluene solution to methanol.

^{1}H NMR measurement was carried out on a JEOL JNM-GX500 NMR spectrometer. ^{2}H NMR spectra were measured on a JEOL JNM-GSX400 NMR spectrometer at 62 MHz in nitrobenzene containing 5 wt% of nitrobenzene-d_5. The ^{2}H NMR chemical shift was referred to the highest-field peak of nitrobenzene-d_5 (δ=7.35 ppm). The gel permeation chromatography (GPC) experiments were performed on a JASCO FLC-A10 chromatograph equipped with Shodex A-80M and KF802.5 GPC columns using tetrahydrofuran as an eluent at room temperature. The GPC-LALLS (low-angle laser light scattering) experiment for polymacromonomer was performed on a Tosoh HLC-801A chromatograph equipped with a detector, LS-8, which was operated with two Tosoh GMH_{xl} columns using chloroform as an eluent at 39°C.

Table 1. Characteristics of highly isotactic and syndiotactic PMMA macromonomers

Macromonomer	Tacticity (%)			Mn^a	$\frac{Mw^b}{Mn}$	$F^{a,c}$
	mm	mr	rr			
iso	95	4	1	2900	1.12	0.96
syn(1)	1	10	89	2720	1.18	0.97
syn(2)	0	9	91	5380	1.15	0.96

[a] Determined by ^{1}H NMR. [b] Determined by GPC.
[c] Number of CH_2=CH- group per chain.

Results and Discussion

The *iso*- and *syn*-PMMA macromonomers were polymerized with AIBN-d_{12} in toluene at 60°C for 24 hr. The results are shown in Table 2. Poly(PMMA macromonomer)s were recovered from the reaction mixtures by reprecipitation from toluene solution to methanol. The ^{2}H NMR spectrum of the poly(*iso*-PMMA macromonomer) is illustrated in Figure 1. The broad resonance centered at 1.05 ppm was assignable to $(CD_3)_2C(CN)$- group attached to styrene unit[5]. The content of deuterium in the polymacromonomer was determined to be 1.55×10^{-4} g·^{2}H/g·polymer from the relative intensity of this signal to the signal of a known amount of nitrobenzene-d_5 added to the solution as an intensity standard. Reliability of the end-group analysis by ^{2}H NMR was established by using *iso*-PMMA prepared with a partially deuterated initiator, $(CD_3)_2C(CH_3)MgBr$[6]. Then, the N

Table 2. End-group analysis of poly(PMMA macromonomer) prepared with AIBN-d_{12} in toluene at 60°C for 24 hr

Macromonomer (mmol)		AIBN-d_{12} (mmol)	Toluene (ml)	Conv.[a] (%)	Mn[b]	Mw/Mn[b]	N[c]	f[d]
iso	0.350	0.0174	6.1	42	55700	1.70	0.72	0.28
syn(1)	0.765	0.0383	13.6	49	69600	1.18	0.65	0.22
syn(2)	0.0541	0.00270	0.84	46	124000	1.31	0.50	0.18

[a] Determined by GPC. [b] Determined by GPC-LALLS.
[c] Number of initiator fragment per polymacromonomer determined by ^{2}H NMR spectroscopy.
[d] Initiator efficiency.

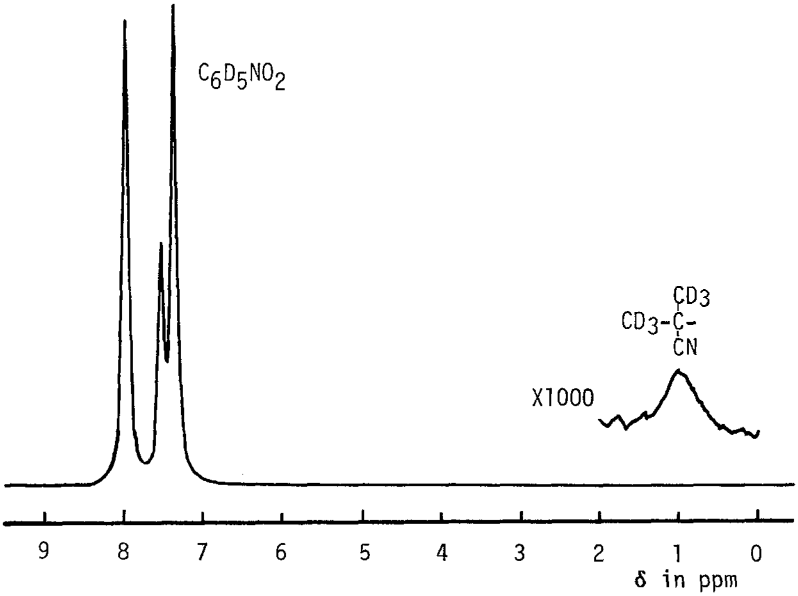

Figure 1. 62MHz ^{2}H NMR spectrum measured in nitrobenzene containing 5 wt% of nitrobenzene-d_5 at 80°C of poly(*iso*-PMMA macromonomer) prepared with AIBN-d_{12} in toluene at 60°C for 24 hr. Macromonomer; Mn=2900, mm:mr:rr=95:4:1, $[M]_0$=0.05 mol/l, $[M]_0/[I]_0$=20 mol/mol.

value was calculated to be 0.72 from the content of the initiator fragment and number average molecular weight, Mn, (55700) of the polymacromonomer. The N's for other polymacromonomers were determined similarly and are shown in Table 2. All the N values were less than unity, suggesting the chain transfer reaction to occur in the radical polymerization of the macromonomer. Many PMMA chains surrounding the propagating radical of the polymacromonomer may restrict normal termination reaction so strongly, as evidenced by extremely smaller k_t values for the polymerization of macromonomer than that of styrene[3,7], that the possibility of chain transfer reaction increases. The investigation is now being made on the type of chain transfer reaction.

The value of N depends on the tacticity of the macromonomer, and poly(*iso*-PMMA macromonomer) had a larger N than poly(*syn*-PMMA macromonomer)s. The radical life time, τ, and the [M·] are given as follows;

$$\tau = \nu/k_p[M] = (1/k_t)^{0.5}(1/2(f\cdot k_d)^{0.5}[I]^{0.5}), \qquad (2)$$

$$[M\cdot] = (1/k_t)^{0.5}(f\cdot k_d[I])^{0.5}. \qquad (3)$$

The k_t for *syn*-macromonomer is much smaller than that for *iso*- one[7], due to lower segmental mobility of *syn*-PMMA chain than *iso*-PMMA chain[8]. The smaller k_t for *syn*-macromonomer polymerization makes the τ and the [M·] larger than those for *iso*-macromonomer polymerization. Therefore, the contribution of chain transfer reaction to the deactivation process of propagating radicals is more important for *syn*-PMMA macromonomer than for *iso*-macromonomer. The tacticity dependence of N mentioned above should reflect this situation.

The N value was also dependent of Mn of the macromonomer. The N value for the *syn*-macromonomer with Mn of 5380 was lower than that for the macromonomer with Mn of 2720. The density of the PMMA segment around the propagating radical becomes higher as the Mn of the macromonomer increases so that the ordinary termination reaction is more restricted in the polymerization of macromonomer with higher Mn as evidenced from the smaller k_t values[3], and thus the transfer reaction may occur more frequently for the higher molecular macromonomer than for the lower molecular one.

The total amount of initiator fragment incorporated into the poly(*iso*-PMMA macromonomer) was calculated as follows;

(Number of initiator fragment per polymacromonomer)
x (Mole of polymacromonomer formed)
=N x (Yield in gram) / (Mn of polymacromonomer)
$=5.50 \times 10^{-3}$ mmol. (4)

Assuming the value of k_d for AIBN-d_{12} to be the same as k_d for AIBN (9.54×10^{-6} s^{-1} at 60°C[9]), the amount of $(CD_3)_2C(CN)\cdot$ radical formed from 0.0174 mmol of AIBN-d_{12} at 60°C during 24 hr was calculated to be 0.0195 mmol. Then, the f value for the *iso*-PMMA macromonomer could be calculated as follows;

$$f = [\text{Incorporated initiator fragment}] / [\text{Generated radical}]$$
$$= 5.50 \times 10^{-3}\ \text{mmol} / 0.0195\ \text{mmol}$$
$$= 0.28. \qquad (5)$$

The values of f for the other macromonomers were calculated similarly, and the results are also shown in Table II. These values were much lower than that for styrene polymerization (0.5~0.7)[10], indicating that a large amount of the primary radicals fail to initiate the polymerization of macromonomer as compared with the case of the polymerization of low molecular weight monomers because the polymerization mixture of macromonomer is highly viscous even in the initial stage of polymerization. The value of f for *iso*-macromonomer was slightly larger than that for *syn*- one, which may reflect the higher mobility of *iso*-PMMA chain.

The f value determined in the present work could be used to estimate k_p values using eq (1). The detailed discussion for the radical polymerization of the PMMA macromonomer based on the kinetic parameters such as k_p and k_t will be published separately[11].

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