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Tacticity dependence of reactivity of stereoregular poly(methyl methacrylate) macromonomers having a methacryloyl function in radical polymerization

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Summary

Radical polymerizations of highly isotactic (*it*-) and highly syndiotactic (*st*-) poly(methyl methacrylate) (PMMA) macromonomers having a methacryloyl function were studied in benzene-d_6 at 60ºC with 2,2'-azobisisobutyronitrile (AIBN). Rate of polymerization (R_p) was determined from the consumption of the macromonomer by means of ^{1}H NMR spectroscopy. The R_p of the *it*-PMMA macromonomer was larger than that of the *st*-PMMA macromonomer. Concentrations of propagating radicals, [M･], were estimated for the polymerization with di-*t*-butyl peroxide in benzene under irradiation of light at 30ºC. The value of [M･] for the polymerization of the *st*-PMMA macromonomer was larger than that for the polymerization of the *it*-PMMA macromonomer. The results indicated that rate constant of propagation (k_p) for the *it*-PMMA macromonomer was larger than that for the *st*-PMMA macromonomer.

Introduction

Since Milkovich reported the idea of macromonomer [1,2], many papers have been published on the syntheses and uses of macromonomers [3–20]. Radical polymerization of macromonomer is one of the most extensively studied areas. Even though a macromonomer is considered to be vinyl monomer having a large substituent, the R_p in radical polymerization is comparable to those of the corresponding low-molecular-weight monomers [3–6].

We have studied tacticity dependence of reactivity of stereoregular PMMA macromonomers having a styrene-type function (Eq. 1) in radical polymerization [11–13]. The *it*-PMMA macromonomer showed larger reactivity than the *st*-PMMA macromonomer in homopolymerization as well as in copolymerization with styrene, which was ascribed to the higher segmental mobility of *it*-PMMA than that of *st*-PMMA [21]. The similar phenomenon was observed in Ziegler polymerization [13]. We also reported that the stereoregularity of PMMA macromonomer having a

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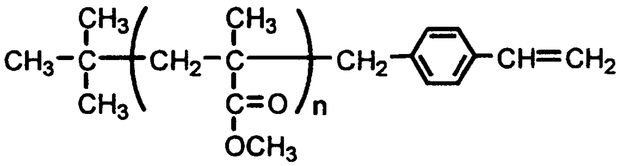
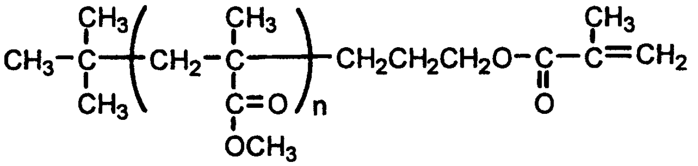
methacryloyl function (Eq. 2) affected its reactivity in anionic homopolymerization [14] and anionic copolymerization with methyl methacrylate [15,16], that is, the *it*-PMMA macromonomer showed larger reactivity than the *st*-PMMA macromonomer. All the results suggest that *it*-PMMA macromonomers have larger reactivity than the corresponding *st*-PMMA macromonomers irrespective of polymerizable function and polymerization mechanism.


(1)


(2)

$$CH_3-C(CH_3)_2-\left(CH_2-C(CH_3)(C(=O)OCH_3)\right)_n-CH_2CH_2CH_2O-C(=O)-C(CH_3)=CH_2$$

In this work, radical polymerizations of *it*- and *st*-PMMA macromonomers having a methacryloyl function (Eq. 2) were studied in order to confirm the tacticity dependence of PMMA macromonomers in their reactivity.

Experimental

Materials

Stereoregular PMMA macromonomers having a methacryloyl function (Eq. 2) were prepared according to the procedures described in the previous papers [15,16]. The characteristics of the *it*- and *st*-PMMA macromonomers used are shown in Table 1.

Benzene was purified in the usual manner and dried over sodium. Benzene-d_6 was obtained commercially and used as received. AIBN was purified by recrystallization from ethanol. Di-*t*-butyl peroxide and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Tempol) were obtained commercially and used without further purification.

Polymerization

The macromonomer was dissolved in benzene or benzene-d_6 containing an initiator. The solution was placed in an NMR or ESR sample tube (5mm o.d.) under nitrogen and degassed by freeze-thawing method and the tube was sealed off under nitrogen. The polymerization was carried out in the NMR probe or ESR cavity, the temperatures in which were set at the polymerization temperatures. Some of the polymerizations were carried out in the ESR cavity under irradiation of light from a 500W ultra-high-pressure mercury lamp (USHIO USH500D).

Measurements

^1H NMR spectra were recorded on a JNM GX500 NMR spectrometer (JEOL) at 500 MHz. ESR spectra were recorded on a JES-RE2X ESR spectrometer (JEOL) with 100 KHz modulators (frequency 9.40 GHz).

Table 1. Characteristics and rate of propagation (R_p) [a] of stereoregular PMMA macromonomers having a methacryloyl function (Eq. 2)

Tacticity of PMMA Macromonomer	Triad Tacticity (%)[b]			$\bar{M}_n$[b] (DP[c])		Functionality b	$R_p \times 10^7$
	mm	*mr*	*rr*				mol/l·s
Isotactic	96	3	1	3010	(28.2)	0.84	5.11
Syndiotactic	1	8	91	3050	(28.7)	0.83	3.75

[a] For the polymerization with AIBN in benzene-d_6 at 60℃; $[M]_0$=0.05 mol/l, $[M]_0/[I]_0$=5.
[b] Determined by ^{1}H NMR. [c] Degree of polymerization.

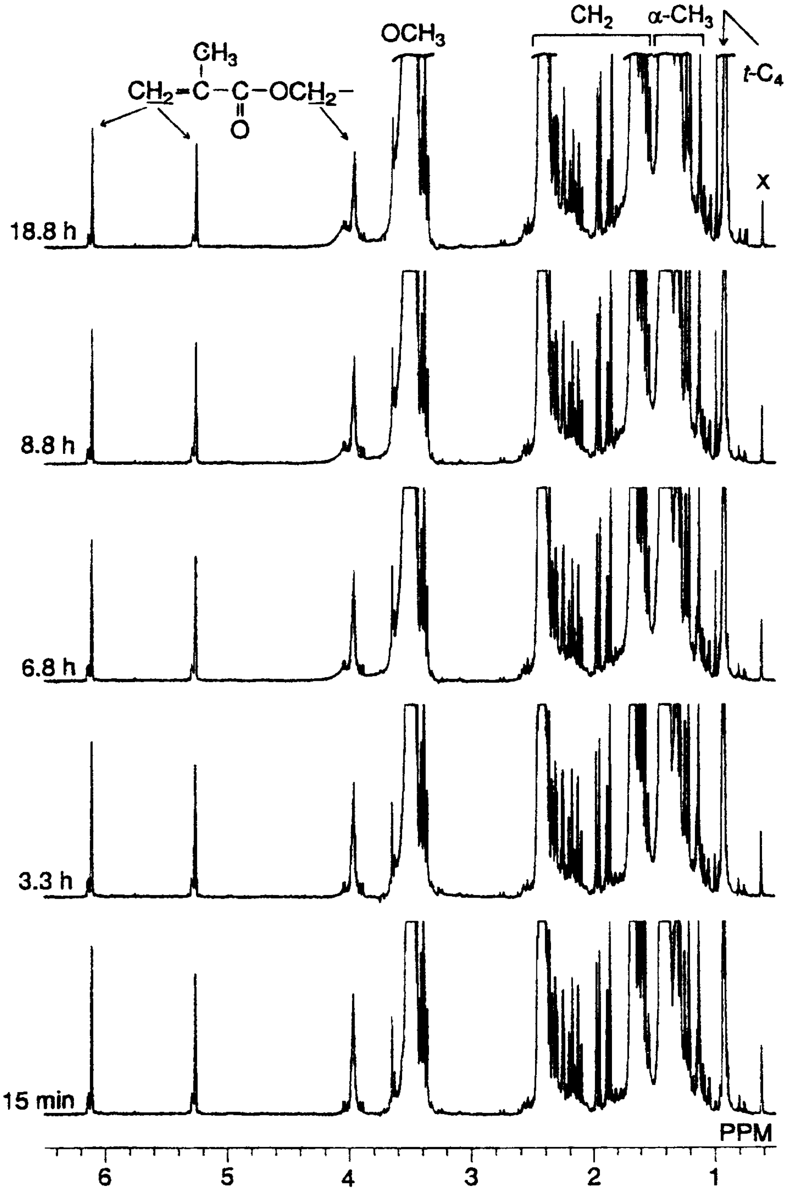


Figure 1. 500 MHz ^{1}H NMR spectra of polymerization mixture of *it*-PMMA macromonomer with AIBN in benzene-d_6 at 60°C. $[M]_0$=0.05 mol/l, $[M]_0/[I]_0$=5. X: Signal due to an impurity

Polymerizations of the *it*- and *st*-PMMA macromonomers were carried out with AIBN in benzene-d_6 at 60°C in NMR sample tubes and followed by ^{1}H NMR spectroscopy for 24h. Figure 1 shows the spectral change for the polymerization mixture of the *it*-PMMA macromonomer, as an example. As the polymerization proceeded the peak intensity of the vinylidene proton signals at 5.3 and 6.1 ppm decreased and the signals of methoxy (3.5 ppm) and *t*-C_4H_9- groups (0.94 ppm) became broader. The concentrations of the macromonomer [M] in the reaction mixture at different polymerization times were determined by measuring the intensities of vinylidene proton signals and that of *t*-C_4H_9- proton signal and are plotted against the time in Figure 2. The plots indicate clearly the larger reactivity of the *it*-PMMA macromonomer than the *st*-PMMA macromonomer. From the slopes of tangents to the curves at the time of zero, the R_p values for the polymerization of the *it*- and *st*-PMMA macromonomers were determined and are shown in Table 1. The R_p value for the polymerization of the *it*-PMMA macromonomer is 1.36 times larger than that for the polymerization of the *st*-PMMA macromonomer. This result is consistent with those of PMMA macromonomers having a styrene-type function (Eq. 1) [11–13].

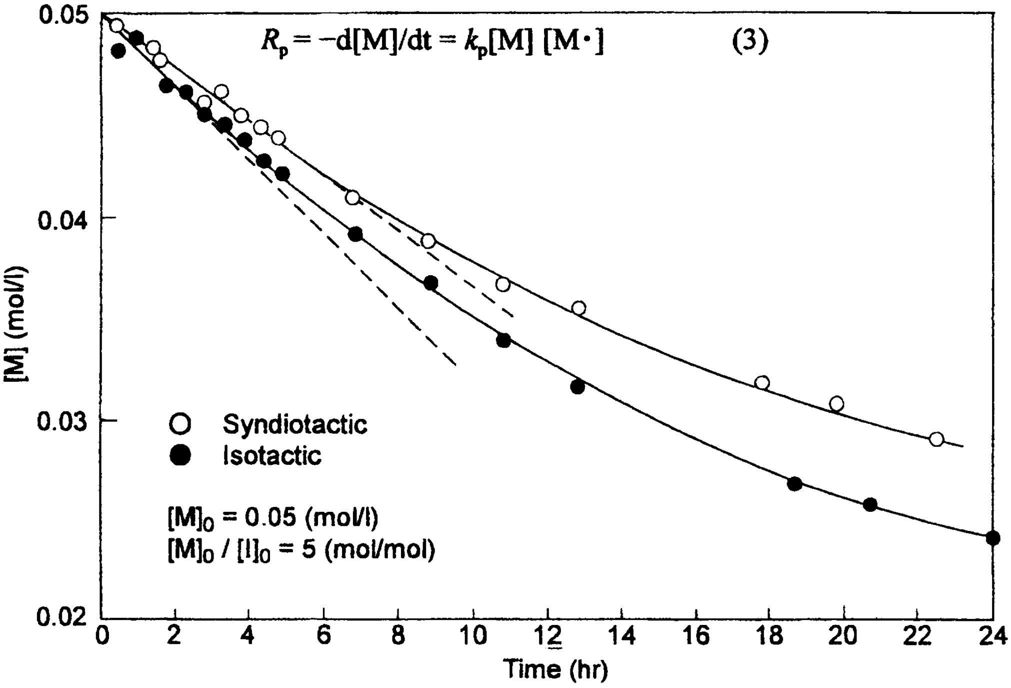


Figure 2. Effect of tacticity on the polymerization rate of PMMA macromonomer with AIBN in benzene-d_6 at 60°C.

R_p is expressed as Eq. 3 and k_p can be determined when concentration of propagating radicals [M•] is known.

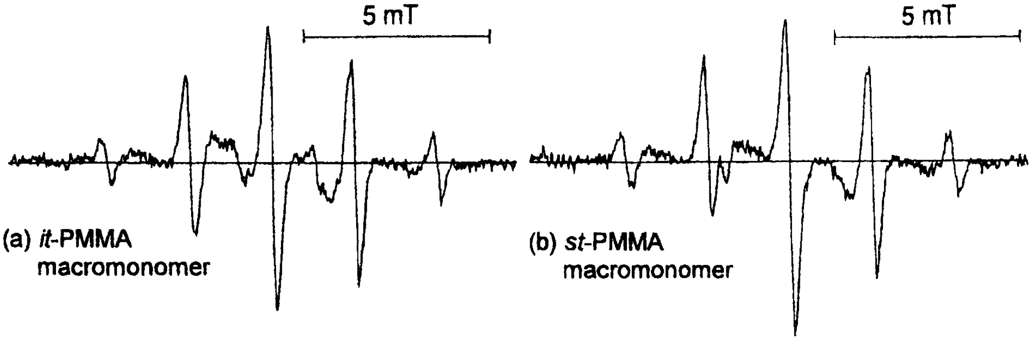
$$R_p = -d[M]/dt = k_p[M][M\cdot] \qquad (3)$$

The [M•] values could be obtained by ESR spectroscopy and the k_p values were determined for radical polymerization of polystyrene macromonomers with a methacryloyl function and with a styrene-type function [10], of poly(ethylene oxide) macromonomers with a styrene-type function [17], and of PMMA macromonomers having a styrene-type function [12,13].

Polymerizations of the *it*- and *st*-PMMA macromonomers having a methacryloyl function were carried out with AIBN in benzene-d_6 at 60°C in ESR sample tubes. The signal of the propagating radicals observed was too weak to determine accurately the [M •] value. However, comparison of the two ESR signals due to the propagating radicals of the *it*- and *st*-PMMA macromonomers clearly indicates that the [M•] value for the latter radicals is larger or at least no less than that for the former ones, that is, the k_p value for the *it*-PMMA macromonomer is larger than that for the *st*-PMMA macromonomer.

In order to obtain intense and clear ESR signals for the propagating radicals, photo-irradiated polymerizations of the *it*- and *st*-PMMA macromonomers were carried out at 30°C. Figure 3 illustrates the ESR spectra of the propagating radicals of the PMMA macromonomers. The spectra showed nine-line pattern which consists of five strong signals and four weak peaks between two neighboring strong signals. These are ascribable to propagating radicals of methacrylate monomers [22]. The [M•] value for the *st*-PMMA macromonomer was found to be 2.0×10^{-6} l/mol·s using Tempol of known amount (4.69×10^{-6} mol/l) in benzene solution of *st*-PMMA and 1.25 times larger than that for the *it*-PMMA macromonomer (1.6×10^{-6} l/mol·s). The fact that the [M•] value for the *st*-PMMA macromonomer is larger than that for the *it*-PMMA macromonomer is a support for the larger k_p value of the *it*-PMMA macromonomer in the polymerization at 60°C without irradiation as compared with that of the *st*-PMMA macromonomer.

An attempt to follow the decay of radical concentration after turning off the light was not successful due to very rapid decay and thus the accurate determination of rate constant of termination was difficult.



(a) *it*-PMMA macromonomer

(b) *st*-PMMA macromonomer

Figure 3. ESR spectra observed for the polymerizations of (a) *it*- and (b) *st*-PMMA macromonomers with di-*t*-butyl peroxide in benzene at 30°C under irradiation by ultra-high-pressure mercury lamp. (9.40 GHz, modulator frequency; 100KHz). $[\mathrm{M}]_0$=0.05 mol/l, $[\mathrm{M}]_0/[\mathrm{I}]_0$=10.

In conclusion, the R_p and k_p values for the polymerization of *it*-PMMA macromonomer having a methacryloyl function is larger than those for the polymerization of the corresponding *st*-PMMA macromonomer. The present results, together with the previous ones [11–16], confirm that the reactivity of *it*-PMMA macromonomer is larger than that of *st*-PMMA macromonomer irrespective of polymerizable function and polymerization mechanism.

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References

1. Milkovich R, Chiang MT (1974) US Patent 3786116
2. Milkovich R (1980) Polym Prepr, Polym Chem Div, Am Chem Soc 21:40
3. Yamashita Y (1981) J Appl Polym Sci: Appl Polym Symp 36:193
4. Rempp PF, Franta E (1984) Adv Polym Sci 58:1
5. Asami R, Takaki M (1985) Makromol Chem, Rapid Commun 12:163
6. Rempp P, Lutz P, Masson P, Franta E (1985) Makromol Chem, Suppl 13:471
7. Kennedy JP, Hiza M (1983) J Polym Sci, Polym Chem Ed 21:1033
8. Muehlbach K, Percec V (1987) J Polym Sci, Polym Chem Ed 25:2605
9. Tsukahara Y, Mizuno K, Segawa A, Yamashita Y (1989) Macromolecules 22:1546
10. Tsukahara Y, Tsutsumi K, Yamashita Y, Shimada S (1990) Macromolecules 23:5201
11. Hatada K, Kitayama T, Ute K, Masuda E, Shinozaki T, Yamamoto M (1989) Polym Bull 21:165
12. Masuda E, Kishiro S, Kitayama T, Hatada K (1991) Polym J 23:847
13. Hatada K, Kitayama T (1994) Stereoregular macromonomers with respect to main chain and/or side chain. In: Mishra MK (ed) Macromolecular Design: Concept and Practice (Macromonomers, Macroinitiators, Macroiniferters, Macroinimers, Macroiniters, and Macroinifers) Polymer Frontiers International, Inc. New York (pp 85-127)
14. Kitayama T, Nakagawa O, Hatada K (1996) Polym J 28:150
15. Kitayama T, Nakagawa O, Kishiro S, Nishiura T, Hatada K (1993) Polym J 25:707
16. Kitayama T, Nakagawa O, Hatada K (1995) Polym J 27:1180
17. Nomura E, Ito K, Kajiwara A, Kamachi M (1997) Macromolecules 30:2811
18. Lu J, Kamigaito M, Sawamoto M, Higashimura T, Deng YX (1997) J Polym Sci, Part A:Polym Chem 35:1423.
19. Hayashi M, Nakahama S, Hirao A (1999) Macromolecules 32:1325
20. Shimano Y, Sato K, Kobayashi S (1999) Polym J 31:219
21. Hatada K, Kitayama T, Okamoto Y, Ohta K, Umemura Y, Yuki H (1978) Makromol Chem 179:485.
22. Kamachi M (1987) Adv Polym Sci 82:207