ELSEVIER

Polymer 40 (1999) 729–734

polymer

The tacticity of the backbone chain of poly(macromonomer)s of ω-methacryloyloxyethyl polystyrene macromonomers prepared by radical chain polymerization

Yasuhisa Tsukahara*, Kenjiro Yai, Kyoji Kaeriyama

Department of Chemistry and Materials Technology, School of Engineering and Art, Kyoto Institute of Technology, Kyoto 606-8585, Japan

Received 17 October 1997; accepted 1 April 1998

Abstract

The effect of the polystyrene chain as a bulky long ester group of methacrylate monomer on the chain tacticity was investigated in the radical chain polymerization of ω-methacryloyloxyethyl polystyrene macromonomers of different molecular weights. The macromonomers and 3-phenylbutyl methacrylate (3PBMA), which corresponds to the unimer model of the macromonomer, were synthesized and polymerized with azobisisobutylonitrile in benzene at 60°C. The polymers obtained were converted to poly(methyl methacrylate)s by acid hydrolysis reaction followed by methyl esterification with diazomethane to estimate the chain tacticity of the original polymers by ^{1}H- and ^{13}C-n.m.r. It was found that the backbone chains of poly(macromonomer)s as well as the poly(3PBMA) chain had a syndiotactic triad in the range of 58–62%, but the chains still had a similar tactic structure comparable with those of poly(methacrylate)s having a short alkyl chain and the fractions of tactic triads obeyed the Bernoullian statistics. This fact indicates that the specific multibranched structure around the propagating radicals as well as the ester polymer chain of the macromonomer does not have much effect on the chain tacticity, although the molecular conformation of the central backbone chain of the formed poly(macromonomer)s is strongly affected by the polystyrene branch chains of high branch density, as described previously.

Keywords: Tacticity; Poly(macromonomer); Poly(3-phenylbutyl methacrylate)

1. Introduction

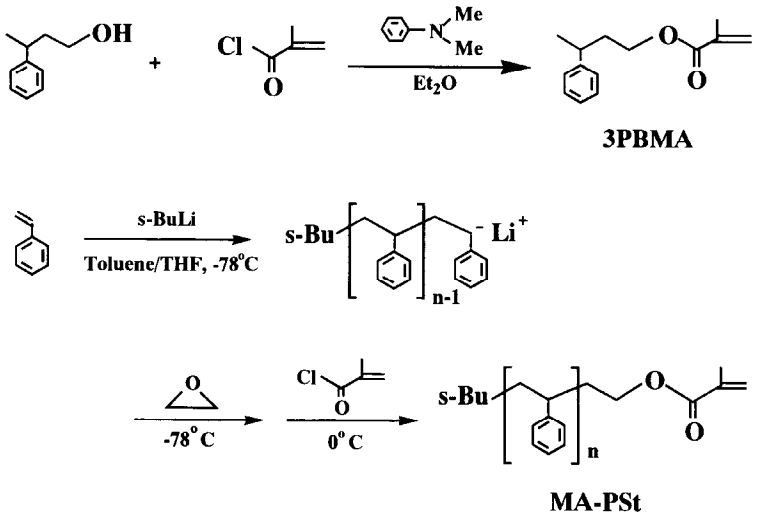
Polymerization behaviours of macromonomers have been reported by several researchers [1]. Ito et al. [2] reported on the radical polymerization of ω-vinylbenzylalkyl poly(oxyethylene) macromonomers in micelles, and Kobayashi et al. [3] recently reported the synthesis and polymerization of ω-vinylbenzyl amylose macromonomers. On the other hand, Kitayama et al. [4,5] reported stereospecific polymerizations of ω-methacryloyl stereoregular poly(methyl methacrylate) macromonomers by anionic polymerizations. We have been studying the radical polymerization behaviour of ω-methacryloyloxyethyl and ω-vinylbenzyl polystyrene macromonomers of narrow molecular weight distributions to investigate the influence of the presence of the polymer chain coupled to the polymerizable end group [1,6–10]. However, there have been no reports on the tactic structure of the backbone of poly(macromonomer)s prepared by radical chain polymerizations so far.

On the other hand, chain polymerizations of end-vinyl macromonomers produce multibranched polymers of well-defined structure, in which every repeating unit of the backbone chain of the polymerization products has one long branch at all times [6–8]. Thus, the branch density is extremely high. In addition, the branch length and the branch number of poly(macromonomer)s can be controlled by the molecular weight of the macromonomer and the polymerization conditions. Such multibranched polymers show very unique and interesting properties, which are very different from those of the corresponding linear polymers [11–18]. For better understanding of the molecular properties of poly(macromonomer)s, it is of great importance to know the chain tacticity of the central backbone, which can affect the molecular conformation reflecting the conformation of the central backbone chain.

In this context, we have investigated here the chain tacticity of the central backbone of the poly(macromonomer)s formed by the radical polymerizations of ω-methacryloyloxyethyl polystyrene macromonomers.

* Corresponding author.

0032-3861/98/$ - see front matter
PII S0032-3861(98)00281-X



Scheme 1. Synthesis of 3PBMA and MA-PSt macromonomers.

2. Experimental

2.1. Materials

ω-Methacryloyloxyethyl polystyrene macromonomers (MA-PSts) were synthesized by the living anionic polymerization technique in previous work [8,9,11]. The number-average molecular weights of MA-PSts are 800 and 2900, with the polydispersity index (M_w/M_n) being 1.11 and 1.07, respectively. 3-Phenylbutyl methacrylate (3PBMA), which corresponds to the unimer model of the macromonomer, was synthesized by a condensation reaction of 3-phenylbutyl alcohol with methacryloyl chloride. Isolation of 3PBMA was carried out using a silica gel column using hexane/ethyl acetate (9:1) mixed solvent. The productions of MA-PSts and 3PBMA were confirmed by ^{1}H-n.m.r. spectra using GE QE-300 (300 MHz) and Varian XL500 (500 MHz) instruments. Azobisisobutylonitrile (AIBN) was purified by recrystalization from a methanol solution.

2.2. Polymerizations

These macromonomers, as well as 3PBMA, were polymerized with AIBN in benzene at 60°C for 24 h. The reaction mixtures were placed in glass ampoules and degassed and sealed under vacuum. After the polymerization, the products were precipitated in a large amount of methanol to remove unreacted compounds, and then freeze-dried from benzene solutions. Methyl methacrylate (MMA) monomer was also polymerized under the same conditions for comparison.

2.3. Tacticity measurements

The polymers obtained were converted to poly(methyl methacrylate)s (PMMAs) by acidic hydrolysis reaction followed by methyl esterification with diazomethane. The acidic hydrolysis was carried out using conc. H_2SO_4 at room temperature (ca. 25°C) for 2 days. The reaction mixture was poured into water and then the water-insoluble fraction was solubilized into methanol to recover poly(methacrylic acid). Methyl esterification of the poly(methacrylic acids)s produced was carried out by adding a diethyl ether solution of diazomethane into each polymer/benzene mixture at room temperature. The addition of diazomethane solution was completed in ca. 60 min and then the mixture was stirred overnight. The hydrolysis products became soluble in benzene as the reaction with diazomethane proceeded. The PMMA was recovered by precipitation of a benzene-soluble fraction into methanol. After this, the PMMAs were purified by precipitation into methanol and freeze-dried with benzene. Tacticity of the PMMAs, which reflects the tacticity of the original polymers, was determined by the signal intensity of α-methyl protons in ^{1}H- and ^{13}C-n.m.r. spectra.

The hydrolysis of the ester groups by conc. H_2SO_4 was confirmed by the disappearance of the phenyl proton signals in the ^{1}H-n.m.r. spectra of the converted polymers. Hydrolysis using HCl (35%) was not successful in the case of the poly(macromonomer)s. When a large fraction of the reaction mixture after the hydrolysis was insoluble in methanol, the insoluble fraction was recovered and the hydrolysis reaction was repeated.

3. Results and discussion

MA-PSts and 3PBMA were synthesized according to Scheme 1. The ^{1}H-n.m.r. spectrum of MA-PSt800 is shown in Fig. 1. In this figure, clear peaks of the α-sec-butyl protons and ω-end vinyl protons are seen at around 0.6–0.7 and 5.4–5.9 ppm, respectively. The peak intensity

[1] As far as we know, there is no report on the synthesis of 3PBMA. The synthesis and polymerization of 4PBMA and tacticity of the obtained polymer have been reported [19].

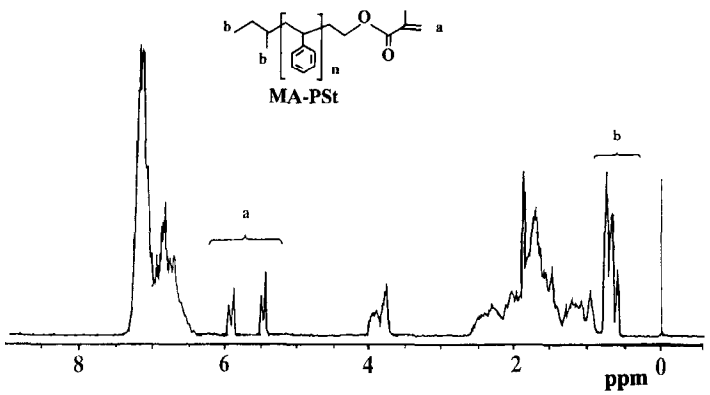


Fig. 1. ^{1}H-n.m.r. spectrum of MA-PSt800 macromonomer in $CDCl_3$.

ratio of the ω-end vinyl protons to the α-sec-butyl protons gives the end group functionality $f = 0.99$. Fig. 2 shows the ^{1}H-n.m.r. spectrum of 3PBMA, where the relative signal intensity of the peaks a–f indicates the formation of 3PBMA[1].

The polymerization conditions of MA-PSt macromonomers and 3PBMA and the molecular weights of the polymerization products are shown in Table 1. The data for MMA monomer are also included. Polymerization solutions were completely transparent, which shows that polymerizations were taking place under homogeneous reaction conditions. The degrees of polymerization (DPs) of all polymer samples obtained are greater than 100.

Fig. 3 shows the ^{1}H-n.m.r. spectrum of poly(MA-PSt2900) after conversion to PMMA. Determination of the chain tacticity of PMMA by n.m.r. spectroscopy has been well established [20,21]. Triad tacticity was determined by the corresponding signal intensity of α-methyl protons in the ^{1}H-n.m.r. spectrum. There are no phenyl proton signals at all. This indicates that the hydrolysis reaction was complete. Fig. 4 shows the ^{13}C-n.m.r. spectrum of PMMA converted from poly(MA-PSt2900), where the signals corresponding to rr, mr and mm triads are indicated in the figure. The relative signal intensity of the tactic triads in ^{13}C-n.m.r. spectra for all samples were almost the same as those in ^{1}H-n.m.r. spectra. These spectra indicate that the PMMAs, and thus the original poly(MA-PSts), as well as poly(3PBMA), have syndiotactic-rich atactic structures.

The fractions of rr, mr and mm triads estimated from the relative signal intensity of α-methyl proton peaks are summarized in Table 2. In this table, the values for PMMA are also included for comparison. It is seen that the values of rr triad fraction for all polymers in Table 2 are 58–62%, while the fractions of mm triad are 5–7%. The values for rr triad of poly(MA-PSts) are 62%, which is slightly larger than that of poly(3PBMA), but the difference is small. This indicates that the presence of the long bulky polystyrene chain does not have much effect on the chain tacticity. The fractions of tactic triads of poly(3PBMA) are also similar to those of PMMA, indicating that the 3-phenylbutyl ester group, which

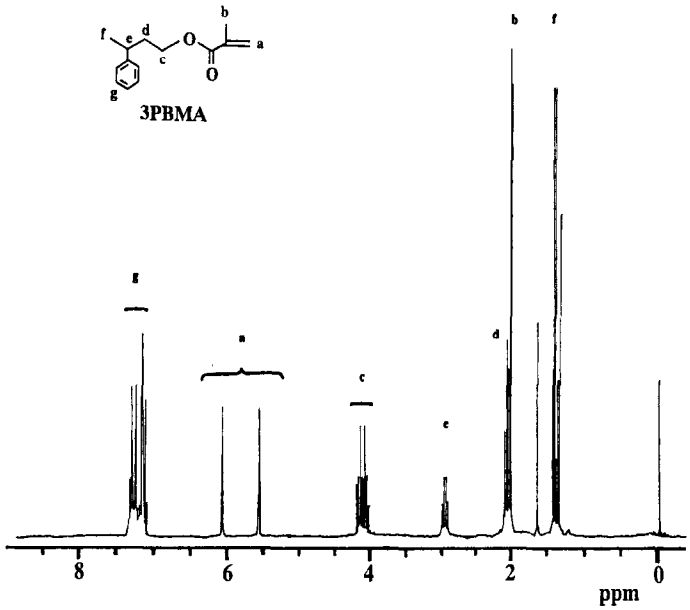


Fig. 2. ^{1}H-n.m.r. spectrum of 3PBMA in $CDCl_3$.

Table 1
Polymerization conditions and characterization of original polymers[a]

Code	[M]	[AIBN]	Time	Polymer			
	(mol l^{-1})	(mol l^{-1})	(h)	M_w [b] ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n [b]	DP
MMA	3.1	0.015	24	117	64.3	1.83	643
3PBMA	1.4	0.02	24	93.4	51.9	1.80	238
MA-PSt800	0.10	0.016	24	140	80.0	1.75	100
MA-PSt2900	0.12	0.016	24	1569	1164	1.35	401

[a]Polymerizations were carried out at 60°C
[b]Molecular weights of poly(macromonomer)s were determined by using g.p.c. equipped with a low angle laser light scattering detector (LALLS) and that of poly(3PBMA) was determined from g.p.c. with a calibration curve with polystyrene standards

corresponds to the root of the polymer chain in MA-PSt, does not affect the stereochemistry of polymerization.

Mays and co-workers [19] investigated the chain tacticity of poly(4-phenylbutyl methacrylate) prepared by radical polymerization with AIBN at 50°C. The polymer obtained was reported to have tactic triads of rr/mr/mm = 63:29:8, which is similar to the tacticity of the poly(3PBMA) obtained in this study, indicating that the difference in position of the phenyl ring has almost no influence.

It should be noted here that PMMAs obtained from the poly(macromonomer)s and the poly(3PBMA) were purified by precipitation in methanol, in which methanol-soluble oligomers might be removed and their stereostructures are unknown. However, the triad tacticity of poly(MA-PSt800), the DP of which is 100, is very similar to that of poly(MA-PSt2900), whose DP is 401. This indicates that the chain tacticity is not very dependent on the molecular weight and the soluble oligomer may not affect the above discussion, although further study is necessary to clarify this point.

The probabilities of an isotactic triad I, syndiotactic triad S and heterotactic triad H are given by:

$$I = P_m^2 = (1 - P_r)^2$$

$$S = (1 - P_m)^2 = P_r^2$$

$$H = 2P_m(1 - P_m) = 2(1 - P_r)P_r,$$

with the assumption that the chain tacticity obeys the Bernoulli trial process; here, P_m and P_r are the probabilities of generating a meso diad and a racemo diad, respectively, and $P_m + P_r = 1$. The calculated values using the above relation are shown in Table 2, in which the P_r value was determined from the rr triad fraction instead of P_m for better accuracy. It is seen from the table that the observed values of I and H are consistent with the calculated values. These results indicate that the backbone chain tacticity of poly(MA-PSts) as well as poly(3PBMA) obeys the Bernouli trial process, as does that of PMMA.

Judging from these results, we can conclude that the multibranched structure around the propagating radical

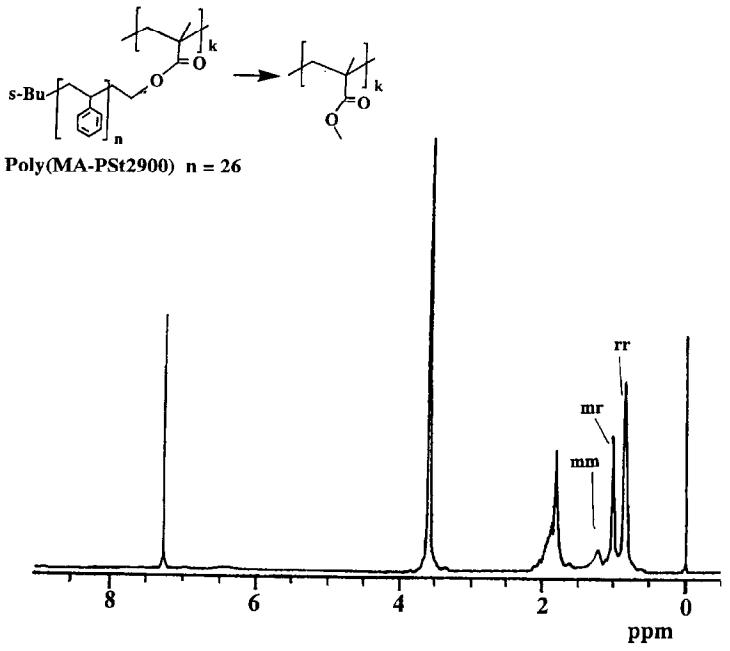


Fig. 3. ^{1}H-n.m.r. spectrum of PMMA converted from poly(MA-PSt2900) in $CDCl_3$.

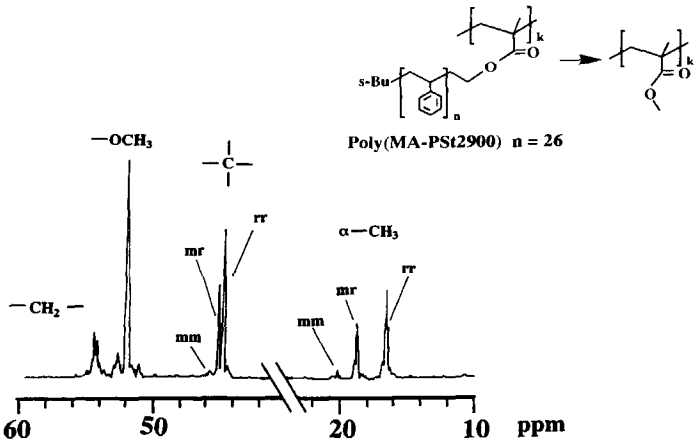


Fig. 4. ^{13}C-n.m.r. spectrum of PMMA converted from poly(MA-PSt2900) in $CDCl_3$.

Table 2
Tacticity of PMMA derived from the original polymer

Original polymer	Observed[a] rr/rm/mm (%)	Bernoulli[b] rr/rm/mm (%)	P_r/P_m (%)
PMMA	57:37:6	57:37:6	76:24
Poly(3PBMA)	58:35:7	58:36:6	76:24
Poly(MA-PSt800)	62:33:5	62:33:5	79:21
Poly(MA-PSt2900)	62:33:5	62:33:5	79:21

[a]Determined by the relative peak intensity of α-methyl protons in the ^{1}H-n.m.r. spectrum of PMMA derived from the original polymer
[b]Calculated by P_r determined from the peak intensity of the α-methyl proton of the syndiotactic triad under the assumption of Bernoulli trial process

site and the presence of the polystyrene chain coupled to the polymerizable end group have no, or only slight, influence on the chain tacticity of the central backbone of poly(macromonomer)s under the polymerization conditions used in this paper, although the rate constants for propagation and termination in the radical polymerization of MA-PSt macromonomers are very different from the values of MMA under similar polymerization conditions [6,9,10].

Recently, Nakano et al. [22] reported that free radical polymerizations of triphenylmethyl methacrylate (TrMA) gave highly isotactic polymers under appropriate conditions. The isotactic triad fraction exceeded 98% due to the bulky triphenylmethyl ester group, which could induce the helical structure of the propagating radical. The difference between the polymerizations of TrMA and MA-PSts might be ascribed to the difference in the chemical structure in the vicinity of the ester linkage. The polystyrene chain of MA-PSt is bulky; however, the polystyrene chain is connected to the carbonyloxy group via two methylene units. Therefore, the bulkiness of the polystyrene chain cannot directly influence the steric crowdedness around the ester linkage to affect the backbone chain tacticity.

This fact is interesting because the polystyrene side chains can strongly affect the conformation of the central backbone of poly(macromonomer)s, where the effect is so strong that the backbone chain is highly extended and poly(macromonomer)s behave as rod-like molecules in solution [12,15–17,23]. It is worthwhile noting here that the highly extended backbone chain cannot take a fully *trans* zig-zag conformation, but might be extended with a certain fraction of *trans-gauche* conformation according to the fraction of each tactic triad obtained in this work [18].

In conclusion, the stereochemistry of the radical polymerization of methacrylate monomers appeared to be sensitive to the local structure near the ester linkage, i.e. the number and shape of the substituent on the ester linkage, but not to the linear polystyrene branch chain. Further study on macromonomers possessing modified end groups is in progress and will appear elsewhere.

Acknowledgements

We wish to thank the Ministry of Education, Science, Sports and Culture for a support through Grant-in-Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (277/08246233) and on Basic Research Area (C/09650997).

References

[1] Yamashita Y. Chemistry and industry of macromonomers. Location: Huthig & Wepf, 1993.
[2] Ito K, Tanaka K, Tanaka H, Imai G, Kawaguchi S, Itsuno S. Macromolecules 1991;24:2348.
[3] Kobayashi K, Kamiya S, Enomoto N. Macromolecules 1996;29:8670.
[4] Kitayama T, Nakagawa O, Kishiro S, Nishimura T, Hatada K. Polym J 1993;25:707.

[5] Kitayama T, Nakagawa O, Hatada K. Polym J 1996;28:150.
[6] Tsukahara Y. In: Mishra MK, editor. Macromolecular design: concept and practice. Location: Polymer Frontier International, 1994:161.
[7] Tsukahara Y. In: Salamome JC, editor. The polymeric materials encyclopedia. Boca Raton, FL: CRC, 1996:3918.
[8] Tsukahara Y, Mizuno K, Segawa A, Yanashita Y. Macromolecules 1989;22:1564.
[9] Tsukahara Y, Tsutsumi K, Yamashita Y, Shimada S. Macromolecules 1989;22:2869; 1990;23:5201.
[10] Tsutsumi K, Okamoto Y, Tsukahara Y. Polymer 1994;35:2205.
[11] Tsukahara Y, Tsutsumi K, Okamoto Y. Macromol Chem, Rapid Commun 1992;13:409.
[12] Wintermantel M, Schmidt M, Tsukahara Y, Kajiwara K, Kohjiya S. Macromol Chem, Rapid Commun 1994;15:279.
[13] Tsukahara Y, Kohjiya S, Tsutsumi K, Okamoto Y. Macromolecules 1994;27:1662.
[14] Tsukahara Y, Inoue J, Ohta Y, Kohjiya S. Polymer 1994;35:5785.
[15] Tsukahra Y, Ohta Y, Senoo K. Polym Prepr Jpn 1995;43:121; Polymer 1995;36:3413.
[16] Wintermantel M, Schmidt M, Kajiwara K. Angew Chem 1995;107:1606.
[17] Wintermantel M, Schmidt M, Kajiwara K, Tsukahara Y. Macromolecules 1996;29:978.
[18] Unayama S, Nakajima K, Ikehara T, Nishi T, Tsukahara Y. Jpn J Appl Phys 1996;35:2280.
[19] Chen Y, Mays JW, Hadjichristidis N. J Polym Sci, Polym Phys Ed 1994;32:715.
[20] Bovey FA. Polymer conformation and configuration. New York: Academic Press, 1969.
[21] Chujo R, Hatada K, Kitamaru R, Kitayama T, Sato H, Tanaka Y. Polym J 1987;19:413.
[22] Nakano T, Matsuda A, Okamoto Y. Polym J 1991;28:556.
[23] Halperin A, Tirrell M, Lodge TP. Adv Polym Sci 1991;100:31.