Polymer Journal, Vol. 31, No. 11-2, pp 1001—1004 (1999)

Uniform Regular and Irregular Three-Arm Star Poly(methyl methacrylate)s

Tatsuki KITAYAMA ,† Takafumi NISHIURA, Mayumi TSUBOTA, Hironobu NAKANISHI, and Koichi HATADA‡

Graduate School of Engineering Science, Osaka University
Machikaneyama 1-3, Toyonaka, Osaka 560-8531, Japan
‡ Department of Applied Physics and Chemistry, Fukui University of Technology
3-6-1 Gakuen, Fukui-shi, Fukui 910-8505, Japan

(Received June 11, 1999)

ABSTRACT: Isotactic (*it*-) and syndiotactic (*st*-) uniform poly(methyl methacrylate)s (PMMAs) with hydroxyl group at the chain end (PMMA-OH's) were prepared by fractionating the corresponding non-uniform PMMAs by means of supercritical fluid chromatography (SFC). The uniform PMMA-OH's with degrees of polymerization (*DP*s) of 16, 26 and 33 were each allowed to react with a trifunctional coupling agent, 1,3,5-benzenetricarbonyl trichloride, to obtain three-arm star polymers with uniform PMMA arms. Intrinsic viscosities of a series of the star PMMAs were measured in tetrahydrofuran at 40℃ by using a differential viscometric detector connected with a size exclusion chromatograph. Tacticity dependence was observed not only in the viscosity but also in shrinking factor g_η. A three-arm star PMMA with one arm with *DP*=16 and two arms with *DP*=31 (irregular star PMMA) was also prepared in a similar manner with the aid of SFC fractionation. The viscosity of the irregular star PMMA was found larger than that of the regular star PMMA with the same total number of monomer units.

KEY WORDS Uniform PMMA / Stereoregular Star Polymer / Irregular Star PMMA / Branching Effect / Solution Viscosity /

Control of polymerization reactions is the first step toward the precise control of polymer structures, leading to the control of their properties and functions. Polymer chemists have witnessed rapid advances of synthetic utility of living polymerizations that afford polymers with well-defined structures such as predictable molecular weight, narrow molecular weight distribution (MWD), and end functionality.

In 1980's we found living polymerizations of methacrylate that afford stereoregular polymers; isotactic- (*it*-) specific polymerization with *t*-BuMgBr,[1] syndiotactic- (*st*-) specific one with *t*-BuLi/R_3Al.[2] Recently, a combination of *t*-BuLi with a bulky aluminum phenoxide, bis(2,6-di-*t*-butylphenoxy)methylaluminum [MeAl(ODBP)$_2$] was found to give heterotactic (*ht*-) polymers with narrow MWD.[3] Stereospecificity of the polymerization with *t*-BuLi/MeAl(ODBP)$_2$ strongly depends on the ester group of the monomer, and, in particular, allyl methacrylate gives highly heterotactic polymers (*mr*=96% at −95℃) with narrow MWD.[4] In sharp contrast, polymerization of trimethylsilyl methacrylate (TMSMA) under the same conditions gives highly *st*-polymers (*rr* =98% at −95℃), which are easily converted to *st*-poly(methacrylic acid) [poly(MAD)].[5] Copolymerization of TMSMA with ethyl methacrylate (EMA) was found to proceed in a monomer-selective manner to give a stereoregular block copolymer that comprises *ht*-poly(EMA) and *st*-poly(MAD) blocks.[6] Thus the polymerizations with *t*-BuLi/MeAl(ODBP)$_2$ provide us with multiple control of polymer structures, including molecular weight and its distribution, stereoregularity in the main chain, end group, and, in some cases, monomer sequence.

Though living polymerizations provide us with narrow MWD, advanced mass spectrometry such as matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) mass spectrometry[7] as well as chromatography such as supercritical fluid chromatography (SFC)[8-13] has revealed unavoidable distribution of molecular weight of the "well-defined polymers". We have shown that SFC is a powerful means for isolating synthetic uniform polymers from narrow MWD polymers obtained by living polymerizations.[9-13] Uniform poly(methyl methacrylate)s (PMMAs) thus obtained have been used to study dependence of melting temperature and glass transition temperature[14] on the degree of polymerization (*DP*) as well as stereocomplex formation in solution.[9]

Based on the stereospecific living polymerizations mentioned above, *it*- and *st*-PMMAs having hydroxyl group at the chain end (PMMA-OH's) were prepared from the corresponding living PMMA anions.[15,16] By applying SFC fractionation, uniform *it*- and *st*-PMMA-OH's could be isolated, which were used to prepare uniform polymers with more elaborated structures. The uniform *it*- and *st*-PMMA-OH's were coupled with sebacoyl dichloride to form uniform stereoblock PMMA.[17,18] Uniform PMMA macromonomer with methacryloyl group was also obtained by SFC separation, which has been used to obtain uniform branched polymers.[19] Uniformity in molecular weight of these uniform polymers allows us to discuss the dependence of properties of the polymers on structural features other than molecular weight, such as tacticity, chemical structures and branching without ambiguity due to the distribution of molecular weight.

We have reported preliminary results on the preparation of uniform star PMMA having three *st*-PMMA arms, demonstrating the clear evidence of branching effect on solution viscosity.[20] In this article, three sets of uniform three-arm star polymers with *it*- and *st*-PMMA arms were prepared by the coupling reaction of the corresponding uniform PMMA-OH's with a trifunctional core-forming compound, and their solution viscosities were measured in tetrahydrofuran (THF) by using a differential viscometer (DV) connected with size exclusion chromatograph (SEC). The results clearly indicated the effect of tacticity on the solution viscosity of the branched PMMAs.

The SFC fractionation provides us with the end-functional uniform PMMAs as a series of homologues. Thus two kinds of uniform *st*-PMMA-OH's of different *DP*s (*DP*=16 and 31) were used for the coupling reaction to intentionally introduce irregularity in the arm length of the star PMMA molecules. Though the reaction product contains four kinds of star polymers with PMMA arms of different *DP*s ([16,16,16], [16,16,31], [16,31,31] and [31,31,31]), SFC fractionation was proved effective to separate a mixture into each component. The star polymer with arm *DP*s of [16,31,31] was used to examine the effect of irregularity of arm length on the viscosity by comparing with that of a regular three-arm star PMMA with arm *DP* of 26 ([26,26,26]), the total number of monomeric unit (78) being identical with each other.

---

† To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Stereoregular PMMA-OH's of different number-average *DP*s were prepared according to the previous report[15,16]; *it*-PMMA-OH; *DP*=30.4, $\bar{M}_w/\bar{M}_n$=1.18, *mm/mr/rr*=97/2/1, end functionality 0.98, *st*-PMMA-OH's; (1) *DP*=14.2, $\bar{M}_w/\bar{M}_n$=1.12, *mm/mr/rr*=1/9/90, end functionality 0.91, (2) *DP*=32.7, $\bar{M}_w/\bar{M}_n$ =1.04, *mm/mr/rr*=1/11/88, end functionality 1.00. A trifunctional coupling agent, 1,3,5-benzenetricarbonyl trichloride (1,3,5-BTC) (Aldrich), was used without further purification as THF solutions.

SFC fractionation

The instrumental set-up of SFC using a JASCO SUPER-200 chromatogram is described elsewhere.[9] Fractionation of PMMA-OH's was performed on a silica gel column (Develsil 100-5, Nomura Chemical Co., Ltd., column size;10 mm *i.d.* ×250 mm, particle size 5 μm) with liquefied CO_2 as mobile phase (flow rate 8 – 9 cm^3 min^{-1}) and methanol as entrainer (flow rate 1.5 – 2.5 cm^3 min^{-1}) at the fluid pressure of 200 kg cm^{-2} and column temperature of 80 – 100℃ with the cooling rate of 1.0 ℃ min^{-1}. These conditions were optimized for each PMMA-OH sample of different *DP*. The amount of sample charged was *ca.* 25 mg each.

Measurements

SEC measurements were performed on a JASCO 880-PU chromatograph equipped with Shodex SEC columns KF803 (8.0 mm *i.d.* × 300 mm, maximum porosity = 7 × 10^4) and KF802.5 (8.0 mm *i.d.* × 300 mm, maximum porosity = 2 × 10^4) using THF as eluent. The flow rate was 1.0 cm^3 min^{-1} and the column temperature was 40℃. SEC curves were recorded using a JASCO UV detector operated at a wavelength of 234nm.

Mass spectra were recorded on a JEOL JMS-DX303HF spectrometer operated at the field-desorption (FD) mode. ^{1}H NMR spectra were measured on a JEOL JNM GX-500 spectrometer in nitrobenzene-d_5 at 110℃.

SEC-differential viscometry (SEC-DV) analysis was made by using a VISCOTEK model 110 differential viscometer and an RI detector installed in a TOSOH LS8000 light scattering detector.

Intrinsic viscosity, [η], of a standard PMMA sample ($\bar{M}_n$=22700, $\bar{M}_w/\bar{M}_n$=1.26, *mm*:*mr*:*rr*=0:11:89) was determined in THF at 40.0℃ by an Ubbelohde viscometer to be 0.161(dlg^{-1}). The ratio between the responses of differential viscometer and an RI detector (S_{DV}/S_{RI}) is in proportion to [η].

$$[\eta] = K \times S_{DV}/S_{RI} \qquad (1)$$

The proportional constant K was determined by the [η] and S_{DV}/S_{RI} values of the standard PMMA.

Synthesis of uniform three-arm star polymer

Uniform PMMA-OH were allowed to react with 1,3,5-BTC in THF at 25℃ in the presence of pyridine for 6 days. The amounts of the reagents are listed in Table I. The reaction was carried out in a 5 mm (*i.d.*) glass tube under dried nitrogen. After an excess amount of methanol was added to the reaction mixture, the reaction products were recovered by evaporating volatiles and then dried *in vacuo*. Uniform three-arm star polymer was separated from the products by means of SEC or SFC.

RESULTS AND DISCUSSION

Preparation of uniform regular three-arm star PMMAs

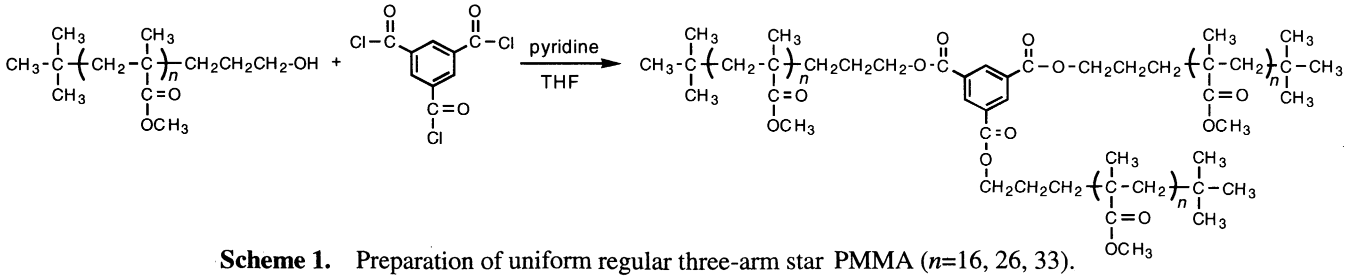
The coupling reactions between uniform PMMA-OH's (*DP* = 16, 26, 33) and 1,3,5-BTC were carried out in THF at 25°C in the presence of pyridine to obtain the uniform three-arm star PMMA (Scheme 1, Table I). After 6 days of reaction, the reaction mixture was further treated with a large excess of methanol to convert the unreacted acid chloride functions to methyl esters since the acidic function to be derived from the acid chloride might hinder the chromatographic separation of the products. Figure 1 shows SEC chromatograms of the reaction mixture of *st*-PMMA-OH (*DP*=26) and 1,3,5-BTC, and that of a reaction mixture from a non-uniform *st*-PMMA-OH (*DP*=32.7, $\bar{M}_w/\bar{M}_n$=1.04) and 1,3,5-BTC. The latter exhibits severe overlap of the peaks of three-arm and two-arm products (Figure 1a), implyin that SEC fractionation of the non-uniform, three-arm star polymer should be difficult. On the other hand, the chromatogram for the uniform polymer (Figure 1b) mainly consists of well-separated three peaks due to three-arm star polymer, two-arm product and one-arm product, with increasing elution volume. The peak due to the one-arm product has a shoulder at larger elution-volume side due to the starting *st*-PMMA-OH remained unreacted. The three-arm star polymer was separated successfully from the mixture by SEC as seen in Figure 1c.

Structural analyses of the uniform star PMMAs thus obtained were carried out using 500 MHz ^{1}H NMR measured in nitrobenzene-d_5 at 110℃. In ^{1}H NMR spectrum of the three-arm star PMMA, a triplet signal was observed at 4.33 ppm due to

Table I. Preparation conditions of uniform three-arm star PMMA

Polymer [*DP*]	mg (μmol)	1,3,5-BTC[a] mg (μmol)	Pyridine mg (μmol)	THF cm^3	Yield[b] %
it-PMMA-OH [16]	18.7 (10.9)	1.47 (5.43)	4.3 (54.3)	0.36	28
it-PMMA-OH [26]	22.0 (8.10)	1.13 (4.17)	3.2 (40.6)	0.27	10
it-PMMA-OH [33]	27.4 (8.01)	1.11 (4.08)	3.2 (40.7)	0.27	12
st-PMMA-OH [16]	18.2 (10.6)	1.45 (5.35)	4.1 (52.1)	0.34	33
st-PMMA-OH [26]	23.9 (8.78)	0.80 (2.96)	3.5 (44.0)	0.30	19
st-PMMA-OH [33]	23.8 (6.96)	0.95 (3.50)	2.8 (34.9)	0.23	26

[a] 1,3,5- B enzenetricarbonyl trichloride.
[b] Yield of three-arm polymer.



Scheme 1. Preparation of uniform regular three-arm star PMMA (*n*=16, 26, 33).

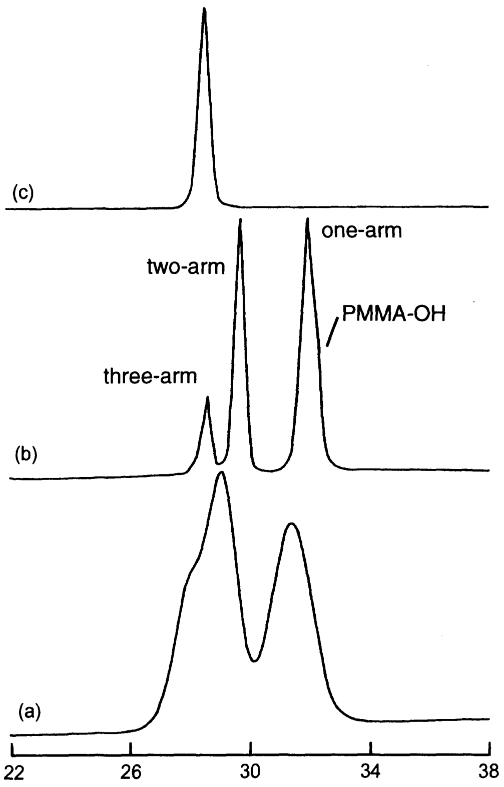


Figure 1. SEC chromatograms of the reaction mixture of non-uniform *st*-PMMA-OH ($\bar{M}n$ = 32.7, $\bar{M}w/\bar{M}n$ = 1.04) and 1,3,5-BTC (a), that of uniform *st*-PMMA-OH (*DP*=26) and 1,3,5-BTC (b), and uniform regular three-arm star PMMA isolated therefrom (c).

-OCH_2- group attached to the linking unit (see Scheme 1), whose intensity corresponded to that of *t*-butyl group observed at 0.82 ppm. The aromatic proton signal was observed at 8.94 ppm as a small singlet due to the core benzene group substituted symmetrically at 1-, 3- and 5-positions.

Tacticity dependence of intrinsic viscosity of uniform regular three-arm star PMMAs

it-PMMA is known to have larger hydrodynamic volume than *st*-PMMA in good solvents such as benzene and chloroform.[21] The tacticity dependence of hydrodynamic volume of *it*- and *st*-PMMAs has recently been demonstrated by using uniform PMMA samples[9]; uniform *it*-PMMA (*DP*=50) shows smaller elution volume in SEC than the corresponding uniform *st*-PMMA in THF at 40℃.

Intrinsic viscosities [η] of the three-arm star PMMAs, and the one- and two-arm coupling products were determined by SEC-DV method in THF at 40℃. Plots of log [η] against logarithmic molecular weight (log MW) are shown in Figure 2a for the syndiotactic series and in Figure 2b for the isotactic series. It is worth noting that the molecular weights of the three-arm and two-arm products are precisely determined based on the uniformity of the starting PMMA-OH's that constitute the arms of the polymers. The values of [η] of the three-arm star *st*-PMMAs (▲in Figure 2a) are smaller than those of the corresponding *it*-star polymers (▲in Figure 2b). The results are consistent with the previous SEC observation for uniform linear *st*- and *it*-PMMAs that hydrodynamic volume of *st*-PMMA is smaller than that of *it*-PMMA with the same *DP*.[9] The plots of log [η] against log MW for *st*-star polymers (▲in Figure 2a) are close to those expected for linear polymer based on Mark-Houwink-Sakurada's equation ([η]=4.2 × 10^{-3} $MW^{0.31}$). The parameters of the equation were determined from the [η] values of linear uniform *st*-PMMAs. On the other hand, the plots for the three-arm star *it*-PMMAs (▲in Figure 2b) deviate clearly from the line for linear *it*-PMMA, as expected for branched polymers.

Zimm and Kilb reported that the ratio of [η] of a branched polymer to that of a linear polymer with the same molecular weight ($g_\eta = [\eta]_{branched} / [\eta]_{linear}$) is expressed by equation (2);[22]

$$g_\eta = (2/f)^{3/2}\,[0.390\,(f-1) + 0.196]\,/\,0.586 \qquad (2)$$

where *f* represents the number of arms. In this formulation, the polymer is assumed to have long, flexible uniform arms in the unperturbed state. The value of g_η obtained from equation (2) with *f* =3 is 0.907. The g_η values for the uniform three-arm PMMAs were summarized in Table II. As mentioned above, the *st*-star PMMAs have [η] values close to those for linear *st*-PMMAs and thus g_η values are all close to unity. The g_η values for the *it*-star PMMAs slightly increased with increasing

Table II. g_η values of uniform regular three-arm star polymers with *it*- and *st*-PMMA arms of different *DP*s

DP of arm	g_η	
	st-Star polymer	*it*-Star polymer
16	0.97	0.84
26	1.00	0.87
33	1.00	0.89

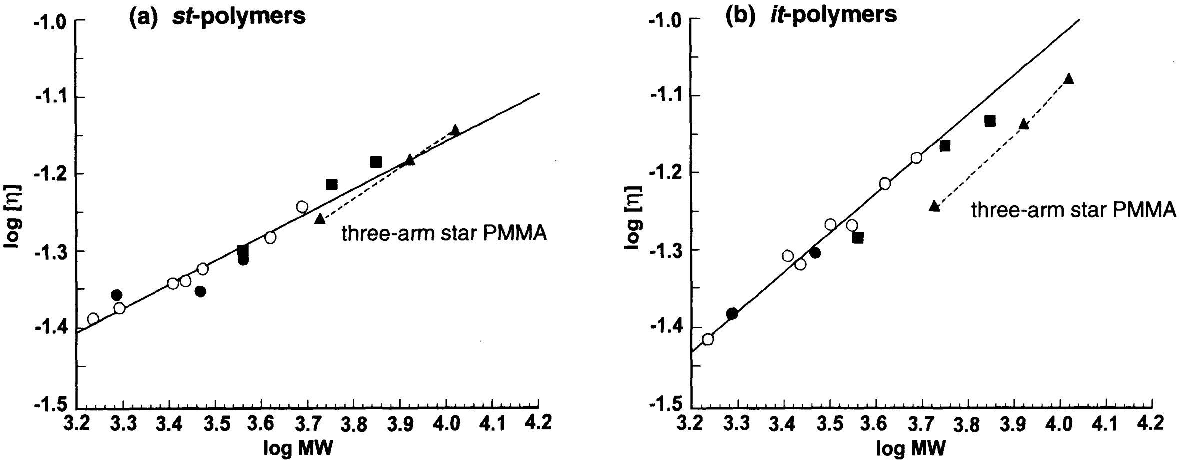


Figure 2. Double-logarithmic plots of [η] measured in THF at 40℃ against molecular weight (MW) of uniform three-arm star *st*-PMMAs and linear *st*-PMMAs (a) and those of *it*-polymers (b). ○; linear PMMA, ●;one-arm byproduct, ■; two-arm byproduct, ▲;three-arm star PMMA. Solid lines represent Mark-Houwink-Sakurada's equations for *st*-PMMA ([η] = 4.2 × 10^{-3} $MW^{0.31}$) and *it*-PMMA ([η] = 8.7 × 10^{-4} $MW^{0.51}$).

DP of arms, and the *it*-star polymer with arm *DP* of 33 showed g_η value of 0.89, which is close to the theoretical value of 0.90_7. The exponent of Mark-Houwink-Sakurada's equation, "a" value for *it*-PMMA (0.51) is close to the value expected for Gaussian chains. The result is apparently consistent with the good fit of g_η value with the theoretical value, even with relatively low molecular weight. In the case of *st*-PMMA, the "a" value (0.31) is smaller than 0.5 at least in the MW range examined. Similar results have been reported for atactic PMMA for MW range of 10^3 to 10^4. The difference in "a" value between *it*- and *at*-PMMA chains has been ascribed to different chain stiffness and local chain conformations.[23] The present results clearly indicate that such difference in chain characteristics arising from the difference in stereochemical structure also affects the branching effect on viscosity.

Uniform irregular three-arm star PMMA

Star polymers synthesized from non-uniform arm precursors should involve intramolecular distribution in the arm length, and thus consist of irregular star polymer molecules that have arms of different *DP*s. To examine the effect of irregularity in arm length on solution viscosity, a uniform irregular three-arm star PMMA having uniform arms of two different *DP*s was prepared. Since we already prepared the regular three-arm star PMMA having three arms of *DP*=26 (78 MMA units in total), an irregular star polymer was intentionally designed to have the same number of MMA units; one arm with *DP*=16 and two arms with *DP*=31. The polymer may be denoted as *star*-[16,31,31].

Thus a 1:2 mixture of uniform *st*-PMMA-OH's with *DP*=16 and 31 was allowed to react with one-third molar amount of 1,3,5-TBC in THF at 25℃ in the presence of 5-fold pyridine for 6 days. Figure 3 shows the SFC chromatogram of the reaction mixture. Peak assignments were tentatively made by elution order, and the objective three-arm product, *star*-[16,31,31], was isolated from the mixture, whose total number of MMA unit was 78. The average *DP* of the arms was confirmed by ^{1}H NMR analysis to be 26.

The *star*-[16,31,31] thus obtained and the regular three-arm star PMMA, *star*-[26,26,26], were subjected to SEC-DV analysis in THF at 40℃ (Figure 4). The [η] value of *star*-[16,31,31] was slightly but meaningfully larger than that of *star*-[26,26,26], and, consistently, the elution volume of the former was slightly smaller than the latter. These facts indicate that the hydrodynamic volume of *star*-[16,31,31] is larger than that of *star*-[26,26,26]. Though the observed differences of the properties are rather small, the certainty of the results is well-supported by the molecular-level uniformity of the uniform star polymers. Such a conclusive result on structure-properties relationship would never be obtained without the uniform polymers.

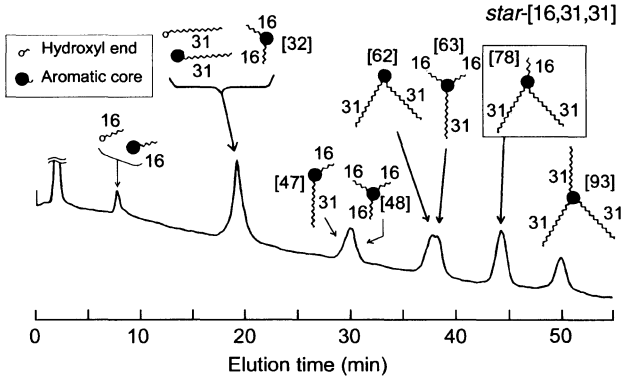


Figure 3. SFC cuve of the reaction mixture of uniform *st*-PMMA-OH's with *DP* of 16 and 31 in 1:2 ratio with 1,3,5-BTC. Figures in brackets represent total number of MMA unit, and figures without brackets the *DP* of arm. Closed circle (●) represents the aromatic core group.

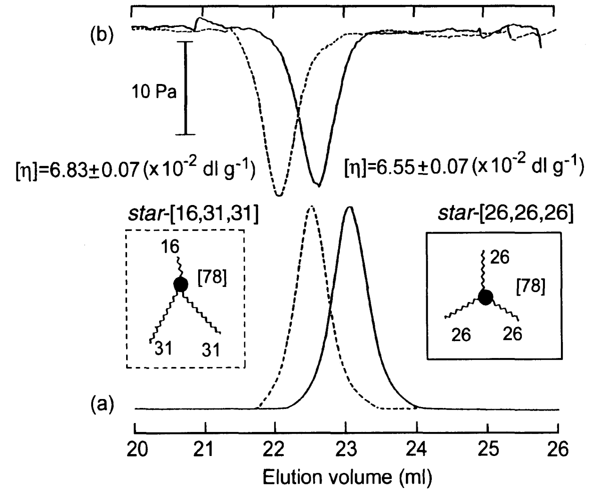


Figure 4. SEC curves, detected with RI (a) and differential viscometric (DV) detectors (b) measured in THF at 40℃, of regular (solid line) and irregular (broken line) three-arm star polymers having *st*-PMMA arms, whose *DP*s in total and in each arm are indicated in the figure. The differences in elution volumes in RI- and DV-detected chromatograms are due to the time lag existing between the detectors.

Acknowledgments. This study was partly supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 0824102) from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, and T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
2. T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, and K. Hatada, *Makromol. Chem., Suppl.*, **15**, 167 (1989).
3. T. Kitayama, Y. Zhang, and K. Hatada, *Polym. J.*, **26**, 868 (1994).
4. T. Hirano, H. Yamaguchi, T. Kitayama, and K. Hatada, *Polym. J.*, **30**, 767 (1998).
5. T. Kitayama, S. He, Y. Hironaka, and K. Hatada, *Polym. J.*, **27**, 314 (1995).
6. T. Kitayama and K. Hatada, "New Macromolecular Architecture and Functions (Proceedings of OUMS'95)", M. Kamachi and A. Nakamura Eds., Springer-Verlag, 1995, p. 31.
7. P. O. Danis and D. E. Karr, *Org. Mass Spectrom.*, **28**, 923 (1993).
8. E. Klesper and W. Hartmann, *Eur. Polym. J.*, **14**, 77 (1977).
9. K. Ute, N. Miyatake, Y. Osugi, and K. Hatada, *Polym. J.*, **25**, 1153 (1993).
10. K. Ute and K. Hatada, "Fractionation by Packed-Column SFC and SFE", M. Saito, Y. Yamauchi, and T. Okuyama Eds, VCH, 1994, p. 231.
11. K. Hatada, K. Ute, T. Kitayama, T. Nishiura, and N. Miyatake, *Macromol. Symp*, **85**, 325 (1994).
12. K. Hatada, K. Ute, and N. Miyatake, *Prog. Polym. Sci.*, **19**, 1067 (1994).
13. K. Hatada and T. Kitayama, "Polymeric Materials Encyclopedia", J. C. Salamone Ed., CRC Press, 1996, p. 8461.
14. K. Ute, N. Miyatake, and K. Hatada, *Polymer*, **36**, 1415 (1995).
15. T. Kitayama, O. Nakagawa, S. Kishiro, T. Nishiura, and K. Hatada, *Polym. J.*, **25**, 707 (1993).
16. T. Kitayama, O. Nakagawa, and K. Hatada, *Polym. J.*, **27**, 1180 (1995).
17. K. Hatada, T. Nishiura, T. Kitayama, K. Ute, and S. Hirotani, *Polym. J.*, **28**, 185 (1996).
18. T. Nishiura, T. Kitayama, and K. Hatada, *Polym. J.*, **28**, 1021 (1996).
19. K. Hatada, T. Nishiura, T. Kitayama, and S. Hirotani, *Macromol. Rapid Commun.*, **18**, 37 (1997).
20. K. Hatada, T. Nishiura, T. Kitayama, and M. Tsubota, *Polym. Bull.*, **36**, 399 (1996).
21. J. M. Cowie, "Solution of Stereoregular Polymers" in "Light Scattering from Polymer Solutions", M. B. Huglin Ed., Academic Press, London, 1972, p. 605.
22. B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959).
23. M. Kamijo, F. Abe, Y. Einaga, and H. Yamakawa, *Macromolecules*, **28**, 1095 (1995).