Poly(ethylene oxide) Macromonomers. 10. Characterization and Solution Properties of the Regular Comb Polymers with Polystyrene Main Chains and Poly(ethylene oxide) Side Chains

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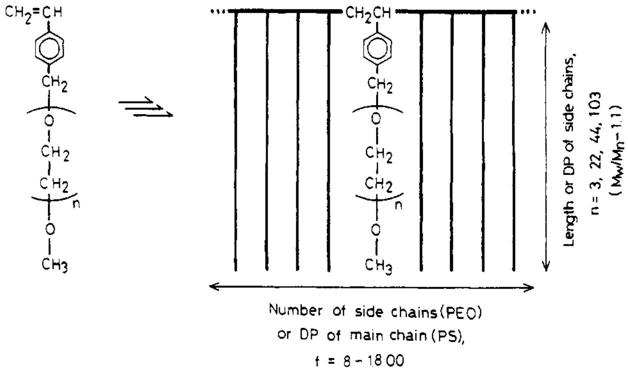
ABSTRACT: A series of regular comb polymers (**2**) prepared by homopolymerization of *p*-vinylbenzyl-ended poly(ethylene oxide) (PEO) macromonomers (**1**) were characterized by means of light scattering (LS), gel permeation chromatography (GPC), and viscosity measurements. The molecular weights, M_w, estimated by LS, coupled with the intrinsic viscosities, both measured in tetrahydrofuran, were successfully applied to construct a universal calibration in GPC. The comb polymers, particularly those with longer, and/or a higher number of, side chains, were found to have very contracted dimensions as compared to the corresponding linear homopolymers of the same molecular weights. The exponent of the Mark–Houwink–Sakurada equation was very low (0.15) and even nearly zero (−0.06) for the comb polymers with side chains of 44 and 103 ethylene oxide units, respectively, suggesting their very densely filled, spherelike conformations. The macromonomers with longer PEO chain lengths were found to polymerize in water to much higher degrees of polymerization in the main chains than those with a tri(ethylene glycol) side chain or styrene, supporting the organized micellar polymerization mechanism of the former as previously proposed.

Introduction

The homopolymerization of macromonomers has recently been of considerable concern in view of a very specific kinetic behavior. Among others, radical polymerizations of polystyrene[1,2] and poly(methyl methacrylate) macromonomers[3,4] have been characterized by very slow diffusion-controlled termination due to their highly crowded, multibranched segments. We have reported that amphiphilic poly(ethylene oxide) (PEO) macromonomers polymerized unusually rapidly in water, very probably as a result of their organization into micelles.[5-7]

Also very interestingly in view of the structure–property relationship, they provide regular comb polymers of a well-defined structure. Thus a PEO macromonomer, **1**,[5] readily polymerizes to afford a polystyrene, **2**, with PEO side chains, which are regularly and densely spaced, each on every benzene ring of the backbone, as in Scheme I.

Scheme I



1 2

The length or the degree of polymerization, *n*, and its distribution of the side chains (arms or teeth) can be either definitely known by independent characterization of the macromonomer used or easily controlled in preparation of the macromonomer by virtue of the living anionic polymerization of ethylene oxide (EO).[5-8] The size of the main chain or the average number of side chains, *f*, may be, at least qualitatively, controlled by changing the feed compositions such as the monomer and the initiator concentrations, denoted by [M] and [I], respectively, in the context of conventional polymerization kinetics.

In our previous work,[5] the micellar polymerization of PEO macromonomers in water was found to be unusually rapid but to follow the usual radical polymerization kinetics, supporting the bimolecular termination of the poly(macromonomer) radicals

$$R_p = k_p(2fk_d/k_t)^{1/2}[M][I]^{1/2} \qquad (1)$$

where R_p is the rate of polymerization, with k_p and k_t standing for the rate constants of propagation and termination and k_d and *f* standing for the decomposition rate constant and the initiator efficiency of the initiator, respectively. Thus the micellar polymerization appears to be most reasonably characterized by a very high k_p and/or a very low k_t. Therefore the degree of polymerization, DP or *f*, should also be very high, according to conventional kinetics as follows[9]

$$DP = [2k_p/(2k_tk_df)^{1/2}][M]/[I]^{1/2} \qquad (2)$$

under the assumption of a recombination termination and no chain transfer. In fact, the molecular weights of the polymers obtained by the micellar polymerization, as estimated by light scattering in benzene, were found to also be of a very high order of magnitude as compared to those expected from eq 2 with k_p and k_t for styrene.[5]

The present paper aims to characterize a series of regular comb polymers, **2**, with various lengths of side chains as well as main chains, denoted by *n* and *f*, respectively, by means of light scattering (LS), gel permeation chromatography (GPC), and viscosity measurements. It will be of fundamental importance not only for examining the mechanism of the micellar polymerization but also for studying general solution properties of branched polymers.[10] In particular, experimental studies appear to have been so far very scarce except for some model branched polymers[11,12] and starlike polymers.[13] The comb polymers, **2**, are expected to exhibit a variety of characteristics depending on the values of *n* and *f*, since a polymer with a very small *n* relative to *f* will represent a linear polymer

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Table I
Characterization of PEO Macromonomers (1)[a]

PEO chain length n	M_n	M_w/M_n
3	(280)	(1.0)
22	1100	1.14
44	2100	1.08
103	4700	1.15

[a] Determined by GPC calibrated with PEO standard samples, except for the monomer of $n = 3$, which is a pure substance.

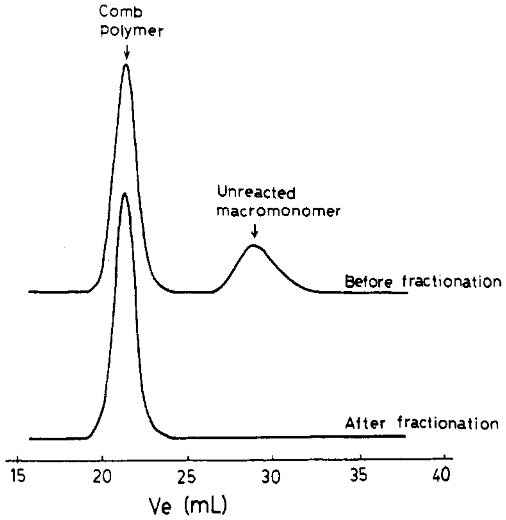

Figure 1. Isolation of a comb polymer (sample code 103-2) by solvent fractionation as monitored by GPC.

on the one hand, while that with a very large n and very small f will behave like a starlike polymer on the other hand. Both large n and f will most probably represent a typical comb or brush polymer. Thus it will be interesting to examine how n and f affect the solution characteristics of the comb polymers.

Experimental Section

Materials. The PEO macromonomer (1) with $n = 3$ was prepared from tri(ethylene glycol) monomethyl ether by reacting with excess sodium hydride and p-vinylbenzyl chloride (VBC) according to a procedure similar to that described previously.[5,8] The other macromonomers with higher n were prepared by polymerization of EO with potassium 2-methoxyethoxide in tetrahydrofuran (THF), followed by termination with VBC, and characterized in a manner similar to that described previously.[5,8] Table I summarizes the characterization of the macromonomers used in this study.

The comb polymers (2) were prepared by radical polymerization of the corresponding macromonomers by appropriately changing the concentrations of the monomer and the initiator. The monomer with $n = 3$ was insoluble in water and so polymerized in benzene at 60 °C for 2 days with 2,2′-azobis(isobutyronitrile) (AIBN) at [M] = 80–360 mmol/L and [I] = 0.2–3 mmol/L. Styrene was also similarly polymerized in benzene for comparison of DP's attained under the same conditions. The polymers were collected by precipitation into hexane, purified by reprecipitation from benzene into hexane, and freeze-dried from benzene. The macromonomers with n = 22, 44, and 103 were polymerized in water, i.e., by micellar polymerization, with 4,4′-azobis(4-cyanovaleric acid) (AVA) at 60 °C. The monomer and the initiator concentrations were varied as [M] = 2–20 mmol/L and [I] = 0.1–3.8 mmol/L, respectively. The polymers were collected by evaporation and fractionated as follows to remove completely the unreacted, or impure without a double bond, macromonomers. To a polymer solution of ca. 1 wt % in benzene was added hexane at 30 °C until turbidity developed; the solution was warmed to 40 °C to give a clear solution, which was then very slowly cooled to 30 °C, by standing overnight, to cause phase separation. The lower layer afforded a pure comb polymer after evaporation of the solvent. Purification was confirmed each time by the absence of any peak due to macromonomers in GPC, as exemplified in Figure 1. Finally the comb polymers were freeze-dried from benzene to constant weights.

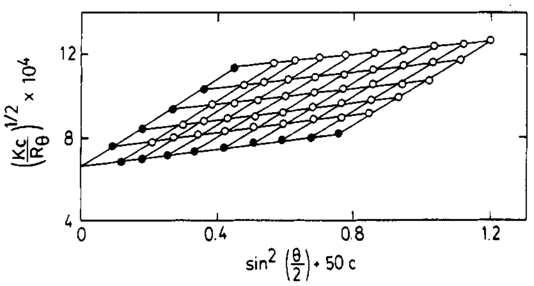

Figure 2. Zimm–Berry plots for a comb polymer (sample code 22-1) measured in THF. $M_w = 2.3 \times 10^6$, $\langle s^2 \rangle = 2.6 \times 10^{-11}$ cm^2, $A_2 = 3.5 \times 10^{-5}$ m^3 mol kg^{-2}.

Measurements. GPC was recorded on a HPLC, TRIROTAR III of Japan Spectroscopic Co., Ltd., equipped with an RI detector, a Shodex SE-11, and columns Shodex A-803 and A-804. THF was used as an eluent at a flow rate of 1 mL/min at 40 °C. Molecular weights were calibrated with the standard samples of linear PEO and polystyrene (PS) from Tosoh Co., Ltd.

LS was measured at 25.0 °C with a photometer system, LS-601, Union Giken Co., Ltd., equipped with a He–Ne laser of 632.8 nm. Sample solutions were filtered through a membrane of pore size 0.2 μm, Toyo Roshi Co., Ltd. The refractive index increment (dn/dc) was measured at 25.0 °C with a refractometer, RM-102, Ootsuka Electronics Co., Ltd. A conventional procedure[14,15] according to the Zimm–Berry plot[16] was followed to evaluate the weight-average molecular weight, M_w

$$\left(\frac{Kc}{R_\theta}\right)^{1/2} = \left[\frac{1}{M_w}\left(1 + \frac{16\pi^2 n_0^{\,2}}{3\lambda_0^{\,2}}\langle s^2\rangle \sin\left(\frac{\theta}{2}\right) + 2A_2 M_w c\right)\right]^{1/2} \quad (3)$$

where

$$K = \frac{4\pi^2 n_0^{\,2}}{N\lambda_0^{\,4}}\left(\frac{dn}{dc}\right)^2 \quad (4)$$

with R_θ the Rayleigh ratio at the scattering angle of observation, θ, which ranged over 20–135°, c the concentration, ranging over ca. 0.02×10^{-2}–3×10^{-2} g/mL, λ_0 the wavelength of the incident light, n_0 the refractive index of the solvent, N Avogadro's number, $\langle s^2 \rangle$ the mean-squared radius of gyration, and A_2 the second virial coefficient.

The viscosity was measured at 25.0 °C with an Ubbelohde-type viscometer. Intrinsic viscosities, $[\eta]$, were determined from extrapolation of the plots of the reduced viscosities, η_{sp}/c and ln η_{rel}/c, vs the concentration.

Results and Discussion

Molecular Weights. In general, determination of the true molecular weights by means of LS is not so simple for block or graft copolymers with some composition distributions.[14,17] The present regular comb polymers, however, should be almost ideally homogeneous in their compositions because they were prepared by *homo*polymerization of the corresponding macromonomers with sharp chain length distributions as given in Table I. A normal Zimm–Berry plot was obtained as shown typically in Figure 2 for a comb polymer of n = 22, measured in THF at 25 °C. The usual procedure to extrapolate to $\theta = 0$ and $c = 0$ afforded $M_w = 2.3 \times 10^6$. LS measurements of the same polymer in benzene and in chloroform gave $M_w = 2.0 \times 10^7$ and $M_w = 3.3 \times 10^6$, respectively, which are too high and similar compared to that measured in THF. Similar trends were observed for the other samples as summarized in Table II, suggesting that the molecular weights measured in THF and chloroform are close to the true values while

Table II
Comparison of Molecular Weights of Comb Polymers (2) As Determined by LS in Various Solvents

	M_w measured in		
sample code[a]	benzene	THF	chloroform
22-1	2.0×10^7	2.3×10^6	3.3×10^6
22-2	7.6×10^6	9.2×10^5	1.2×10^6
22-3	2.1×10^7	5.8×10^5	6.7×10^5
22-4	4.6×10^6	8.3×10^4	
103-1	7.5×10^6	1.2×10^6	1.1×10^6
103-2	5.2×10^6	3.3×10^5	2.9×10^5
103-3	6.4×10^5	2.9×10^5	2.6×10^5
103-4	1.8×10^5	1.3×10^5	1.1×10^5
103-5	1.5×10^5	9.1×10^4	7.0×10^4

[a] The first value such as 22 and 103 stands for the number-average length or DP of the PEO side chain, *n*.

Table III
Characterization of Comb Polymers (2)

sample code[a]	$10^{-4}M_2$(LS)[b]	$10^{-4}M_w$(GPC)[c]	$[\eta]$,[d] dL/g	DP or *f*[e]
3-1	16	10	0.21	554
3-2	5.3	2.6	0.11	190
3-3	2.2	1.0	0.067	80
22-1	229	25	0.81	1760
22-2	92	21	0.46	711
22-3	58	17	0.28	446
22-4	8.3	1.8	0.080	64
22-5	5.4	0.6	0.055	41
44-2	149	13	0.16	648
44-3	56	12	0.12	244
44-4	3.0	3.4	0.09	13
44-5	1.8	1.8	0.08	8
103-1	116	18	0.22	215
103-2	33	14	0.21	61
103-3	29	12	0.22	51
103-4	13	8.1	0.26	24
103-5	9.1	5.1	0.24	17

[a] See footnote in Table II. [b] M_w determined by LS in THF. [c] M_w determined by GPC calibrated with linear PEO standard samples. [d] Intrinsic viscosity in THF at 25 °C. [e] Average degree of polymerization or average number of side chains calculated from M_w(LS) divided by M_w of the corresponding macromonomer.

those measured in benzene, together with those previously reported,[5] appear to be much overestimated, probably because of some aggregation of the comb polymers in benzene or for some other reason which is not clear at present. We therefore employed the M_w in THF as the true or nearly true value since this has been supported by universal calibration of GPC data in the same solvent as follows.

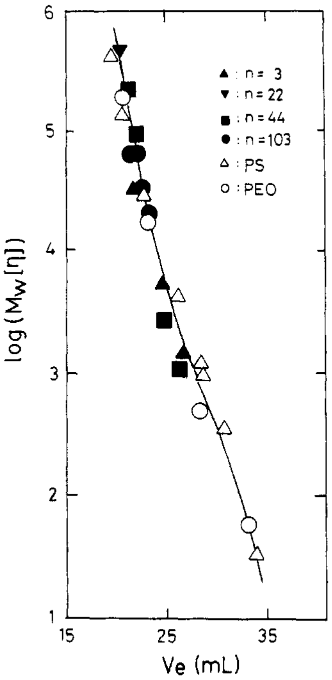

Figure 3. Universal calibration of GPC data for comb polymers and corresponding homopolymers.

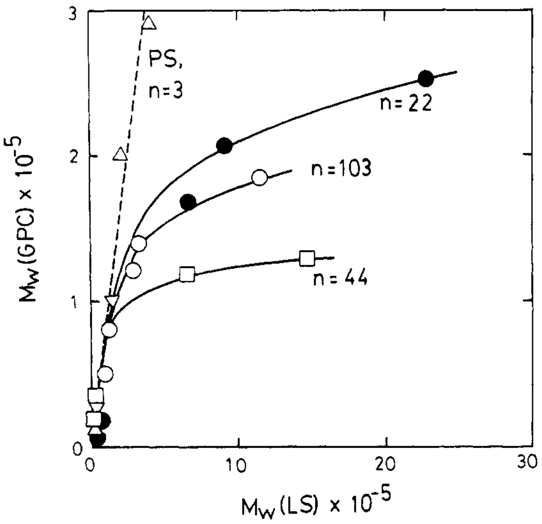

Figure 4. Comparison of molecular weights determined by GPC and LS, measured in THF, for PS (△) and comb polymers of $n = 3$ (▽), $n = 22$ (●), $n = 44$ (□), and $n = 103$ (○). A broken line is theoretical for M_w(GPC) = M_w(LS).

It is well-known[14,18] that GPC, when calibrated only with linear standard polymers as usual, severely underestimates the molecular weight of a branched polymer, which should assume a more compact molecular volume in solution than that of a corresponding linear polymer of the same molecular weight. Since a polymer hydrodynamic volume in solution can be expressed by the product of the molecular weight and the intrinsic viscosity, as in the Flory–Fox theory,[19] the universal calibration[20] requires that this quantity, $M_w[\eta]$, should determine the retention in GPC, irrespective of the structure or the composition of the polymers. Table III summarized all the comb polymers investigated in this study with the results of the characterization of the molecular weight, M_w, measured by LS and those estimated by GPC calibrated with the linear PEO standard samples, together with the intrinsic viscosities, all measured in THF. A universal calibration was constructed in Figure 3 by plotting the logarithm of $M_w[\eta]$, with M_w measured by LS in THF, as a function of the elution volume, V_e, in GPC. All the plots, including the comb polymers as well as the corresponding linear homopolymers, can be clearly represented by a single curve, supporting not only the usefulness of the universal calibration but also the validity of the M_w thus measured by LS. In contrast, the apparent molecular weights based on the GPC calibration with linear standard polymers are severely underestimated, particularly at higher molecular weights, i.e., for the comb polymers with a longer and/or higher number of side chains, as is clear in Figure 4. The polymers with the shortest side chains, $n = 3$, as well as polystyrene (PS) samples fall nearly on the theoretical line with M_w(LS) = M_w(GPC), as expected.

As to the molecular weight distribution of the comb polymers, GPC also yielded poor estimation based on the usual calibration with the linear standard polymers. For an example, a comb polymer of $n = 103$, sample code 103-1 in Table III, the usual calibration gave $M_w/M_n = 1.13$ while recalibration using the M_w data measured by LS in

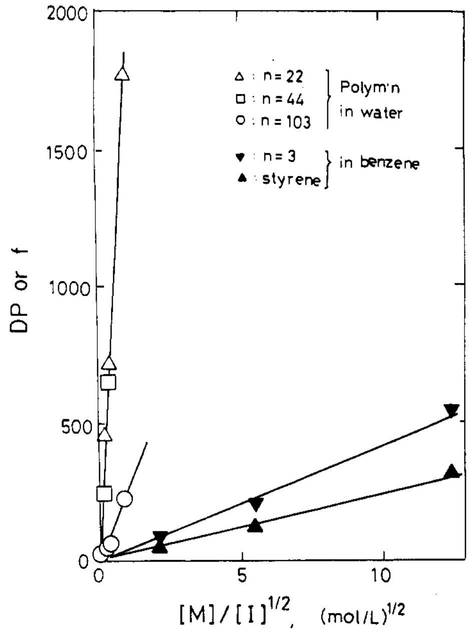

Figure 5. DP or f of comb polymers as a function of the feed composition in polymerization. The macromonomers of $n = 22$ (△), 44 (□), and 103 (○) were polymerized in water with AVA, while the monomers of $n = 3$ (▼) and styrene (▲) were polymerized in benzene with AIBN.

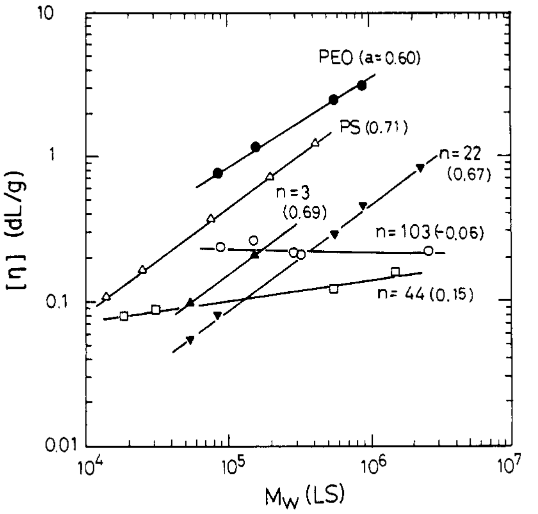

Figure 6. Double-logarithmic plots of $[\eta]$ vs M_w(LS) for PEO (●, $a = 0.60$), PS (△, 0.71), and comb polymers of $n = 3$ (▲, 0.69), $n = 22$ (▼, 0.67), $n = 44$ (□, 0.15), and $n = 103$ (○, −0.06). Values in parentheses denote the exponent a in the Mark–Houwink–Sakurada equation: $[\eta] = KM_w^a$. Data for PS were obtained from the literature.[21]

THF estimated M_w/M_n as high as 3.0–4.9. Similar trends were also true for the other comb polymers. In this manner, the usual GPC calibration based on the linear standard polymers appears to be almost meaningless for branched polymers in that too low values are estimated for M_n, M_w, and M_w/M_n.

Now that we have had the true or nearly true values for M_w, the average degree of polymerization, DP, of the polystyrene main chain or the average number of the PEO side chains, f, was calculated as given in Table III and plotted as a function of the initial concentrations of the monomer and the initiator, according to eq 2. The results in Figure 5 clearly show that the polymerizations in water of the PEO macromonomers of $n = 22$, 44, and 103 attained much higher DPs than those of either the monomer of $n = 3$ or styrene in benzene, supporting the micellar polymerization mechanism of the former, with enhanced k_p and/or depressed k_t.[5] The conventional bimolecular termination mechanism is also supported to control the DPs for the micellar polymerization in water. Somewhat low DPs for the macromonomers of $n = 103$, as compared to those for $n = 22$ and 44, appear to result from a less organized, micellar polymerization because of a too enhanced hydrophilicity of this monomer. These trends parallel those found for the polymerization rates.[5]

Solution Properties. From the results of characterization by means of LS and GPC, as described above, it is already clear that the present comb polymers assume very compact dimensions in solution as compared to those of the linear polymers of the corresponding molecular weights. Although they have somewhat broad distributions in the backbone chain lengths, with M_w/M_n around 3–5, it will be interesting to examine what conformations they should have in solution depending on the length of the side chains.

Figure 6 shows the double-logarithmic plots of the intrinsic viscosity and the M_w by LS, both measured in THF at 25 °C, according to the Mark–Houwink–Sakurada equation.[14,19]

$$[\eta] = KM_w^{\,a} \tag{5}$$

The values of the exponent a around 0.6–0.7 were observed for the comb polymers with relatively short side chains ($n = 3$ and 22) as well as for linear PEO and PS, clearly supporting their expanded-coil conformations, as expected. Thus each isolated chain in the solutions of these comb polymers apparently behaves like an expanded-coil linear polymer chain, as a whole, although with a much more contracted dimension, as compared to a real linear polymer with the same molecular weight, because of a geometric requirement for the comb structure.

Most striking in Figure 6 is the observation that the comb polymers with longer side chains exhibited very low or even nearly zero values for the exponent at least within the M_w range investigated; $a = 0.15$ for $n = 44$, and $a = -0.06$ for $n = 103$. Since the zero exponent is required for a rigid sphere,[14] the results suggest a very densely filled, nondraining, rigid spherelike conformation, as a whole, for each of these comb polymer chains. Although further extensive studies should remain to confirm more explicit conformations, the nearly zero exponent appears to be the first experimental observation for synthetic branched polymers to our knowledge. At any rate, the little dependence of the viscosity on the molecular weight, as observed for the present regular comb polymers, is very interesting in nature and appears to find applications particularly in the field of paint technology.

Conclusions

Characterization of solution properties of a series of regular comb polymers, 2, by means of LS, GPC, and viscosity measurements has revealed their very compact dimensions, particularly at higher n and f, as compared to their linear counterparts with the same molecular weights. GPC was helpless in estimating their molecular weights unless the universal calibration was made. Very low or even nearly zero exponent factors in the Mark–Houwink–Sakurada equation were observed for the comb polymers with side chains longer than 44 EO units. An organized micellar polymerization mechanism[5] was supported by the much higher DPs attained for the polymerization of the PEO macromonomers in water than those for the lower molecular weight homologues in benzene.

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