On the Intrinsic Viscosity of Poly(macromonomer)s†

Yasuhisa Tsukahara* and Shinzo Kohjiya

Department of Materials Science, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan

Kiyoharu Tsutsumi and Yoshio Okamoto

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

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Polymerizations of macromonomers provide regular multibranched polymers with a very high branch density. The multibranched structure of poly(macromonomer)s leads to very small molecular dimensions in solution compared with the corresponding linear polymers of the same molecular weight. Since both the degree of polymerization and the length of branches may be varied, poly(macromonomer)s are interesting models for the study of branched polymers.[1–4]

Previously, we have reported the radical polymerization behavior of polystyrene macromonomers in a good solvent.[2] A strong diffusion-controlled effect was found in the polymerization reaction depending on the molecular weight and the concentration of the macromonomer. Thus, the degree of polymerization of the poly(macromonomer)s is controlled by both the concentration and the molecular weight of the macromonomer.

In this paper, we report the intrinsic viscosity, [η], of poly(macrononomer)s in toluene, a good solvent. The [η] and the hydrodynamic volumes of the poly(macromonomer)s are discussed in terms of their multibranched structure as functions of the branch number and length. These results are compared with those of the corresponding linear polymers. Investigation of the molecular dimension and the related segment density of poly(macromonomer)s in solution can provide information about the nature of the growing chain of macromonomers in polymerization reactions.[2]

ω-[(Methacryloyloxy)ethyl]polystyrene macromonomers synthesized by living anionic polymerization of styrene with *s*-BuLi followed by addition of ethylene oxide and termination with methacryloyl chloride were polymerized using AIBN initiator in benzene at 60 °C for 24 h. Polymerization products were purified by precipitation–extraction procedures with cyclohexane–petroleum ether mixed solvents to remove unreacted macromonomers. The purification was repeated several times until the sharp peak in the gel permeation chromatograph (GPC), corresponding to the unreacted macromonomer, completely disappeared.

The weight-average molecular weight, M_w, and the polydispersity index, M_w/M_n, of poly(macromonomer)s were determined by GPC (Tosoh HLC802A/LS-8) equipped with a low-angle laser light scattering (LS) detector and a refractive index (RI) detector.[2a,c] The GPC was operated with Tosoh G6000H, G4000H, and G2000H columns on toluene at 25 °C.

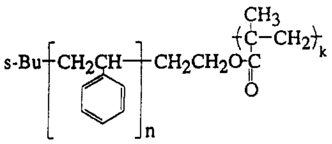
Intrinsic viscosities were measured using an Ubbelohde type capillary viscometer in toluene at 25 °C. The flow time of the solvent was 206 s.

Table 1. Characteristics of Poly(macromonomer)s

	macromonomer		poly(macromonomer)			
sample code	$M_w \times 10^{-3}$	M_w/M_n	$M_w \times 10^{-3}$ [a]	DP	M_w/M_n	[η][b] (dL/g)
MA–PSt800	0.89	1.11	6.1	6.8	1.05	0.0415
			8.4	9.5	1.17	0.0432
			11.3	12.7	1.21	0.0451
			19.5	21.9	1.27	0.0480
			45.0	50.6	1.73	0.0619
			230	258	2.22	0.143
			489	549	2.13	0.275
			1540	1730	2.00	0.571
MA–PSt2900	3.10	1.07	17.6	5.7	1.35	0.0648
			62.7	20.2	1.86	0.0742
			251	81.0	1.30	0.0830
			529	171	2.52	0.113
			1390	448	2.77	0.238
MA–PSt5500[c]	6.10	1.11	4.5	7.4	1.14	0.120
			13.9	22.8	1.35	0.113
			35.9	58.9	2.29	0.114
			132	216	2.08	0.171
			164	269	2.62	0.198
			186	305	1.56	0.219
MA–PSt12400	13.1	1.06	85.5	6.4	1.53	0.166
			153	11.6	1.22	0.184
			236	18.0	1.14	0.169
			321	24.5	2.93	0.169
			437	33.4	1.97	0.169
			5430	415	1.72	0.370
MA–PSt14000	14.6	1.04	158	10.8	1.27	0.246
			228	15.6	1.34	0.245
			280	19.2	1.75	0.232
MA–PSt27000	28.1	1.04	142	5.1	1.42	0.213
			243	8.6	1.73	0.322
			603	21.5	1.73	0.304

[a] Determined by GPC equipped with a low-angle light scattering detector on toluene at 25 °C. [b] Measured in toluene at 25 °C. [c] This macromonomer was prepared by a slightly different procedure and possesses a benzyl group at the α-chain end.

Poly(macromonomer)s in this study have the structure



with different n and k. Values of M_w, M_w/M_n of the macromonomers, the degree of polymerization (DP), and the M_w/M_n of poly(macromonomer)s are summarized in Table 1. The numeral in the sample designation behind MA–PSt represents the number-average molecular weight, M_n, of the macromonomer. The number-average molecular weights of the branches of the poly(macromonomer)s are in the range from 800 to 27 000, and the branch numbers are in the range from 6 to 1730 per molecule. M_w/M_n values are in the range from 1.05 to 2.93 and have a tendency to increase with DP but also depend on the isolation procedure.

Figure 1a exemplifies the GPC curve of the radical polymerization product of macromonomer MA–PSt2900. The right and left peaks correspond to the formed poly(macromonomer) and unreacted macromonomer, respectively. GPC curve b in Figure 1 corresponds to the recovered product after precipitation in cyclohexane/petroleum ether (mixing ratio 1/2 (v/v)), to extract the unreacted macromonomer. This procedure was repeated 2–4 times to isolate the poly(macromonomer). The final GPC curve of the poly(macromonomer) is shown in Figure 1c. In this case, M_w, DP, and M_w/M_n of the poly(macromonomer) determined by the LS detector are 62.7 × 10^3, 20.2, and 1.86, respectively.

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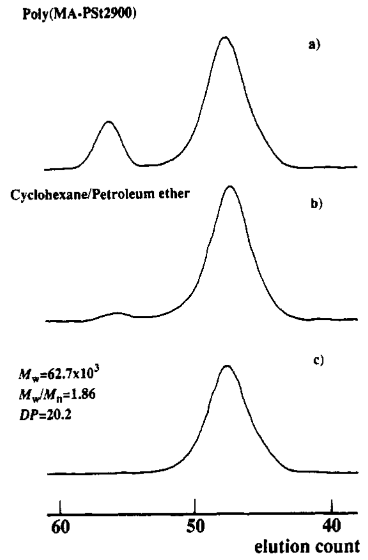

Figure 1. GPC curves of (a) the polymerization product of MA-PSt2900, (b) the recovered product from precipitation in a cyclohexane/petroleum ether mixed solvent, (c) the isolated poly(macromonomer). The polymerization was carried out in benzene at 60 °C for 24 h.

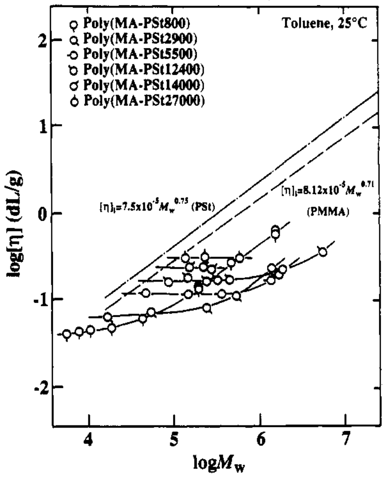

Figure 2. log–log plots of the intrinsic viscosity $[\eta]$ versus the weight-average molecular weight M_w of poly(macromonomer)s. $[\eta]$ was measured in toluene at 25 °C. M_w of branches of poly(macromonomer)s are shown in Table 1. The broken straight line in the figure is the empirical equation for linera poly(methyl methacrylate),[5a] and the broken dotted line is that of polystyrene.[5b]

Figure 2 shows $[\eta]$ of the poly(macromonomer)s in toluene at 25 °C as a function of M_w. The broken straight line in the figure is the empirical equation for linear poly(methyl methacrylate) (PMMA),[5a] and the broken dotted line is that of polystyrene (PSt).[5b] It is seen in the figure that $[\eta]$ versus M_w relationships of the poly(macromonomer)s are quite different from those of the linear PMMA and PSt. The $[\eta]$ values of the poly(macromonomer)s in the low-M_w region are almost independent of the M_w for any given branch length. This behavior is similar to that of poly(macromonomer)s of poly(oxyethylene) macromonomers reported by Ito et al.[4] The value of $[\eta]$ in the low-M_w region increases systematically with an increase of the branch length.

On the other hand, in the high-M_w region, $[\eta]$ increases gradually with M_w. The M_w for the onset of the increase in $[\eta]$ seems to shift toward higher M_w with an increase of the length of the branch chains. The rise of $[\eta]$ is not observed for the poly(macromonomer)s having long branches in this molecular weight range.

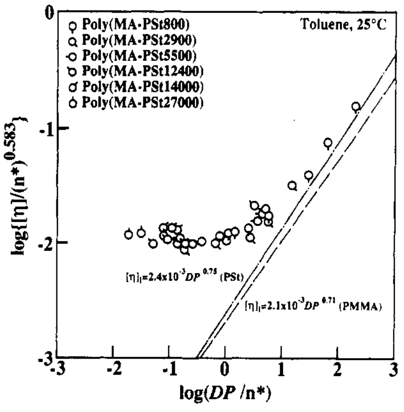

Figure 3. log–log plots of $[\eta]/(n^*)^{0.583}$ versus (DP/n^*) for the poly(macromonomer)s. The broken straight line in the figure is for linear poly(methyl methacrylate), and the broken dotted line is that of polystyrene.

The data in Figure 2 indicate that the poly(macromonomer)s in the low-M_w region behave like rigid spheres with a polymer chain segment density almost independent of the M_w but decreasing with increasing length of the branches. For the rigid molecule, the intrinsic viscosity, $[\eta]$, is expressed by $[\eta] = \phi/\rho$, whereby ϕ is the shape factor,[6] which is 2.5 for the spherical molecule,[7] and ρ is the segment density. Thus, the variation $[\eta]$ with M_w in Figure 2 is related to the change in (ϕ/ρ) with M_w. That is, the constancy of $[\eta]$ at the low-M_w region might be explained by the constancy of (ϕ/ρ) with M_w.

When the branch number increases to a great extent, the chain length ratio of the backbone to the branch becomes large and the molecular shape of poly(macromonomer)s changes gradually from that of the spherical star-branched polymer to the comb-branched polymer. Therefore, if the backbone chain has some extent of chain stiffness due to the high branch density, the shape factor increases with DP and thus $[\eta]$ increases with M_w. On the other hand, when the polymer backbone is flexible in spite of the high branch density, the bending of the backbone chain causes a decrease of the average segment density ρ within the hydrodynamic volume and an increase of $[\eta]$ with M_w. Both of these might explain the rising of $[\eta]$ in the high-M_w region.

In Figure 3, $[\eta]/(n^*)^{0.583}$ is plotted against (DP/n^*) to reduce both the effect of the difference in the branch length and the difference in the chain length ratio of the backbone to the branch, where n^* is the number of MMA residues in the side chain. The empirical relation illustrated in Figure 3 shows that $[\eta]/(n^*)^{0.583}$ can almost be presented as a universal function of DP/n^* for the poly(macromonomer)s of all branch lengths. The exponent 0.583 was obtained from the slope in the double-logarithmic plots of $[\eta]$ at the low-DP region with M_w of the branch. It is also seen in Figure 3 that these plots seem to approach the straight lines for PMMA and PSt as DP/n^* increases. Further study on the poly(macromonomer)s of the great DP is necessary and is now in progress.

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