Polymer Vol. 36 No. 14, pp. 2781–2786, 1995

0032-3861/95/$10.00+0.00

Characterization of poly(methyl methacrylate)-*graft*-polystyrene prepared from methacryloyloxyethyl polystyrene macromonomer

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(Received 8 December 1994; revised 3 February 1995)

Poly(methyl methacrylate)-*graft*-polystyrene was prepared by radical copolymerization of methyl methacrylate and methacryloyloxyethyl polystyrene macromonomer. By means of ^{1}H n.m.r. spectroscopy and static light scattering (SLS), molecular weight distribution (*MWD*) and chemical composition distribution (*CCD*) were investigated for as-polymerized samples and their fractions separated by size exclusion. All fractionated samples had approximately the same chemical composition as those of the unfractionated copolymers. Apparent molecular weight measured by SLS was dependent upon solvent. The following conclusions were deduced from these results: the as-polymerized copolymers had polydispersities in *CCD* and *MWD* that were not correlated with each other. In contrast with the as-polymerized samples, the size-exclusion-fractionated samples showed a strong *CCD*-*MWD* correlation, while the two-dimensional distribution functions of *CCD* and *MWD* for all fractions were similar to each other. In view of the fact that the chain dimension of a long-branched polymer decreases with increasing branch density at the same molecular weight, the present results were consistently explicable.

(Keywords: graft copolymer; characterization; light scattering)

INTRODUCTION

Copolymerization using macromonomers[1] has recently received much attention as a powerful method for designing a vast variety of well-defined graft copolymers. Extensive studies have brought about considerable progress in understanding copolymerization behaviour of the macromonomer, such as effects of degree of polymerization of macromonomer on reactivity of macromonomers and those of solvent quality[2–9]. However, there have been few reports on characterization of copolymers prepared from macromonomers.

Chemical composition distribution (*CCD*) and molecular weight distribution (*MWD*) of copolymes have been investigated by means of thin layer chromatography and cross fractionation[10–12] using two systems with different efficiencies for composition fractionation. Recently, high performance liquid chromatography[13] of adsorption mode and chromatographic cross fractionation[14] have been demonstrated to be reliable methods. On the other hand, static light scattering (SLS) is known to be a useful characterization method without fractionation for copolymers[15–19]. Physical quantities measured by SLS, i.e. apparent molecular weight and apparent radius of gyration, are influenced by both *MWD* and *CCD*, so that we can obtain information of copolymer characteristics by analysis of SLS. These characterization methods have been applied mostly to statistical copolymers[10–14,18,20].

Teramachi and co-workers[20] have investigated the *CCD* by reversed-phase high performance liquid chromatography for products of radical copolymerization of methacryloyloxyethyl polystyrene macromonomer (M-PS) with methyl methacrylate (MMA) monomer, and found that the graft copolymers obtained had a wide *CCD*, which was compared with the *CCD* predicted theoretically[21,22]. A combination of various methods including SLS has to be powerful to obtain more detailed information on *CCD* and *MWD* of copolymers.

In this study, we used size exclusion chromatography (s.e.c.), ^{1}H n.m.r. spectroscopy and SLS to characterize graft copolymers prepared by radical copolymerization of M-PS with MMA, and investigated the *CCD*, *MWD* and their correlation for size-exclusion-fractionated samples as well as for an unfractionated one. Characterizations for both of the fractionated and unfractionated samples provided detailed information of the *MWD* and *CCD* for the product of radical copolymerization of macromonomer/monomer.

EXPERIMENTAL

Radical copolymerization

Solvents and monomers. MMA was purified by

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distillation under vacuum. Toluene was dried over calcium hydride, and purified by fractional distillation. Methacryloyloxyethyl polystyrene macromonomer was a product of SARTOMER, and was used as supplied. Weight-average molecular weight (M_w) and molecular weight distribution index (M_w/M_n) determined by s.e.c. were 8.52×10^3 and 1.10, respectively. Azobisisobutyronitrile (AIBN) was used as supplied commercially.

Copolymerization. Desired amounts of monomers M-PS and MMA with the initiator AIBN were dissolved in toluene in a glass tube. Subsequently, the tube was sealed under vacuum, followed by being placed in an oil bath at 60°C. After copolymerization, the polymers were separated from the product by precipitation with methanol. The unreacted M-PS in the polymers was removed by precipitation using toluene as solvent and hexane as non-solvent. Concentrations of total monomer and AIBN were 50 and 0.1 wt%, respectively, and the composition of M-PS in the monomers was 25 wt%: the ratio of MMA to M-PS was 3:1 (w/w). Monomer conversions were calculated from the ratio of the s.e.c. peak area of the copolymer to that of the unreacted M-PS with the refractive index increments of polystyrene (PS) and poly(methyl methacrylate) (PMMA) in the eluent tetrahydrofuran[23].

Fractionation

Column fractionation was carried out using a preparative s.e.c. apparatus equipped with two Tosoh 5000H columns (600 mm long, 43 mm i.d.) operated at 40°C. Chloroform was used as eluent at a flow rate of $30\,\mathrm{ml\,min^{-1}}$. At first, the graft copolymer R-2 was fractionated into 14 fractions (RN-1–RN-14). A mixture of the fractions RN-1–RN-6 was further fractionated into 16 fractions (RS-1–RS-16).

Evaluations of average molecular weight by s.e.c. and chemical composition by ^{1}H n.m.r.

M_w and M_w/M_n of fractionated and unfractionated graft copolymers were roughly estimated by s.e.c. with PS standard. Chemical compositions were determined from ^{1}H n.m.r. spectra in deuterated methylene dichloride measured by using a 500 MHz n.m.r. spectrometer (JEOL GSX 500).

Static light scatting

Static light scattering measurements were carried out in three solvents, chloroform (CHF), i-amyl acetate (i-AA) and thiophenol (THP), at 30, 60 and 30°C, respectively. THP and i-AA were dried over calcium hydride, and purified by distillation. CHF with stabilizer was used as supplied commercially. Sample solutions were filtered through Millipore filter into light scattering cells, followed by dilution with dust-free solvent to be of desired concentration. The optical cells were subsequently flame-sealed under vacuum.

The light scattering apparatus was especially designed with a He–Ne laser (wavelength 633 nm) as the light source, using the photon-counting method. Details of the light scattering spectrometer have been described elsewhere[24]. The excess Rayleigh ratio (R_{vv}) for vertically polarized incident and scattered light was extrapolated to zero concentration (c) and zero angle (θ) by Zimm or Berry plots to determine the apparent molecular weight (M_{app}) following the form[15]:

$$(R_{vv}/c)_{c\to 0,\theta\to 0} = KM_{app} \tag{1}$$

where the constant K is given by $K = 4\pi^2 n^2 (\partial n/\partial c)^2/(N_A \lambda_0^4)$, with n being the refractive index of the solvent, N_A the Avogadro constant, $(\partial n/\partial c)$ the refractive index increment and λ_0 the wavelength of the incident beam in vacuum. The concentration c is in weight per volume of solution. The apparent molecular weight for a system with polydispersity in both molecular weight and chemical composition, is described as:

$$M_{app} = \sum_i \frac{c_i}{c} M_i \left(\frac{\partial n}{\partial c_i}\right)^2 \Big/ \left(\frac{\partial n}{\partial c}\right)^2 \tag{2}$$

Here, M_i and c_i represent the molecular weight and the concentration of component i, with the relation $c = \sum_i c_i$. The refractive indices and densities of the solvents were obtained by extrapolation of reported values[25–30] to the desired wavelength and temperature (*Table 1*). Using a differential refractometer (Union Giken RM-102), the refractive index increment was measured for PS, PMMA and the graft copolymer (RN-13) (*Table 2*). The measured value for the graft copolymer was in good agreement with the calculated value from the chemical composition with the refractive index increments of PS and PMMA assuming the additivity of $(\partial n/\partial c)$ (*Table 2*).

Table 1 Densities of solvents and their refractive indices[25–30]

Solvent	T(°C)	Density ($\mathrm{g\,ml^{-1}}$)	Refractive index
THP	30	1.07	1.58
i-AA	60	0.767	1.35
CHF	30	1.47	1.44

Table 2 Refractive index increments ($\mathrm{ml\,g^{-1}}$) of PMMA, PS and RN-13 in three solvents

Sample	THP (30°C)	i-AA (60°C)	CHF (30°C)
PMMA	−0.0962	0.103	0.0524
PS	–	0.205	0.141
RN-13	−0.0757(−0.0794[a])	0.123(0.121[a])	0.0677(0.0679[a])

[a] Calculated from $\langle W\rangle(\partial n/\partial c_{PS}) + (1 - \langle W\rangle)(\partial n/\partial c_{PMMA})$. The average value of PS composition for fractionated samples (RN series) is used for $\langle W\rangle$

RESULTS AND DISCUSSION

Conversions of MMA and M-PS

Conversions of M-PS and MMA in copolymerizations in toluene are shown in *Table 3*. PS composition of the copolymer was calculated from the conversions also shown in *Table 3*. Although the conversion of M-PS is lower than that of MMA for the same reaction time, there exists a linear relationship between them as shown in *Figure 1*. One can also see that the composition is independent of the reaction time, which is equivalent to the linear relationship of conversion. The constant composition independent of the reaction time has already been observed for M-PS/MMA/benzene systems by Tsukahara and co-workers[9]. The result suggests that the difference in conversion between M-PS and MMA does not arise from the difference in reactivity between them, but from an incomplete introduction of

Table 3 Monomer conversion data for copolymerizations of M-PS and MMA at 60°C. MMA:M-PS = 3:1 (w/w). Total monomer concentration = 50 wt%. AIBN concentration = 0.1 wt%

Reaction time (h)	Total monomer conversion (wt%)	Conversion[a] MMA (wt%)	Conversion[a] PS (wt%)	Average PS composition[a]	Copolymer code
11.0	40.8	44.5	28.9	0.174	R-1
19.5	66.7	72.7	48.6	0.182	R-2
27.0	85.2	93.6	59.7	0.173	R-3
48.0	91.9	100	66.9	0.179	R-4

[a] Determined by s.e.c.

methacryloyloxyethyl groups to M-PS. It should be noted that this experimental result does not necessarily indicate that the *CCD* is narrow or has no strong correlation with the *MWD*.

Average chemical compositions of fractionated and unfractionated samples

Table 4 lists the average chemical compositions ($\langle W \rangle$) of the fractionated (RN series) and unfractionated (R-2) samples measured by ^{1}H n.m.r. together with the M_w and M_w/M_n estimated by s.e.c. The value of $\langle W \rangle$ of R-2 is in good agreement with that determined from the conversion listed in *Table 3*.

All fractionated samples have approximately the same chemical composition, being equal to that of the unfractionated original sample. This result indicates that even if the *CCD* exists, there is no strong correlation between the *CCD* and *MWD*. Furthermore, recalling the experimental result that the chemical composition is independent of the reaction time, it follows that the *CCD* and *MWD* scarcely change during the course of copolymerization. In this sense, the azeotropic random copolymerization prevails until at least 67% of the total conversion of R-2.

MWD *and* CCD *of fractionated and unfractionated samples*

The M_{app} of the R-2 and RS series are listed in *Table 5*. In all fractions, M_{app} determined by SLS depends on the solvent. The solvent dependence of M_{app} comes from the presence of heterogeneity in the chemical composition through difference in the refractive index increment between the pure component copolymers, which depends on solvent. For an A–B copolymer, which has polydispersity in molecular weight and chemical composition, M_{app} can be expressed as[15]:

$$M_{app} = M_w + 2Pb + Qb^2 \tag{3}$$

$$P = \sum_i \frac{c_i}{c} M_i \delta W_i \tag{4}$$

$$Q = \sum_i \frac{c_i}{c} M_i \delta W_i^2 \tag{5}$$

$$b = \frac{(v_A - v_B)}{v_0} \tag{6}$$

where δW_i is the deviation of A-composition W_i of the type i molecule from the average composition $\langle W \rangle$, i.e. $\delta W_i = W_i - \langle W \rangle$, and v_A, v_B and v_0 are the refractive index increments of pure polymers A, B and the copolymer. Parameters P and Q are related to the heterogeneity in chemical composition: P represents the correlation strength between the *CCD* and *MWD*, while Q primarily represents the broadness of the *CCD**. In the present cases, the respective solvents have different b values, so that the solvent dependence of M_{app} directly indicates the presence of heterogeneity of chemical composition in the fractionated samples. Accordingly, the unfractionated samples must have heterogeneity as well, although M_{app} has a very weak solvent dependence. It is concluded for the copolymerization products as a whole that heterogeneity in both *MWD* and *CCD* exists, although there is no strong correlation between *CCD* and *MWD*.

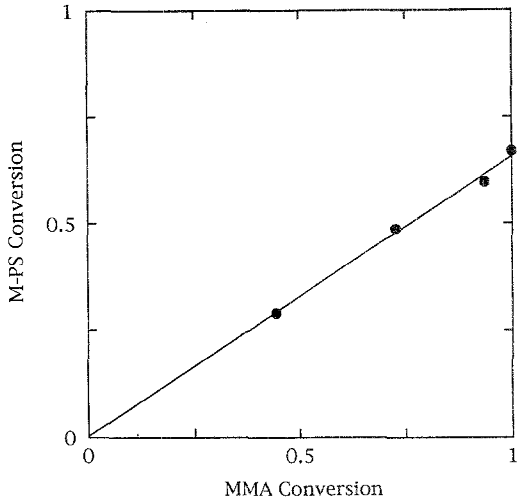

Figure 1 Monomer conversions for copolymerization of M-PS with MMA in toluene at 60°C

Figure 2 shows semi-log plots of M_{app} against b ($\equiv \{v_{PS} - v_{PMMA}\}/v_{copolymer}$) for RS series, demonstrating that M_{app} varies with b in the same way in all fractions. This similarity in the log M_{app} *versus* b plots indicates that the parameters P and Q reduced by M_w are common, and suggests a similarity in the *CCD* and *MWD* for all fractions, as shown below. Dividing equation (3) by M_w, one has:

$$\frac{M_{app}}{M_w} = 1 + 2\tilde{P}b + \tilde{Q}b^2 \tag{7}$$

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*If CCD is monodisperse, i.e. if the copolymer is homogeneous in chemical composition, then one has $P = Q = 0$. If there exists no correlation between *CCD* and *MWD*, then $P = 0$ and $Q = M_W \langle (W - \langle W \rangle)^2 \rangle$

Table 4 Average PS weight fraction $\langle W\rangle$, M_w and M_w/M_n of fractionated and unfractionated samples

Sample	$\langle W\rangle$(wt%)^a	$M_w(\times 10^{-6})^b$	$M_w/M_n{}^b$
Unfractionated			
R-2	0.188	0.652	2.81
Fractionated			
RN-2	0.188	2.82	1.36
RN-4	0.191	1.61	1.32
RN-7	0.170	0.752	1.33
RN-10	0.173	0.460	1.21
RN-12	0.163	0.253	1.19
RN-14	0.167	0.145	1.19

[a] Measured by ^{1}H n.m.r.

[b] Measured by s.e.c. with PS equivalent

Table 5 Apparent molecular weight $M_{app}(\times 10^{-6})$ of fractionated and unfractionated samples in three solvents measured by static light scattering

Sample	THP (30°C)	i-AA (60°C)	CHF (30°C)
Unfractionated			
R-2	3.55	3.49	3.60
Fractionated			
RS-7	5.83	16.8	24.7
RS-9	2.69	7.98	11.6
RS-11	1.42	4.67	6.58
RS-16	1.00	2.62	3.93

$$\tilde{P} = \sum_i \frac{c_i}{c} \frac{M_i}{M_w} \delta W_i \qquad (8)$$

$$\tilde{Q} = \sum_i \frac{c_i}{c} \frac{M_i}{M_w} \delta W_i^2 \qquad (9)$$

The similarity of log M_{app} *versus* b plots implies a similarity in the *CCD* and *MWD*. In other words, the two-dimensional distribution function $C_i/C = f_c(W_i, M_i/M_w)$ is approximately common for the fractionated samples RS-7, 9, 11 and 16. Superposing the log M_{app} *versus* b plots onto those of RS-7 by shifting along the log M_{app} axis, we obtained a master curve for the reduced plots of $M_{app}/[M_w/M_w(RS\text{-}7)]$ against b, as shown in *Figure 3*. By fitting equation (7) to all the points of the master curve and from the shift factor $\log\{M_w/M_w(\text{RS-7})\}$, one could determine $\tilde{P}$, $\tilde{Q}$ and M_w of each fraction, which are shown in *Table 6*. On the other hand, for unfractionated sample R-2, M_w and $\tilde{Q}$ were determined by fitting of equation (7), as illustrated in *Figure 4*, assuming that $P = 0$ since there is almost no

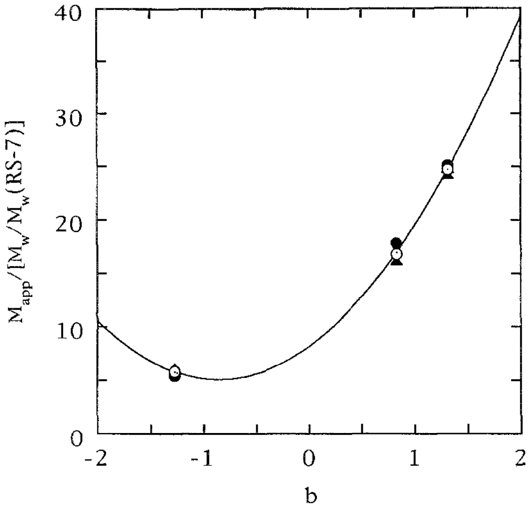

Figure 3 Plots of $M_{app}/[M_w/M_w(\text{RS-7})]$ *versus* b for the fractionated samples (RS series). Solid line was obtained by fitting equation (7) to all the points. Symbols are the same as in *Figure 2*

Table 6 Molecular weight M_w and characteristic parameters $\tilde{P}$ and $\tilde{Q}$ for *CCD* and *MWD*

Sample	$M_w(\times 10^{-6})$	$\tilde{P}$	$\tilde{Q}$
Unfractionated			
R-2	3.4	(0)	0.026
Fractionated			
RS-7	8.2		
RS-9	3.8	0.44	0.51
RS-11	2.1		
RS-16	1.3		

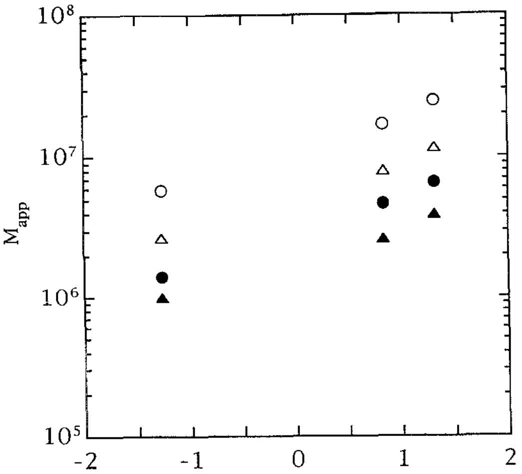

Figure 2 Semi-log plots of apparent molecular weight M_{app} *versus* b for the fractionated samples (RS series). Solvents are THP, i-AA, CHF from left to right. (○) RS-7; (△) RS-9; (●) RS-11; (▲) RS-16

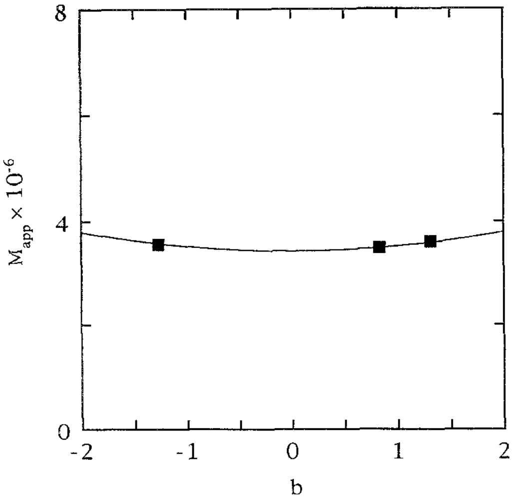

Figure 4 Plot of M_{app} *versus* b for the unfractionated sample (R-2). Solid line was obtained by fitting equation (7) to the experimental data with $P = 0$

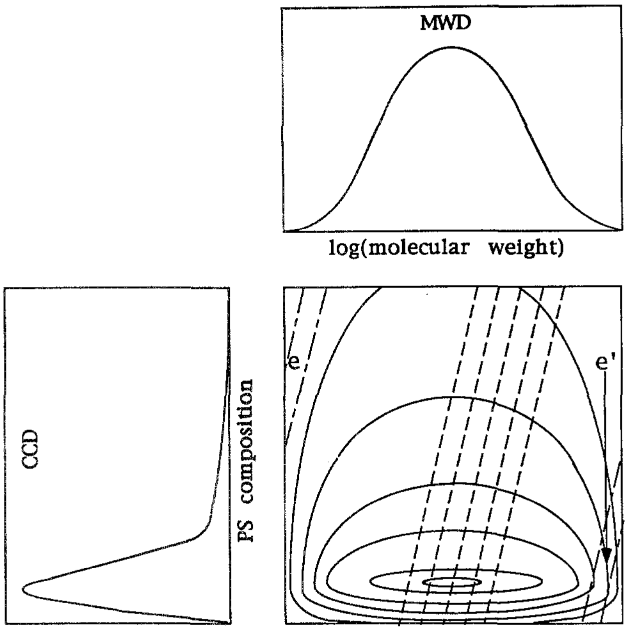

Figure 5 Schematic illustration of a supposedly two-dimensional distribution function for *CCD* and *MWD*. See the text for the description of regions e and e'

correlation between the *CCD* and *MWD* in the unfractionated sample. The obtained values are listed in *Table 6*.

The small value of $\tilde{Q}(= 0.026)$ for R-2 shows that the *CCD* is not so wide in the unfractionated sample. The present results of $\tilde{P}$ and $\tilde{Q}$ of R-2 are comparable to those of anionically polymerized copolymers. For most cases of PMMA-*block*-PS[16,17] or PMMA-*graft*-PS[19], absolute values of $\tilde{P}$ and $\tilde{Q}$ are smaller than 0.1, and for PMMA-*stat*-PS[19], $\tilde{P} = 0$ and $\tilde{Q} = 0.16$.

In contrast with the unfractionated sample, the fractionated samples have large values of $\tilde{P}$ and $\tilde{Q}$. A large positive $\tilde{P}$ value (0.44) indicates a strong correlation between the *CCD* and *MWD* such that the higher molecular weight fractions have the larger composition of grafted PS [see equation (4)].

Interpretations and concluding remarks

The present results can be summarized as follows. Unfractionated copolymerization products of M-PS and MMA have polydispersity in both *CCD* and *MWD*, where *CCD* and *MWD* are not correlated with each other. In contrast with the as-polymerized sample, size-exclusion-fractionated samples show a strong *CCD–MWD* correlation, having large values of P and Q, while the distribution functions $c_i/c = f_c\ (W_i,\ M_i/M_w)$ are almost the same in all fractions. The results are consistently explicable in the following way.

A supposedly two-dimensional distribution function for *CCD* and *MWD* is illustrated in *Figure 5*, where *CCD* and *MWD* are independent. The polymer-chain dimension of long-branched polymers such as the present graft polymer decreases with increasing branch density at the same molecular weight[31,32], so that the molecular weight increases with increasing branch density at the same chain dimension. Consequently, a fraction separated by size exclusion, i.e. by difference in polymer-chain dimension, must show a strong correlation between the molecular weight (*MW*) and the branch density, as is observed here, where the branch density is equivalent to the chemical composition (*CC*). The *CC–MW* distribution of fractionated samples is illustrated by the area cut off by broken lines in *Figure 5*. The higher molecular weight (M_i) fraction in the fractionated one has the larger PS composition. Since the average *CC*, and accordingly the *CC* at the peak position is located at a low PS composition (~ 0.2), the higher M_i fraction in the fractionated sample has a larger δW by the definition of Q, resulting in a large Q value [equation (5) or (9)], whereas the Q value for the as-polymerized sample is much smaller. Here, it should be noted that Q is primarily determined by the width of *CCD*, but also affected by the correlation of the *CCD* and *MWD*, and that a large Q value does not always imply a broad *CCD*.

The similarity in $f_c\ (W_i,\ M_i/M_w)$ among the fractionated samples may primarily come from the non-correlation between the *CCD* and *MWD* of the original sample. Also, it is responsible for the fact that the fractionated samples were cut off from a middle portion of the *MWD* of the original sample. If a fraction (e or e') is separated from the edge of the distribution (*Figure 5*), the *CCD* of this fraction must be different from those of the present fractions. Even the fractions from the middle portion may not be exactly the same as each other. However, this sort of effect is very weak in the fractions around the middle of the distribution, so that the similarity in the distribution function approximately holds for the present fractionated samples.

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