Study of Linear Poly(*p*-chlorostyrene)—Diluent Systems. II. The Conformations in Poly(*p*-chlorostyrene)—Endothermic Solvent (ethylbenzene) and Poly(*p*-chlorostyrene)— Exothermic Solvent (*t*-butyl acetate) by Light and X-ray Small-Angle Scatterings

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ABSTRACT: The conformations of poly(*p*-chlorostyrene) (PPCS) in endothermic solvent (ethylbenzene, $\theta_U = -14.7^\circ\text{C}$) and in exothermic solvent (*t*-butyl acetate, $\theta_L = 65.4^\circ\text{C}$) were determined by light and x-ray small-angle scattering on the condition that the molecular sizes were equal as a whole (*i.e.*, at 30°C). θ_U is the theta temperature of the endothermic system and θ_L that of the exothermic one. The values of the radius of gyration $\langle s^2 \rangle_z^{1/2}$ and the second virial coefficient A_2 obtained from light-scattering measurements were 2.23×10^{-6} and 5.56×10^{-5} for PPCS—ethylbenzene system, and 2.18×10^{-6} and 5.55×10^{-5} for PPCS—*t*-butyl acetate system, respectively.

In X-ray scattering measurements, both the pure solvent (after the absorption correction and the corresponding monomer solution which had the same numbers of chlorine atoms as the PPCS solution, were employed as substances for the standard subtraction to obtain a excess scattering from the solution. Differences between the two subtraction methods appeared at angles larger than about 3° . 1 and 2% solutions were measured to take into account of the concentration dependences. The effect on the scattering curve was negligible at angles more than 0.4° . The smearing effect of the slit was analyzed according to the procedure of Schmidt. The determination of the persistence length a was possible after elimination of the cross-section factor. The values of persistence length a and the radius of gyration of cross-section factor R_q were comparable with those of polystyrene and its derivative in the published data according to Kratky, *et al*. The a values obtained from X-ray small-angle scattering were somewhat smaller than the values calculated from the hydrodynamic length L and the radius of gyration $\langle s^2 \rangle_z^{1/2}$ assuming a Gaussian coil. The values of a and R_q seem to be little affected in both endothermic and exothermic systems. However, differences of the conformations in the two systems appeared in the rod-like region of the scattering curve.

KEY WORDS Poly(*p*-Chlorostyrene) / Endothermic Solvent / Ethylbenzene / Exothermic Solvent / *t*-Butyl Acetate / X-Ray Small-Angle Scattering / Persistence Length / Cross-Section Factor / Subtraction Effect /

The X-ray small-angle scattering curve for an ideal worm-like chain molecule, whose cross-

section is negligible in comparison with the length, has been separated into three parts by Kratky, Porod, Peterlin and others.¹⁻⁷ (1) The first makes the major contribution at very small angles due to the coil conformation as a whole and is approximated by a Gaussian curve. (2) The second is due to the effect of sections of

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the molecule which represent the random arrangement of scattering masses. This part of the scattering appears at somewhat larger scattering angles and is given by $1/(2\theta)^2$ using the scattering angle 2θ . (3) The contribution from the smaller sections of the molecule appears gradually at larger angles, and approaches to that of a rod, $1/(2\theta)$. Plotting $I(2\theta)^2$ against (2θ) , the second region becomes a plateau and the third is a straight line passing through the origin which means that the product is proportional to the scattering angle, where I is a de-smear scattering intensity. The value $(2\theta)^*$ for the intersection of these two straight line gives an transition point from which the persistence length a is derived.

A finite cross-section in a real macromolecule brings the characteristic change in the second and third parts of the X-ray small-angle scattering.⁸⁻¹² In this case, a transition point is given by a discontinuity of the differential coefficient of the scattering curve and the value of the persistence length calculated using the discontinuity is equal to the value obtained through the correction of the finite cross-section.¹⁶

Furthermore, Kratky, Kirste, and their co-workers have clarified that the other factors, such as tacticity (configuration),¹³ solvent effect,¹⁴ subtraction method,^{2,15,16} and concentration effect^{8,16} also have effects on the form of the scattering curve in the same regions.

On the other hand, as shown in a previous paper,¹⁷ both the entropy parameter ϕ_1 and the enthalpy parameter κ_1 are positive in the endothermic system, while both are negative in the exothermic system. The dissolution behavior in each system is different; that is, the enthalpy plays the major role in the endothermic system, whilst the entropy does in the exothermic one.²³ This suggests that there is an appreciable degree of local order of pendant groups on a polymer chain in the latter system.²⁴

In this paper, the conformations of poly(*p*-chlorostyrene) (PPCS) both in endothermic solvent (ethylbenzen, $\theta_U = -14.7^\circ\text{C}$) and in exothermic solvent (*t*-butyl acetate, $\theta_L = 65.4^\circ\text{C}$) were determined by light and X-ray small-angle scattering on the grounds that the molecular sizes were almost equal as a whole. The concentration effect, the subtraction method, the

influence of the stability of the X-ray apparatus and the slit smearing effect have been also discussed as attendant problems. The results were compared with the recent data on polystyrene and its halogen derivative reported by Kratky, *et al.*^{16,18}

THEORETICAL

Persistence Length a

According to Heine, Kratky, and Roppert,⁷ the persistence length a is related to the position of the transition point $(2\theta)^*$ by

$$a = 2.3\lambda/2\pi(2\theta)^* = 2.3/s^* \quad (1)$$

where λ is the wavelength. The transition point $(2\theta)^*$ can be also obtained from the plot of $I(2\theta)$ against $1/(2\theta)$ according to Zipper, *et al.*¹⁹ Zipper, *et al.*, also gave another method for ascertaining the persistence length from the smeared curve,¹⁹ which was by plotting $[-d\bar{I}/d(2\theta)]$ against (2θ) with a smeared scattering intensity $\bar{I}$. In this plot, a discontinuity of the derivative gives a transition point.

Radius of Gyration of the Cross-Section R_q

According to Kratky, *et al.*,^{18,20} a scattering curve for a rod is given by

$$I/I_q = 1/\theta \quad (2)$$

where I_q is the so-called cross-section factor, from which the cross-section size is determined. If the cross-section is, to a certain extent, isotropic and I_q does not greatly differ from the Gaussian form (Guinier's approximation on a cross-section), the cross-section factor is given by

$$I\theta = I_q \exp(-KR_q^2\theta^2) \quad (3)$$

Equation 3 indicates that the radius of gyration of the cross-section R_q is obtained from the inclination $(\tan \alpha)_0$ in a plot of $\log I_q$ against θ^2 at low angles, *i.e.*,

$$R_q = [-(\tan \alpha)_0/K]^{1/2} \quad (4)$$

using constant $K = 16\pi^2/2\lambda^2$.

Relations among Hydrodynamic Length L , Radius of Gyration $\langle s_0^2 \rangle^{1/2}$ (or Mean Square End-to-End Distance $\langle r_0^2 \rangle^{1/2}$) and Persistence Length

For sufficiently long chains, the following relation holds well:^{2,22}

$$\lim_{L \rightarrow \infty} 3\langle s_0^2 \rangle = La, \quad \lim_{L \rightarrow \infty} \langle r_0^2 \rangle = 2La \quad (5)$$

where the hydrodynamic length L is the fully extended length of the real chain.

EXPERIMENTAL

Materials

The methods used for the synthesis of *p*-chlorostyrene are the same as in the previous paper.¹⁷ PPCS was prepared by radical polymerization for about two days using α, α' -azobisisobutyronitrile as the initiator at 60°C and fractionated into five fractions. The middle fraction was used in this work. The purification of the solvents was described in the previous paper.¹⁷

Measurements

The technical details for light-scattering and viscosity measurements have been described in the previous paper.¹⁷

The measurements of X-ray small-angle scattering were performed with a Rigaku Denki X-ray generator with a Philips line-focus copper target tube at 35 kV and 20 mA. The monochromatization was accomplished by a scintillation counter in combination with an impulse height discriminator and a Ni filter to separate Cu-K α (1.54 Å). Two types of slit systems were employed: one was a modified U slit made by Rigaku Denki Co., Ltd, which has been used at the lower angles from 0.2 to 3.6°, and the other was an adequately long conventional slit system for the larger angles up to 6°.

The sample cell was made from a 2-mm thick brass plate with a rectangular window (5 mm $\times$ 25 mm), to both sides of which were fixed thin mica films (*ca.* 100 μ thick) using Syanobond 5000. A constant volume of a solvent or a solution was inserted and withdrawn by an injection-syringe through the small screwed hole made in the cell. This hole was precisely closed with a small bolt when measuring. The sample holder held a pair of cells, one of which was a reference cell enclosing a pure solvent as a standard and the other was used for solutions. The sample holder was set on a sliding rail and details are shown in Figure 1. The measurement was performed alternately for each cell by sliding the holder. The sample was kept at $30.0 \pm 0.2^\circ\text{C}$ by circulating thermostated water to the cell housing. At least 10^4 pulses were recorded for each measurement, which corresponded to a statistical error of $\pm 1\%$ (see the later section and Table II).

In order to obtain the real scattering of the polymer molecules in solution, two methods were applied according to Kratky, *et al.*¹⁶ One was the method in which the scattering curve originating from the solution of the monomer (it contained an equal number of heavy atoms per unit volume) was subtracted from the scattering curve of the solution of the polymer (subtraction method I). *p*-Chlorotoluene instead of *p*-chlorostyrene was employed, as this was practically identical in the scattering effects. The other was the method in which the scattering of the pure solvent was subtracted

Figure 1. X-ray small-angle cell: A, direct beam; B, circulating pass of thermostated water; C, sliding rail; D, cell holder; E, cell; F, mica window; G, tefton packing; H, cell holder; I, board of Bakelite; J, a small screwed hole (0.6 mm in diameter) for inserting and withdrawing sample.

from the scattering of the solution of the polymer after the absorption effect was corrected (subtraction method II). The absorption correction was carried out by using the Cu-K α line which was monochromatized by the crystal of Al in addition to Ni filter at the wide angle and changing both the thickness and the concentration of the sample, since the absorption coefficient of X-ray in Ni filter strongly depend on the wavelength.²⁵ Although both subtraction methods are not introduced on a theoretical basis, a more suitable procedure has not been found at the present time.^{15,16}

RESULTS AND DISCUSSION

Viscosity and Light Scattering

The dependence of intrinsic viscosity $[\eta]$ on the temperature is shown in Figure 2. Figure 2 shows that the $[\eta]$ of PPCS—ethylbenzene system increases with increasing temperature, whilst that of PPCS—*t*-butyl acetate decreases with increasing temperature. The values of $[\eta]$ for the two systems are almost equal at 30°C, which means that the excess free energy in both of the systems is almost the same when the unperturbed dimensions are not affected by the solvent.

The Zimm (root) plots for two systems are shown in Figures 3 and 4. The results of the viscosity and light scattering measurements at 30°C are compiled in Table I. In Table I, k' ,

Figure 2. Plot of intrinsic viscosity against temperature for PPCS—ethylbenzene (open circles) and PPCS—*t*-butyl acetate (filled circles).

Table I. Light scattering and viscosity data at 30°C

Parameters	PPCS—Ethylbenzene	PPCS— <i>t</i> -Butyl acetate
$[\eta]$	0.637	0.640
k'	0.53	0.47
M_w	53.3×10^4	59.7×10^4
A_2	5.56×10^{-5}	5.55×10^{-5}
$\langle s^2 \rangle_z^{1/2}$	2.23×10^{-6}	2.18×10^{-6}
ϕ	2.17×10^{21}	2.27×10^{21}

M_w , A_2 , $\langle s^2 \rangle_z^{1/2}$, and ϕ denote the Huggins constant, the weight-average molecular weight, the

Figure 3. Plot of $(Kc/R\theta)^{1/2}$ against $\sin^2(\theta/2) + 10^3 c$ for PPCS—ethylbenzene at 30.0°C.

Figure 4. Plot of $(Kc/R\theta)^{1/2}$ against $\sin^2(\theta/2) + 10^3c$ for PPCS—*t*-butyl acetate at 30.0°C.

second virial coefficient, the *z*-average root mean-square radius, and the universal constant, respectively. From the comparison between the Φ values for the two systems and the theoretical value calculated from consideration of the molecular weight distribution, it is deduced that the $\langle s^2 \rangle_z^{1/2}$ values obtained from the light scattering measurement are reasonable. The *a* values obtained from eq 5 by using the values of $\langle s^2 \rangle_z$ from light scattering measurements and *L* (as

calculated below are 14.6 Å for PPCS—ethylbenzene and 13.9 Å for PPCS—*t*-butyl acetate, respectively. *L* was calculated from $L = (M_w/M_0) \times 2l \sin(\theta/2)$ with $M_w = 56.5 \times 10^4$ (the average value of two systems), $M_0 = 138.5$, $l = 1.54$ Å and $\theta = 109.5^\circ$.

Small-Angle Measurements

Counting Error Analysis. As shown in Figures 5 and 6, the difference between the scattering intensity of the solution and that of the solvent

Figure 5. Smeared scattering curves $\tilde{I}$ of PPCS—ethylbenzene solution at 30.0°C (2%).

Figure 6. Smeared scattering curves $\tilde{I}$ of PPCS-*t*-butyl acetate solution at 30.0°C (2%).

(or monomer solution) at higher angles is so small that the difference can only be distinguished by highly accurate measurements. In order to check the stability of the present apparatus, the counts per minute against a incident beam through a Ni filter were measured over a long period. After a lapse of three hours after the X-ray generator began working, the counts magnitude became almost constant at $ca. 2 \times 10^4$ counts/min. However, the fluctuation was slightly more than the expected statistical error depending on the time of measurement. This suggested that the present apparatus was not in the same condition over a long period of time, whilst it was stable for a short period. Accordingly, in

the present measurement, one measurement run was performed within a period short enough to keep the stability of the apparatus constant and the same measurement was repeated until the fluctuation in the integrated value of the corresponding points in each run was within the statistical error of 1%. In addition to this procedure, the observed values in each run were corrected by comparing them with the average value of the counts measured at a fixed angle before and after each run. However, it has been found that the counts obtained by such careful treatment agreed with the counts obtained by the simple average (without correction at a fixed angle) within ± 0.2 counts/min. after the dif-

Table II. Scattering intensity in pure ethylbenzene at 30°C and $2\theta=1^\circ$ (count/min)^a

115	103	96	89	95	99	93	108	109	109	101.6/100.2	101.4
114	106	106	109	94	109	104	101	97	89	102.9/100.9	102.0
92	93	96	103	96	102	105	102	103	108	100.0/101.3	98.7
96	96	112	87	99	94	97	98	98	105	98.2/102.4	95.9
112	112	106	95	106	117	113	100	101	102	106.4/107.9	98.6
105	110	109	112	104	115	111	101	106	107	108.0/108.7	99.4
113	97	114	111	116	105	105	113	105	114	109.3/110.1	99.3
107	112	109	107	107	103	111	118	97	107	107.8/111.0	97.1
118	114	105	112	109	109	100	107	96	101	107.1/107.4	99.7
117	113	111	113	106	102	111	105	118	116	111.2/109.1	101.9
Average											99.4

^a Mean value, 99.4 count/min; probable error, ± 1.3 count/min.

Figure 7. Plot of $(\tilde{I}/c)$ against 2θ on double logarithmic scale of smeared scattering curves of PPCS—ethylbenzene: open circles, subtraction method I; filled circles, subtraction method II.

Figure 8. Plot of $(\tilde{I}/c)$ against 2θ on double logarithmic scale of smeared scattering curves of PPCS—*t*-butyl acetate: the significance of the symbols is the same as in Figure 7.

ference between the absolute values of both counts was adjusted. The integrated value of

each point was more than 10^4 counts. An example is shown in Table II, which indicates that the counting error deduced by means of the above treatment reaches 1.3 counts/min. Figures 5 and 6 were the results obtained through this treatment.

Comparison of Subtraction Methods. The smeared, real scattering curves of PPCS—ethylbenzene and PPCS—*t*-butyl acetate in the plot of $(\tilde{I}/c)$ against 2θ on double logarithmic scale are shown in Figures 7 and 8. The open circles show the result obtained by applying the subtraction method I and the filled circles are these obtained by applying method II. The concentration dependence is not observed in the range of angles 0.4 – 6.0° , which is considered to be the transition region, as in the recent results by Kratky, *et al.*^{16,18}

The real scattering curves obtained by both subtraction methods coincide with each other in the small angle region as shown in Figures 7 and 8. This region reflects the effect of the dimensions of the macromolecule as a whole and it is not influenced by small molecules and the small parts of macromolecules. This is the reason why both the subtraction methods gave the same results. The two scattering curves are gradually separated with increasing angle. The range of higher angles is clearly influenced by the subtraction method, although the relative merits of both subtraction methods is not clear on the basis of the present theory of X-ray small-angle scattering.

In the present work, the real scattering curves have been desmeared to the pinhole slit system by Schmidt's procedure²¹ by assuming that the beam is infinitely long. This treatment is considered to give a result adequate for the comparison of the scattering curves of both the endothermic and exothermic systems which is the main object of this work. In the present work, the same slit correction was applied to the results obtained by both subtraction methods unlike the case of Kratky, *et al.*¹⁶

Comparison of Cross-Section Factors and Persistence Lengths in Both Systems

The desmeared scattering curves of the both systems are shown by the solid lines in Figures 9 and 10, respectively. In these Figures, $I(2\theta)^2$

Figure 9. Plot of $I(2\theta)^2$ against (2θ) for determination of persistence length of PPCS—ethylbenzene system for subtraction methods I and II: dotted curves, scattering curves after removal of the cross-section factor.

Figure 10. Plot of $I(2\theta)^2$ against (2θ) for determination of persistence length of PPCS—*t*-butyl acetate system for subtraction method I and II: dotted curves, scattering curves after removal of the cross-section factor.

Figure 11. Guinier plot of cross-section factors $I(\theta)$ of PPCS—ethylbenzene for subtraction method I and II.

Figure 12. Guinier plot of cross-section factors $I(\theta)$ of PPCS—*t*-butyl acetate for subtraction methods I and II.

Figure 13. Plot of $I(2\theta)$ against $1/(2\theta)$ for determination of persistence length of PPCS—ethylbenzene for subtraction methods I and II.

Figure 14. Plot of $I(2\theta)$ against $1/(2\theta)$ for determination of persistence length of PPCS—*t*-butyl acetate for subtraction methods I and II.

Figure 15. Plot of $[-d\tilde{I}/d(2\theta)](2\theta)$ against 2θ for determination of persistence length of PPCS—ethylbenzene (denoted by EB and EB—PCT) and PPCS—*t*-butyl acetate (denoted by *t*BA and *t*BA—PCT) from the smeared scattering curves for subtraction methods I and II.

is plotted against 2θ . As seen in these Figures, the shape of the curves obtained through the same subtraction method in both systems is almost the same as each other. However, the scattering curves in both systems differ from the theoretical curve for a very long, infinitely thin worm-like chain and resemble qualitatively the theoretical curves⁸⁻¹² obtained through consideration of the effect of the cross-section of a main chain.

The cross-section factors are evaluated from eq 3 according to Kratky, *et al.*,¹⁸ as shown in Figures 11 and 12. The scattering curves divided with these factors are also shown by broken lines in Figures 9 and 10. These corrected curves apparently show the typical transition length. The persistence length can also be evaluated by using the plot of $I(2\theta)$ against $1/(2\theta)$ as shown in Figures 13 and 14. Moreover, the persistence length a can be determined from the discontinuity of the derivatives mentioned above even when using the smeared scattering curve as shown in Figure 15. The values of the persistence length a and the radius of gyration of the cross-section R_q are compiled in Table III. Agreement among the values of persistence length are good in spite of the different evaluations. The error in the a value obtained by the third method is somewhat larger because of the differential operations. The corresponding values for the homologous

Table III. Persistence length a and radius of the cross section R_q

System	Subtraction	$a, \text{\AA}^a$		$R_q, \text{\AA}$	
PPCS—ethylbenzene	I	11.6 ^b	13.3 ^c	11.9 ^d	4.9
	II	11.9 ^b	13.3 ^c	12.8 ^d	5.5
PPCS— <i>t</i> -butyl acetate	I	12.0 ^b	13.0 ^c	13.6 ^d	5.1
	II	12.0 ^b	13.0 ^c	14.5 ^d	5.6
POBS—benzene	I	16.5 ^b			4.56
	II	16.5 ^b			4.35
PS—cyclohexane	II	12.2 ^b			4.1

^a $a = 2.3\lambda/2\pi(2\theta)^*$, $\lambda = 1.54 \text{\AA}$

^b Values calculated from the transition point of the plot of $I(2\theta)^2$ against 2θ .

^c Values calculated from the discontinuity of the plot of $I(2\theta)$ against $1/(2\theta)$.

^d Values obtained from the discontinuity of the plot of $[-d\tilde{I}/d(2\theta)](2\theta)$ against 2θ .

polymer series are quoted from the papers of Kratky, *et al.*,^{16,18} for comparison. a and R_q values for PPCS are comparable to those of polystyrene (PS) and poly(*o*-bromostyrene) (POBS) and the R_q values of PPCS is slightly larger than the others. This probably will have reflected the difference of atoms in the side groups in the *para*-position. However, it will be necessary to investigate the effects of the solvent and the temperature on a and R_q values in order to discuss the corresponding values of

these homologous polymer series in more detail. The a values obtained from X-ray small-angle scattering are somewhat smaller than the values calculated from the hydrodynamic length L and radius of gyration $\langle s^2 \rangle_z^{1/2}$ assuming a Gaussian coil. A small disagreement between the obtained a values may be natural even if the theory connecting L and $\langle s^2 \rangle_0^{1/2}$ is correct, because the $\langle s^2 \rangle_z^{1/2}$ at 30°C is employed in the present calculation instead of $\langle s^2 \rangle_0^{1/2}$. These a and R_g values do not seem to be affected appreciably by whether the system is endothermic or exothermic. However, the details of the scattering curves are different as shown in Figures 9–12. The rod-like part in the system of PPCS—ethylbenzene in Figure 11 is about 1.5 to 2 times longer than that of PPCS—*t*-butyl acetate in Figure 12. This discrepancy is probably due to the differences in the conformations in the submolecular range of both systems, because there is an appreciable degree of local order of a pendant group on a polymer chain in the exothermic system 24. The courses of the side of small angles in both curves are different as shown in the plot of Figures 9 and 10, although the forms of the curves at the same angles are almost the same in the plot of Figures 7 and 8. It is not clear whether this difference as seen in Figures 9 and 10 is due to the difference in the conformations of the polymer as a whole or to the incorrectness of the extrapolated value to zero angle used in the desmearing method. Further investigation of X-ray scattering over the range of even smaller and higher angles will be necessary to clarify the detail of the conformations in both systems.

CONCLUSIONS

The following results are obtained from the study of PPCS—ethylbenzene and PPCS—*t*-butyl acetate systems:

(1) The values of persistence length a and radius of gyration of the cross-section R_g do not strongly depend on whether the endothermic system or the exothermic one is used in the condition of equal molecular sizes as a whole. However, the difference between the conformations in these two systems appears in the rod-

like part of the chain molecule. a and R_g values obtained for PPCS are comparable to those of PS and POBS, which are given by Kratky, *et al.*

(2) The subtraction methods are noticeably different at the larger angles.

(3) The concentration effect on the scattering curves in the range of concentrations used in this work is almost negligible at angles above 0.4°.

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