

## Poly(n-octadecyl acrylate)의 용액물성 및 분자형태에 관한 연구

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## Dilute Solution Properties and Molecular Conformation of Poly(n-octadecyl acrylate)

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**Abstract:** The dilute solution properties and conformational characteristics of poly(n-octadecyl acrylate) have been studied. The comb-like polymer obtained by radical polymerization of octadecyl acrylate was fractionated by both methods of fractional precipitation and fractional solution. The average molar mass and the polydispersity index for the polymer fractions studied were found to be in the range of  $0.62\text{--}80.9 \times 10^2$  kg/mol and 1.12–1.76, respectively. The solubility parameter found for the polymer was  $8.65 \text{ (cal.cm}^{-3})^{1/2}$ . A phase equilibrium experiment yielded the  $T_\theta$  as  $11.5^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ . The unperturbed chain dimension of the polymer was calculated by using intrinsic viscosity data. The conformational characteristics under unperturbed state were analyzed by an application of theories for both the flexible chain and semi-flexible worm-like model. The results indicate that the flexibility of the backbone chain of the polymer is reduced to an extent that can be comparable with a typical semi-stiff chain.

### INTRODUCTION

Since the first appearance of polymer containing long branches of same size in its backbone chain, a considerable weight of study has been given for the evaluation of structure-properties relations of this type of polymers<sup>1-5, 7, 8</sup>. With respect to this so called uniform comb-like polymer, however, few studies have been reported so far on the determination of unperturbed molecular dimension or the calculation of molecular parameters pertaining to the space-filling properties of polymer molecules.

The intention of this work is to examine the conformational behavior of poly(n-octadecyl acrylate) (PODA) in dilute solution. The reason for this polymer being selected lies on the characteristics which are especially attractive for the study of conformational properties. The long n-alkyl side chain attached to the ester group in each monomer unit is considered to give an effect to the conformation of main chain.

In 1966, a relationship between the intrinsic viscosity and molar mass for the foregoing polymer was once established by Jørdon, Jr. and

coworkers<sup>6</sup>, but they did not make any kind of evaluation of molecular parameters for the unperturbed chain dimension. In the meantime, a systematic research on the effect of size and structure of side groups on the conformation of polymer molecules and the equilibrium rigidity of their main chain has been carried out by Tsvetkov et al.<sup>7</sup> for the homologous series of poly(alkyl acrylate) and poly(alkyl methacrylate), concluding that the increase in the length of the side substituents leads to a two- to fourfold increase in the equilibrium rigidity of the backbone chain. Similarly, Zhongde and coworkers<sup>8</sup> have examined the influence of n-alkyl side chain length on the unperturbed chain dimensions of poly(alkyl metacrylates) by making comparisons of values of characteristic ratios up to poly(docosyl methacrylate). Following their results, interactions between lateral chains caused the increase in characteristic ratio as a function of side chain length. However, those studies conducted so far are rather limited on the theory of flexible coil model for the analysis of their results.

This paper presents our experimental findings pertaining to those molecular parameters related to the chain dimension and conformation of atactic PODA. An emphasis is given to the interpretation of the experimental results in terms of both theories for the flexible chain and semi-flexible worm-like model.

## EXPERIMENTAL

**Polymer** The polymerization of n-octadecyl acrylate, prepared by a known procedure<sup>11</sup>, was carried out in a sealed glass ampoule under reduced pressure (40 mmHg) with 2,2-azo-bis(isobutyronitrile) as the initiator, in a water bath controlled at 60°C for 12 to 24 hrs.. The polymer obtained, a fiber form of solid, was purified by repeated dissolution and precipitation followed by drying under reduced pressure. The conversion of n-octadecyl acrylate into polymer was 82.3%. Data from IR analysis were in good agreement with those expected from the structure.

**Fractional Precipitation** The precipitation of

polymer from the dilute solution was carried out by a conventional procedure starting with 0.5% of toluene solution. An addition of non-solvent up to the first cloudiness was followed by thermal dissolution and reequilibration at  $25 \pm 0.1^\circ\text{C}$ . After settling overnight, the dilute phase was separated from the concentrated phase. The fraction thus obtained was successively purified and dried under reduced pressure. In this manner, 11 fractions were obtained. The non-solvent used was methanol.

**Fractional Solution** Those polymer samples selected for the measurements of dilute solution properties were imposed to refractionation by column extraction to minimize the polydispersity in molar mass. The sample to be fractionated was firstly deposited on the surface of glass beads (dia. 0.5 mm) in a column containing non-solvent only, and then successive elution was carried out with a liquid of increasing solvent power, by forcing the fluid eluants to pass through the column upward with constant flow rate at 25°C. The polymer fractions extracted were recovered from the collections of eluted fractions.

**Viscometry** The dilute solution viscosity was measured in an Ubbelohde viscometer where pure solvent flow time was at least 120 sec. The intrinsic viscosity values were determined by the usual extrapolation to zero concentration of  $\eta_{sp}/C$  vs.  $C$  and  $\ln \eta_{rel}/C$  vs.  $C$ <sup>12,13</sup> data.

**Gel Permeation Chromatography (GPC)** The average molar masses and polydispersity indices of the various polymer fractions were estimated by size exclusion chromatography. The GPC experiment was performed on a Waters Associates Model 201, with THF or toluene as the eluant. The elution was conducted with a flow rate of 1 mL/min. A series arrangement of four  $\mu$ -styragel columns, with upper porosity ratings of  $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Å, was employed. The average molar mass of each polymer fraction was calculated from the values of  $\log [\eta] M$  of universal calibration curve corresponding to the elution volume at the maximum peak of chromatogram.

**Solubility Parameter** The value of solubility parameter of the polymer studied has been deter-

mined by the maximum intrinsic viscosity method<sup>14</sup>. Values of the solubility parameters for various organic solvents used were in the range of 7.3-9.5 (cal. cm<sup>-3</sup>)<sup>1/2</sup>.

**Cloud Point Curves** The critical precipitation temperatures ( $T_c$ ) were determined from the cloud point curves for four fractions of polymer samples in CH<sub>2</sub>Cl<sub>2</sub>. An initial solution was prepared with polymer concentration approximately twice the critical volume fraction. In each measurement, a glass tube containing 5 mL of solution was immersed in a bath, first kept at 25°C. The temperature then lowered gradually at a rate of 0.1°C/min, while the solution being constantly shaken. The temperature at which an incipient cloudiness was recognized by visual inspection was recorded as the precipitation temperature ( $T_p$ ). The  $\theta$ -temperature ( $T_\theta$ ) was calculated from the  $T_c$ 's obtained from the higher molar mass fractions using Schultz and Flory's expression<sup>10</sup>. The value of partial specific volume of the polymer used was 1.062 mL/g, determined by the dilatometric method<sup>17</sup>.

## RESULTS AND DISCUSSION

**Molecular Characteristics** It is now well recognized that the conformational behaviors between oligomers and high molar mass homologues are quite different. Therefore, it is an important pre-

quisite to have samples covering a wide span of molar masses for the conformational study of a polymer. To be more precise, such samples must be as homogeneous as possible in molar mass.

Molecular characteristics evaluated for the polymer fractions selected are summarized in Table 1. Values of number average molar mass ( $\bar{M}_n$ ) appeared in the first column of Table 1 were calculated from the intrinsic viscosity data, using Jordon's expression<sup>6</sup>. These well agree with values obtained from the GPC. The highest degree of polymerization found was about 25,800 and the lowest was only 200. This wide span of degree of polymerization for the selected samples is considered to be quite satisfactory for the present conformational study.

The results of polydispersity index determined by GPC are also listed in Table 1. As can be seen, the values of  $\bar{M}_w/\bar{M}_n$  for each of the fractions are moderately low except for the case of F-1, and show a tendency of increasing sharpness with decreasing molar mass. A similar trend is also reported by Barrales-Rienda et al.<sup>18</sup> who have studied the dilute solution properties of poly[N-(octadecyl) mal-imide]. This behavior suggests that the first few fractions, as may be the case for F-1, contain materials of low molar mass due to the phenomenon known as false cloud point<sup>19</sup> which is subjected to some degree of criss-crossing or entanglement of

**Table 1.** Molecular Characteristics of Poly(n-octadecyl acrylate)

Sample code	$\bar{M}_n \times 10^{-2}$ (kg/mol) <sup>a</sup>	$\bar{M}_n \times 10^{-2}$ (kg/mol) <sup>b</sup>	$\bar{M}_w/\bar{M}_n$ (gpc)	$[\eta]$ (dL g <sup>-1</sup> ) <sup>c</sup>	$[\eta]$ (dL g <sup>-1</sup> ) <sup>d</sup>	$[\eta]$ (dL g <sup>-1</sup> ) <sup>e</sup>
F-1	80.9	76.4	1.76	6.85	—	—
F-2	39.5	34.2	1.34	4.40	3.04	2.07
F-3	29.0	28.1	1.30	3.61	2.50	1.73
F-4	15.8	16.1	1.27	2.45	1.45	1.10
F-5	5.16	4.8	1.23	1.20	0.82	0.61
F-6	2.73	3.0	1.17	0.80	0.62	0.47
F-7	1.15	1.4	1.12	0.46	—	0.28
F-8	0.62	0.6	1.24	0.31	—	—

<sup>a</sup>Determined by Jordon's data. <sup>b</sup>Determined by GPC. <sup>c</sup>Benzene at 30°C. <sup>d</sup>CH<sub>2</sub>Cl<sub>2</sub> at 30°C. <sup>e</sup> $\theta$ -condition.

short chains to the large molecules.

**Solubility Parameter** Since the value of solubility parameter, defined as the square root of the cohesive energy density in the amorphous state at room temperature<sup>20, 21</sup>, of a polymer can not be determined directly from the enthalpy of vaporization, the maximum intrinsic viscosity method<sup>14</sup> has been used to determine the solubility parameter for the polymer investigated. The values  $[\eta]$  are plotted against the solubility parameters known of various organic solvents<sup>22</sup> in Fig. 1 from which a value of  $8.65 \text{ (cal. cm}^{-3})^{1/2}$  is obtained. This value is appeared as lower than 9.73 for poly(methyl acrylate), 9.20 for poly(ethyl acrylate)<sup>20</sup>. The long lateral alkyl group of the comb-like polymer is expected to cause the ester groups of the polymer to be hindered from solvation by those polar solvent molecules.

In contrast, a calculation of solubility parameter according to the group contribution theory<sup>15, 16</sup> yielded a value of 8.56 which is found to be slightly smaller than that obtained from the foregoing intrinsic viscosity method. This discrepancy is considered to be arisen from the fact that the experimental determination has involved a moderate intermolecular interaction between solvent and solute, whereas group contribution theory assumes

no specific polymer-solvent interactions.

**Phase Equilibrium** The theory of Schultz and Flory<sup>10</sup>, known to describe adequately the behavior of flexible linear polymer in solvent, allows the determination of the  $T_\theta$  by studying the cloud point curve for several fractions of molar masses. Actually, the validity of this theory for comb-like polymers has been confirmed by Chinai et al.<sup>9</sup> and Barrales-Rienda<sup>23</sup>.

The theoretical critical volume fractions are calculated by using an equation of the form<sup>24</sup>,

$$(\phi_2)_{\text{crit}} = 1/X^{1/2} \quad (1)$$

$$\text{with } X = \bar{M} \bar{v} / V_1 \quad (2)$$

where  $\bar{v}$  is the partial specific volume,  $V_1$  is the molar volume of solvent, and  $\bar{M}$  is the average molar mass of polymer fraction. Temperatures ( $T_p$ ) at which precipitation occurs on cooling  $\text{CH}_2\text{Cl}_2$  solutions of four fractions are shown by the points plotted against the concentration expressed by volume fraction in Fig. 2. All the cloud point curves shown in Fig. 2 are in shapes of dissymmetry, due mainly to the size difference of molecular size of the two components involved.

The maximum points in the cloud point curves, representing the critical precipitation temperatures

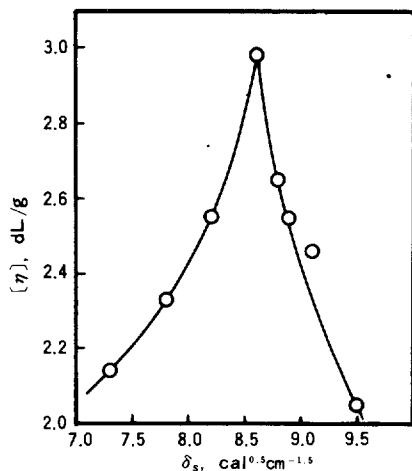


Fig. 1. Plot of intrinsic viscosity of poly(n-octadecyl acrylate) as a function of the solubility parameter of various organic solvents.

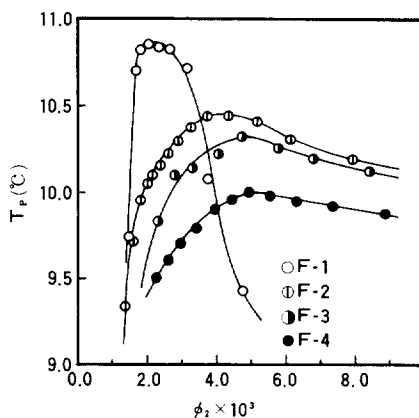


Fig. 2. Cloud point curves for poly(n-octadecyl acrylate) fractions with  $\text{CH}_2\text{Cl}_2$  in the region of high molar masses.  $\phi_2$  represents the volume fraction of polymer.

( $T_c$ ) for each fraction, are summarized in Table 2. A higher  $T_c$  was found at the fraction of higher molar mass. This appearance is known to be typical of system consisting with a polymer fraction in a single solvent component<sup>25</sup>.

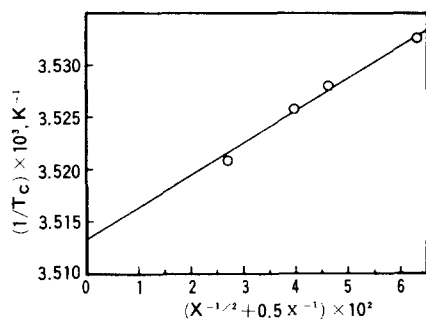
Reciprocals of the values of  $T_c$  are plotted against the function  $X^{-1/2} + 0.5 X^{-1}$  to obtain  $T_\theta$ , according to the Flory-Schultz equation<sup>10</sup> of the following form,

$$1/T_c = 1/T_\theta [1 + (1/\psi) (1/X^{1/2} + 1/2X)] \quad (3)$$

where  $T_\theta$  is  $\theta$ -temperature,  $\psi$  is the entropy of dilution parameter,  $X$  is the ratio of molar volume of polymer and solvent. As is shown in Fig. 3, data points follow a straight line, in good agreement with the Flory's theory. The  $T_\theta$  obtained from the intercept is 11.5°C. To confirm the accuracy of  $T_\theta$  determined, on the other hand, values of intrinsic viscosities obtained at 11.5°C in  $\text{CH}_2\text{Cl}_2$  are plotted against molar masses, which yields a value of 0.504 for the exponent of Mark-Houwink-Kuhn-Sakurada (MHKS) equation, as is shown in Fig. 4. This result

**Table 2.** Values of  $T_c$  for the Four Fractions Selected

Sample code	$\bar{M}_n \times 10^{-2}$ , (kg/mol)	$T_c$ , (°C)
F-1	80.9	10.85
F-2	39.5	10.45
F-3	29.0	10.32
F-4	15.8	10.00



**Fig. 3.** Reciprocal critical precipitation temperature ( $1/T_c$ ) of poly(n-octadecyl acrylate) fractions in  $\theta$ -solvent plotted against  $X^{-1/2} + 0.5 X^{-1}$ .

suggests that the  $T_\theta$  determined by the phase equilibrium study is the one quite close to the real  $\theta$ -temperature of the system studied.

**Chain Dimension** The evaluation of unperturbed chain dimension can conveniently be accomplished by measuring intrinsic viscosity of polymer under  $\theta$ -condition. The intrinsic viscosity in the unperturbed state,  $[\eta]_\theta$ , is proportional to the square-root of the molar mass for flexible chains with no hydrodynamic interactions and can be expressed in the form<sup>26</sup>,

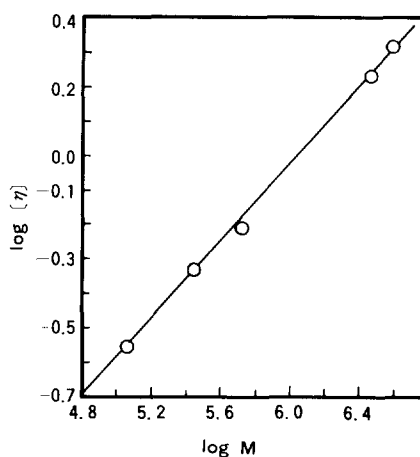
$$[\eta]_\theta = K_\theta \bar{M}^{1/2} = \Phi [\langle R^2 \rangle_\theta / \bar{M}]^{3/2} \bar{M}^{1/2} \quad (4)$$

where  $K_\theta$  denotes the unperturbed dimension in  $\text{dL g}^{-3/2} \text{mol}^{1/2}$ ,  $\Phi$  is the hydrodynamic constant, and  $\langle R^2 \rangle_\theta$  is the unperturbed mean square end to end distance. A simple rearrangement of the equation (4) yields an equation of the following form,

$$\langle R^2 \rangle_\theta^{1/2} = (K_\theta / \Phi) \bar{M}^{1/2} \quad (5)$$

from which an unperturbed root mean square end to end distance can be estimated. The subscript  $\infty$  serves as a reminder that the ratio has been assigned its limiting value.

From the intercept of the straight line shown in Fig. 4, the value of  $K_\theta$  was obtained as  $8.22 \times 10^{-4} \text{ dL g}^{-3/2} \text{mol}^{1/2}$ , which led to formulate an empirical equation



**Fig. 4.** Double-logarithmic plot of intrinsic viscosity of poly(n-octadecyl acrylate) as a function of the average molar mass under unperturbed state.

$$[\eta]_0^{11.5^\circ\text{C}} = 8.22 \times 10^{-4} \bar{M}^{1/2} \quad (6)$$

where  $[\eta]_0$  is expressed in dL/g. This determination of  $K_\theta$  then allows to evaluate the unperturbed root mean square end to end distance with the aid of predominant  $\Phi$  value as  $2.87 \times 10^{21} \text{ mol}^{-1}$  (with  $[\eta]$  expressed in dL/g)<sup>27,28</sup>. The values of  $\langle R^2 \rangle_0^{1/2}$  thus obtained for the five fractions were given in Table 3, and made it possible to formulate a semi-empirical relation of the form,

$$\langle R^2 \rangle_0^{1/2} = 0.659 \times 10^{-8} \bar{M}^{1/2} \text{ (in cm)} \quad (7)$$

Whereas, measurements of intrinsic viscosities carried out under non- $\theta$ -condition yielded directly the chain dimensions perturbed by excluded volume from the simple relation like equation (8),

$$[\eta] = K \bar{M}^a = \Phi [\langle R^2 \rangle^{1/2} / \bar{M}] \quad (8)$$

so that

$$\langle R^2 \rangle^{1/2} = [K \bar{M}^{1+a} / \Phi]^{1/3} \quad (9)$$

where  $\langle R^2 \rangle^{1/2}$  is the perturbed root mean square end to end distance and  $K$  and  $a$  are the preexponential and exponential terms of MHKS equation, respectively. With measured values of  $K$  and  $a$  in  $\text{CH}_2\text{Cl}_2$  at  $30^\circ\text{C}$ , the perturbed chain dimensions were estimated for the five fractions, and are shown in Table 3.

The values of molecular expansion factor,  $\alpha_R$ , a dimensional change of molecule due to the excluded volume effect, are also listed in Table 3. The  $\alpha_R$  values were calculated by using the following relation<sup>29,30</sup>.

$$\alpha_R = [\langle R^2 \rangle / \langle R^2 \rangle_0]^{1/2} \quad (10)$$

**Table 3.** Values of Chain Dimension and Molecular Expansion Factor of Poly(n-octadecyl acrylate)

Sample code	$\langle R^2 \rangle^{1/2}(\text{nm})^a$	$\langle R^2 \rangle_0^{1/2}(\text{nm})$	$\alpha_R$
F-2	160.4	131.0	1.22
F-3	135.9	112.2	1.21
F-4	98.3	82.8	1.18
F-5	54.1	47.3	1.14
F-6	38.5	34.4	1.12

<sup>a</sup>Determined under non- $\theta$ -condition.

An examination of the results for the  $\alpha_R$  reveals a definite increase with increasing molar mass. This confirms the theory which predicts the alteration of molecular dimensions by excluded volume effect in a manner which increases with increasing molar mass without apparent limit. The reason for the more extended chain posture for the higher molar mass is explicable in terms of net repulsion increment between polymer segments, which subsequently introduce perturbations to the random walk. These perturbations may increase with increased branching, so that the expansion factor also increases.

Following Flory<sup>29</sup>, the characteristic ratio,  $C_\infty$ , can be used for a comparison of the average dimensions of unperturbed random coils, and can be written as

$$C_\infty = \lim_{n \rightarrow \infty} [\langle R^2 \rangle_0 / nb^2] = \lim_{n \rightarrow \infty} \left[ \frac{\langle R^2 \rangle_0 / \bar{M}}{(n' / M_0) b^2} \right] \\ = (K_\theta / \Phi)^{2/3} (M_0 / 2b^2) \quad (11)$$

where  $n$  is the number of backbone chain bonds,  $n'$  is the number of bonds per monomer unit,  $b^2$  is the mean square average bond length, and  $M_0$  is the molar mass of monomer. For the comb-like polymer here,  $b$  and  $M_0$  are taken as  $1.54 \text{ \AA}$  and  $324 \text{ g/mol}$ , respectively. The resulting value of  $C_\infty$ , by the use of foregoing values for  $K_\theta$  and  $\Phi$ , is given in Table 4 along with values for polymers with long lateral chains available from various literatures and compilation<sup>28, 31-34</sup>. The results in Table 4 show that the value of  $C_\infty$  for the PODA investigated is appeared as quite larger than the ones for usual random coil polymers such as atactic PMMA or polystyrene, and is still higher than those polymers with long lateral n-alkyl groups which are known to possess a semiflexible conformational characteristics<sup>28, 32</sup>. As a consequence, it has become apparent that the conformation of the comb-like polymer in this work assumes to be more extended in its backbone chain than has been expected.

In view of the fact that the value of  $C_\infty$  obtained here comes out as far exceeding the range that a usual random coil polymer exhibits, it has been attempted to determine the polymer chain stiffness

parameter,  $\sigma$ <sup>35</sup>, which is a measure of the hindrance to internal rotation about the C-C single bonds of the backbone chain molecule under unperturbed state. This dimensionless ratio is given as follows:

$$\sigma = [\langle R^2 \rangle_0 / \langle R^2 \rangle_{of}]^{1/2} \quad (12)$$

where  $\langle R^2 \rangle_{of}$  is the mean square end to end distance, assuming completely free rotation around the C-C bonds of the polymer chain. The resulting value is listed in the second column of Table 4 and is compared with values of other polymers. As the case of  $C_\infty$ ,  $\sigma$  for the PODA exceeds those for PMMA and polystyrene, and is found to be comparable with poly(hexadecyl methacrylate), but shows lower value than that of cellulose trinitrate (4.7)<sup>31</sup>. The main contribution to the large values for both the  $C_\infty$  and  $\sigma$  is very likely the stiffening effect of the backbone chain due mainly to the presence of long pendant groups which probably hinder the backbone internal rotations by establishing orientational correlations between themselves. Actually, there have been lots of experimental evidences informing that those interactions between long lateral chains can lead to orientationally ordered structures<sup>32, 36</sup>. Thus it is believed that such interactions, at least in part, can cause the observed enhancement in  $C_\infty$ .

This exceptional chain rigidity of the polymer in consideration has prompted us to interpret the

result obtained in terms of such a model for chain stiffness. According to the theory of Yamakawa-Fujii<sup>37</sup>, the conformational characteristics of stiff chain macromolecules can be analyzed on the basis of a continuous worm-like cylinder model which is characterized by the contour length  $L$ , molecular diameter  $d$ , and Kuhn statistical segment length  $\lambda^{-1}$  with which an absolute measure of chain stiffness for all types of real chains can be made. Defining the molar mass per unit contour length,  $M_L = M/L$ ,  $\lambda^{-1}$  can be expressed in terms of unperturbed dimension and  $M_L$  as follows<sup>38</sup>:

$$\lambda^{-1} = [\langle R^2 \rangle_0 / \bar{M}]_\infty M_L \quad (13)$$

In addition, Maeda and coworkers<sup>39</sup> have shown that the best  $M_L$  can be obtained by taking  $L$  as the length of the chain fully extended to the all-trans conformation by keeping the valence angle constant. This approach has made it possible to calculate the contour length of our polymer by assigning the skeletal C-C <sup>$\alpha$</sup> -C and C <sup>$\alpha$</sup> -C-C <sup>$\alpha$</sup>  bond angles as 112° and 114°<sup>33</sup>, respectively, with following relation:

$$L = nb/2 [\sin(\theta_1/2) + \sin(\theta_2/2)] \quad (14)$$

where  $n$  is the number of bonds of backbone chain,  $b$  is the C-C bond length (1.54 Å), and  $\theta_1$  and  $\theta_2$  are bond angles equivalent to  $\angle C-C^\alpha-C$  and  $\angle C^\alpha-C-C^\alpha$ , respectively (see Fig. 5). The value of  $M_L$  thus calculated is given in Table 5.

**Table 4.** Values of Characteristic Ratio and Steric Factor of Poly(n-octadecyl acrylate) and Various Other Polymers

Polymer	$C_\infty$	$\sigma$	Ref.
Poly(methyl methacrylate) (atactic)	5.7-8.65	1.69-2.08	31
Polystyrene (atactic)	7.2-13.1	1.90-2.56	31
Poly(methyl acrylate)	8.4		33
Poly[N-(n-octadecyl) maleimide]	15.0-20.0		28
Poly(stearyl methacrylate)	20.4		32
Poly(docosyl methacrylate)	23.6		32
Poly(hexadecyl methacrylate)	25.1	3.54	31
Poly(n-octadecyl acrylate)	29.7	3.94	this work

As has been pointed out by Bohdanecky<sup>40-41</sup>, the estimation of  $[\langle R^2 \rangle_0 / \bar{M}]_\infty$  or  $\lambda^{-1}/M_L$  (see eq. 13) for stiff chain polymer from the intrinsic viscosity data has been most frequently carried out by means of the plot of  $\bar{M}/[\eta]$  vs.  $\bar{M}^{1/2}$  which is based on the following relation:

$$M/[\eta] = A_n + \bar{M}^{1/2}/B_n \quad (15)$$

where  $B_n$  and  $A_n$  are given by

$$B_n = \Phi (\lambda^{-1}/M_L)^{3/2} \quad (16)$$

$$A_n = (M_L^2 / \Phi \lambda^{-1}) \cdot (-1.23 - 1.97 \ln d/\lambda^{-1}) \quad (17)$$

Accordingly,  $\lambda^{-1}$  and  $d$  can be estimated from the slope and intercept of the plot of  $\bar{M}/[\eta]$  vs.  $\bar{M}^{1/2}$ , respectively. Such a plot is given in Fig. 6 which shows a good linearity. In Table 5 are summarized

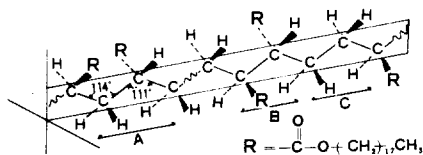


Fig. 5. A portion of hypothetically extended zig-zag chain of poly(n-octadecyl acrylate) with the lateral chains in the staggered conformation. A: head to tail configuration, B: head to head configuration, C: tail to tail configuration.

the values of  $\lambda^{-1}$  and  $d$  obtained by the procedure just described and are also included the corresponding values for other polymers for a comparison.

A brief comparison of the Kuhn statistical segment lengths in Table 5 makes it clear that the chain stiffness of the PODA is quite different from those of PHIC and PBLG whose conformations are known as a typical rod and a  $\alpha$ -helix, respectively<sup>41-43</sup>. Furthermore, a distinctly small value for the number of monomer units per Kuhn segment is found for the PODA (37 units), in-

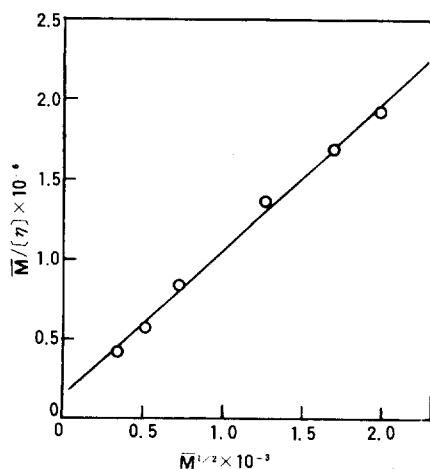


Fig. 6. Plot of  $\bar{M}/[\eta]$  vs.  $\bar{M}^{1/2}$  for poly(n-octadecyl acrylate) in  $\text{CH}_2\text{Cl}_2$  at  $11.5^\circ\text{C}$ .

Table 5. Values of Molecular Parameters of Poly(n-octadecyl acrylate) and Some Stiff-Chain Polymers

Polymer	Solvent	$M_L(\text{nm}^{-1})$	$\lambda^{-1}(\text{nm})$	$d(\text{nm})$	Ref
PODA <sup>a</sup>	$\text{CH}_2\text{Cl}_2$	1,261	6.61	1.45	this work
PODA <sup>b</sup>	$\text{CH}_2\text{Cl}_2$		5.48		"
PMI-18	benzene	1,415	8.1	1.1	28
PHIC	hexane	710	84	1.7	41
PBLG	DMF	980-1,040	84-94	0.8-1.9	47
PCBL	DMF	1,500-1,680	79-88	0.8-1.75	46

<sup>a</sup>Values are estimated from the worm-like cylinder model.

<sup>b</sup>The value of  $\lambda^{-1}$  is estimated from the random-coil model. Abbreviations: PHIC, Poly(n-hexyl isocyanate); PBLG, Poly( $\gamma$ -benzyl-L-glutamate); PCBL, Poly( $\epsilon$ -carbobenzoxyl-L-lysine); PMI-18, Poly [N-(n-octadecyl) maleimide]; PODA, Poly(n-octadecyl acrylate).



dicating that the chain stiffness of PODA is far less than the PCBL (430 units) by over an order of magnitude. However, the fact that the value of  $\lambda^{-1}$  of PMI-18, known to have a semistiff backbone chain<sup>18</sup>, is just comparable with our polymer suggests that the backbone chain of the latter is clearly stiffened even its main chain is consisted with C-C single bonds only. This result, together with the results of  $C_\infty$  or  $\sigma$ , can be interpreted as a consequence of severe steric interference between the long n-alkyl side chains that connected to the planar ester group, which leads to a conformational posture of the long substituents to be oriented perpendicular to the plane defined by the two adjoining skeletal bonds. There is, really, a study on the optical anisotropy of poly(alkyl acrylate) and poly(alkyl methacrylate) asserting that high orientational order in the long alkyl side chain has led to an increase in the anisotropy of the side chain and to a certain decrease in the equilibrium flexibility of the main chain<sup>14</sup>.

Moreover, experimental evidences that showing the  $\bar{g}$  conformation of poly(methyl acrylate) imposes severe steric overlaps between atoms of the ester group<sup>33</sup>, and the long side n-alkyl groups attached to the poly(methacrylate) do not exhibit aggregation via side group association in dilute solution<sup>32</sup>, make it possible to confirm that the energetically accessible conformers of the PODA are limited to the trans and gauche forms. Considering, however, that the polymer synthesized here has no stereoregularity, the population of trans-trans conformer with substituents in the staggered conformation is more favourable at the sites of head-to-tail or tail-to-tail configuration due to stronger repulsion originated by dense populations of side chains, but conversely, at the sites of head-to-head configuration is assumed to have a trans-gauche form due possibly to the less dense populations of side chains. In addition, a rough rule stating that an overwhelming proportion of the head-to-tail addition occurs when the monomer is extremely asymmetric makes it possible to postulate that the majority of the conformer of the backbone chain are

the trans-trans with the long substituents to be oriented in the opposite directions. These facts, it is considered, can serve as the reason why the backbone chain of PODA demonstrates stiffness which is hardly expectative from a usual coil molecule.

The root mean square end-to-end distance ( $\langle R^2 \rangle_0^{1/2}$ ) calculated for the Gaussian coil of 18 C-C bonds is 0.92 nm, which is slightly lower than the value found for the molecular diameter (1.45 nm) as is shown in Table 5. This implies, in a qualitative sense, that the cross-sectional diameter of the PODA lies in the region of the dimension occupied by one side chain which is somewhat extended from the Gaussian coil of the lateral n-alkyl chain.

On the other hand, the Kuhn statistical segment length obtained from the worm-like cylinder model is compared with the one calculated from the value of  $K_\theta$  determined previously under  $\theta$ -condition, by the use of following relation:

$$\lambda^{-1} = [K_\theta / \Phi]_\infty^{2/3} M_L \quad (18)$$

which can be derived simply by a combination of eq. 5 and 13. The value found with flexible coil model is 5.48 nm. Although it is very difficult to explain the result of discrepancy in  $\lambda^{-1}$ s between unlike models at present, but those values are clearly far above the range of 1.5–3.0 nm<sup>45</sup> which usual flexible chain molecules reveal. Obviously, this result is a consequence of the peculiar behavior of the interactions between the side chains.

In conclusion, the conformational behavior of poly(n-octadecyl acrylate) under unperturbed state can be characterized as a semiflexible chain molecule. As is revealed by the analysis of viscometric results, the molecular parameters are found to be 1.45 nm for the cross-sectional diameter and  $6.05 \pm 0.56$  nm for the Kuhn statistical segment length. It seems appropriate to consider that the orientation correlations between the long lateral chains are responsible for the stiffness of backbone chain, but it is desired that a more detailed analysis on the spatial characteristics of this polymer must be carried out by the application of rotational isomeric state calculation.

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