Polymer Bulletin 39, 45–52 (1997)

Polymer Bulletin

Interpolymer complex formation between form I helical and form II helical poly(L-proline) and poly(carboxylic acids)

Hyun-Don Kim[1], Sung-Ho Jin[1], Sang Bae Lee[2], Jung-Sung Yang[2]

[1] Samsung General Chemicals Technology Center, 103-6, Moonji-Dong, Yusong-Gu, Taejeon 305-380, Korea
[2] Department of Chemistry, Kyungnam University, Masan 631-701, Korea

Received: 4 March 1997/Revised version: 21 April 1997/Accepted: 28 April 1997

SUMMARY

Interpolymer complex formations between Form II helical poly(L-proline)[(PLP(II)] and Form I helical poly(L-proline)[PLP(I)] and poly(carboxylic acids) such as polyacrylic acid(PAA), atatic polymethacrylic acid(at-PMAA), and syndiotatic polymethacrylic acid(st-PMAA) have been studied by FT-IR, X-ray diffraction, and light scattering measurements. It was found that the interpolymer complexes were formed *via* hydrogen bonding. The helical PLP(II) formed polymer complex more favorably with PAA and at-PMAA having a disordered structure than wih st-PMAA having a ordered structure. In contrast, the helical PLP(I) formed polymer complex more favorably with st-PMAA than with PAA and at-PMAA. In addition, PLP(II) helix was destroyed on the complexation with PAA and at-PMAA, but the PLP(II) helix was perserved on the complexation with st-PMAA. However, the PLP(I) helix was all perserved on the complexation with poly(carboxylic acids). These findings could be explained in terms of molecular conformation of the complementary polymers associated with the complex formation.

INTRODUCTION

Interpolymer complex formation has been noted by many authors as the clue to solve the problems of a complicated macromolecular interactions. The polymer complexes are formed, almost stoichiometrically, by the association of two or more complementary polymers through electrostatic forces, hydrophobic interactions, hydrogen bonding, van der Waals forces or combinations of these interactions(1-3). The formation of polymer complexes between a basic polymer[e.g, poly(ethylene oxide) (PEO), poly(N-vinyl pyrrolidone) (PVP)], and a acidic polymer[e.g, poly(acrylic acid)(PAA) and poly(methacrylic acid)(PMAA), poly(glutamic acid)(PGA), poly(aspartic acid)(PAsA)] *via* hydrogen bonding in organic or aqueous media has attracted a continuing interest as a model of biological systems (4-10).

Recently, we studied extensively on molecular conformation-dependent complexation between basic-polypeptide such as poly(L-proline) Form II [PLP(II)] with a left-handed 3_1 helix (or poly(L-proline) Form I[PLP(I)] with a right-handed 10_3 helix) and acidicpolypeptides such as L-form PGA (or PAsA) with helical and random coil structure *via* hydrogen bonding in solution (11-13). Park et. als studied the formation of complex between PLP(II) and at-PMAA in aqueous media, and they noted that helical PLP(II) conformation was destroyed on the complex (14).

In this paper, we invesitigated extensively the conformational effect of helical PLP(I) and helical PLP(II) as basic-polymer to the complex formation with poly(carboxylic acids) as acidic-polymer such as PAA, at-PMAA, and st-PMAA. This study was conducted by the analysis of solid state complexes which were precipitated by 1:1 equimolar mixture of basic- and acidic-polymer in solution.

EXPERIMENTAL

Materials

PLP(Form II,M_v=19,000) was purchaced from Sigma Chemical Co., Ltd., and identified by IR spectra and specific optical rotation ($[\alpha]_D$=-540 in water) measurement. PAA(MW=220,000) were purchased from Aldrich . The at-PMAA was prepared by the method similar to that of Sasaki and Yokoyma(15) and M_v=330,000 was determined from the viscosity measurement(16). The st-PMAA was prepared by the well-known method and the molecular weight of st-PMAA was estimated as M_v=250,000 by the equation of PMMA(polymethyl methacrylate) in chloroform at 25℃ M_v(PMAA)= 0.86×M_v(PMMA) (17,18). The propanol was used with Merk Grade and three-times distilled water was used.

Sample Preparation

Both PLP(II) and PLP(I) solution were prepared by the following method; the conformational transition of PLP(II)→PLP(I) was initiated by one volume of solution of PLP(II) in water by adding 9-volume of propanol. The specific optical rotation ($[\alpha]_D$) was -400 at first in water/propanol(1/9 v/v), and the transition was progressed with the change of $[\alpha]_D$ and the transition was ended at $[\alpha]_D$=-15 after about 7 days (19, 20). In here, $[\alpha]_D$=-400 exhibited pure PLP(II) conformation and $[\alpha]_D$=-15 exhibited pure PLP(I) conformation.

The preparation of solide state complexes was conducted as following; the precipitates were obtained by the 1:1 equimolar mixture of PLP(I,II) and poly(carboxylic acids) ([PLP(I,II)]=[polycarboxylic acids]=5×10^{-5} unit mole/mL]. The complexes precipitated were separated from the supernant solution, and dried for 30hr at 55℃ under vacuum.

Measurements

FT-IR : FT-IR measurement of samples were conducted by KBr parllet method by using Bomem Michelsom Series MB-100 FT-IR spectroscopy. A total 32 scans at resolution of 1cm^{-1} were signal averaged.

X-ray Diffractometer : X-ray diffraction patterns were recorded using a Cu, Ka beam in *ab* X-ray diffractometer(Rigaku D-MAX IIIB).

Light scattering : the light scattering measurement was carried out using the Brookhaven instrument (Model BI-2030) equipped with a He-Ne laser light source, the scattering angle(θ) and the wavelength(λ) of the incident light employed being 90°and

500 nm respectively.

RESULTS and DISCUSSION

(A) FT-IR Measurements of PLP(II)[PLP(I)]/Poly(carboxylic acids) Complexes

Figure 1 shows the FT-IR spectra of pure PLP(II) and PLP(II)/Poly(carboxylic acids) complexes such as PLP(II)/PAA, PLP(II)/at-PMAA, and PLP(II)/st-PMAA. The measuremens was conducted for the precipitates which were produced by the interpolymer complexes. The precipitates were obtained by the 1:1 equimolar mixture of PLP(II) and Poly(carboxylic acids) in water/propanol(1/9 v/v) solvent. In Fig. 1a, the IR spectrum for pure PLP(II) is consistent with the reported result (21). The frequency 16 40cm^{-1} exhibits the stretching band of -C=O group of PLP(II), and the 1332cm^{-1} exhibits the characteristic absorption peak of PLP(II). It is noted that the streching band, ν(C=O) for *pyrrolidine-C=O* group of PLP in all complexes shows lower frequency shift than ν(C=O) of the pure PLP. This is indicative of the fact that the main factor of complex formation is the hydrogen bonding between -C=O group of PLP(II) and -COOH of poly(carboxylic acids). As shown in Table 1, the low frequency shifts in the complexes are shown as the following order: PLP(II)/PAA$\geq$ PLP(II)/at-PMAA> PLP(II)/st-PMAA, indicating that PLP(II) forms the interpolymer complex more strongly with the PAA and at-PMAA than with st-PMAA.

Figure 2 also shows the FT-IR spectra of PLP(I)/Poly(carboxylic acids) complexes and pure PLP(I). The PLP(I) was obtained after about 7 day at 25 ℃ after dissolution of PLP (II) to water/propanol(1/9 v/v) solvent ($[\alpha]_D$=-15). In Fig. 2a, the IR spectra for pure PLP(I) is consistent with the reported result (21). The frequency 1648cm^{-1} exhibits the stretching band of -C=O group of PLP(I), and the 960, 1332cm^{-1} exhibit the characteristic absorption peaks of PLP(I). The result exhibits low frequency shift of ν (C=O) for PLP(I) in all complexes compared to that of the PLP(I), indicating that the main factor of complex formation is the hydrogen bonding between -C=O group of PLP (I) and -COOH of poly(carboxylic acids). The low frequency shifts of ν(C=O) in PLP (I) in the complexes are shown as the following order; PLP(I)/st-PMAA> PLP(I)/at-PMAA$\geq$ PLP(I)/PAA, indicating that PLP(I) forms the interpolymer complex more strongly with st-PMAA than with PAA and at- PMAA. It is opposite to the result of PLP(II)/Poly(carboxylic acids) complexes.

The difference in the ability of complex formation between PLP(I)[or PLP(II)] and poly(carboxylic acids) is due to the conformation of PLP(II) and PLP(I) as well as the conformation of Poly(carboxylic acids). The PLP(I) with a left-handed 3_1 helical structure is more accessible to PAA and at-PMAA having a random coil structure than st-PMAA with a planar zig-zag helical structure. However, the PLP(I) having a right-handed 10_3 helical structure may be more accessible to st-PMAA than PAA and at-PMAA .

On the basis of FT-IR result itself, we cannot persist perfectly the above suggestion for tne conformational effect on the complex formation because the ν(C=O) in macromolecules is able to be changed by the conformation generally. However this effect for PLP seems to be small in the complexes because the conformational change of PLP is small because the characteristic absorption peaks of PLP(II)(1332cm^{-1}) and PLP(I) (960, 1332cm^{-1}) on the complexes still exist.

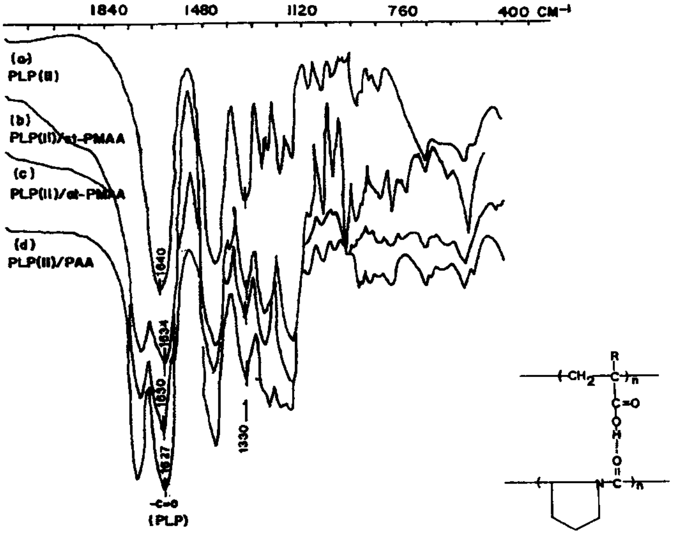

Figure 1. FT-IR spectra for (a)PLP(II), (b)PLP(II)/st-PMAA complex, (c)PLP(II)/at-PAA complex, and (c)PLP(II)/PAA complex.

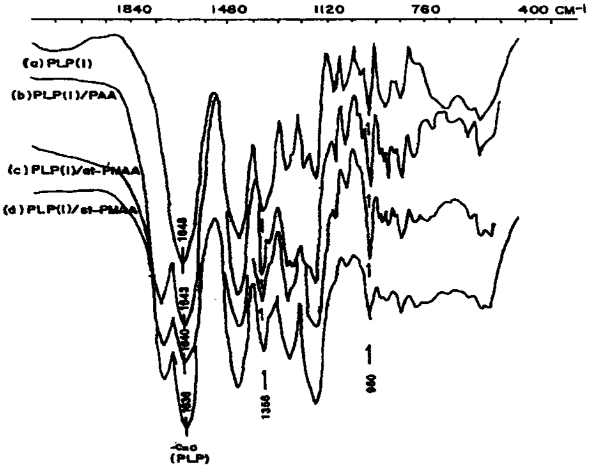

Figure 2. FT-IR spectra for (a)PLP(I), (b)PLP(I)/PAA complex, (c)PLP(II)/at-PAA complex, and (c)PLP(I)/st-PMAA complex.

Table 1. The frequency (cm^{-1}) of -C=O group of PLP at the pure PLP(II) and PLP(I), PLP (II), PLP(I)/Poly(carboxylic acids) complexes.

	ν(C=0)	$\Delta\nu$		ν(C=0)	$\Delta\nu$
PLP(II)	1640		PLP(I)	1648	
PLP(II)/PAA	1627	13	PLP(I)/PAA	1643	5
PLP(II)/at-PMAA	1630	10	PLP(I)/at-PMAA	1640	8
PLP(II)/st-PMAA	1634	6	PLP(I)/st-PMAA	1634	12

$\Delta\nu = \nu$(C=O)(pure PLP) - ν(C=O)(PLP for the complexes)

Moreover, the conclusions reached by the results of FT-IR on the complexation is also well supported by the following X-RAY diffraction and light scattering measurement results.

(B)X-ray Diffraction Measurements of PLP(II)[PLP(I)] and Poly(carboxylic acids) Complexes

Figure 3 shows the X-ray diffraction peaks on pure PLP(II) and PLP(II)/Poly (carboxylic acids) complexes such as PLP(II)/PAA, PLP(II)/at-PMAA, and PLP(II)/st-PMAA. The solide state complexes are also prepared by the same method as in Fig. 1.

In Figure 3, (a) exhibits the diffraction peaks for the pure PLP(II) which was obtained by freeze-dry in aqueous solution (specific optical rotation $[\alpha]_D$=-540) and (b) exhibits the diffraction peaks for the PLP(II) precipitated from the water/propanol(1/9 v/v) solution by ether within a short time after mixing 9-volume propanol to the 1-volume of water PLP(II) solution($[\alpha]_D$=-400). For the result of pure PLP(II) in (a), the strong diffraction peaks appear at 2θ=14.48(d=5.956), 17.76(d=4.990) and weak diffraction peaks appear at 2θ=20.56(d=3.695), 32.48(d=2.754). These peaks are good aggreement with the reported result (14,20). However, two broad diffraction peaks only appear at 2θ around 14.60, 17.48 in (b) for the PLP(II) precipitated from water/propanol(1/9 v/v). The difference in (a) and (b) is due to the dissolved solvent conditions prior to the precipitation. This result was elucidated already by Gornick et. al. (20).

It is noted in Fig. 4 that the strong diffraction peaks around 2θ=14.60 and 17.48 for pure PLP(II) do not appear in (c)PLP(II)/PAA and (d)PLP(II)/at-PMAA, on the contarary, the peaks appear in (e)PLP(II)/st-PMAA. This suggests that PLP(II) with a ordered left-handed 3_1 helix is destroyed on the complexation with the PAA and at-PMAA having a random coil structure, however, the PLP(II) helix is perserved on the complexation with st-PMAA having a planar zig-zag helical structure.

On the basis of the results of FT-IR(Fig. 1) and X-ray(Figs. 3) measurements, a strong complexation between PLP(II) and PAA, at-PMAA exists, exhibiting that the high value in $\Delta\upsilon$(C=O)(low frequency shift) of PLP(II) and the distruction of helical structure of PLP(II), but a weak complexation between PLP(II) and st-PMAA exists, exhibiting that the low value in $\Delta\upsilon$(C=O) of PLP(II) and the perservation of helical structure of PLP(II).

Figure 4 shows the X-ray diffraction peaks on the state of the PLP(I)/Poly(carboxylic acids) complexes such as PLP(I)/PAA, PLP(I)/at-PMAA, and PLP(I)/st-PMAA as well as pure PLP(I). The solide state complexes were prepared by the same method in Fig. 2.

For the pure PLP(I) in Fig. 4a, the strong and broad peaks at 2θ=10.76(d=8.215) and 20.18(d=4.360) are well aggreement with the reported result(20) and the broadeness of diffraction peaks is also caused by the specific effect of propanol on the crystallization process as mentioned before (Fig. 3). In Fig 4b-d, the diffraction peaks for pure PLP(I) appear in all the complexes, indicating that a ordered right- handed 10_3 helical PLP(I) is not destroyed on the complexation with PAA, at-PMAA, and st-PMAA. The peservation of PLP(I) helical structure in the complexes is due to the rigidity and compactness of PLP(I) helix compared to PLP(II) helix in which has

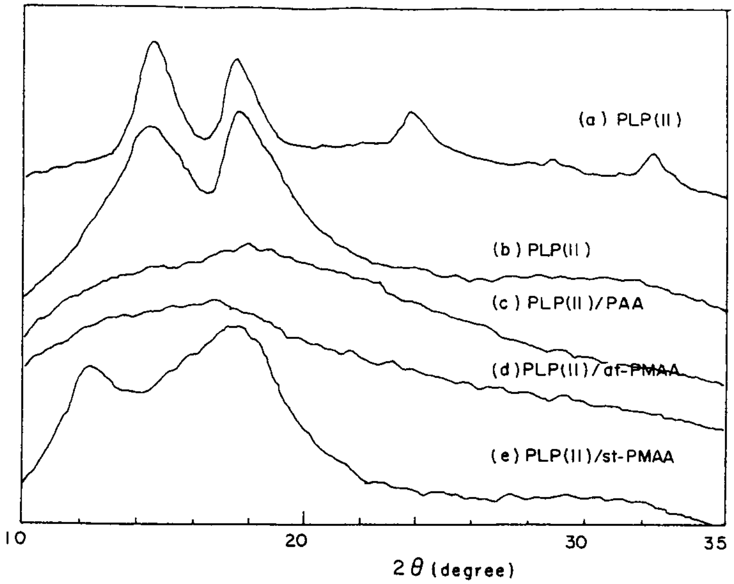

Figure 3. X-ray diffraction patterns for (a)PLP(II) precipitated from the water, (b)PLP(II) precipitated from the water/propanol(1/9 v/v) by ether,(c)PLP(II)/PAA complex, (d)PLP(II)/at-PMAA complex, and (e)PLP(II)/st-PMAA complex

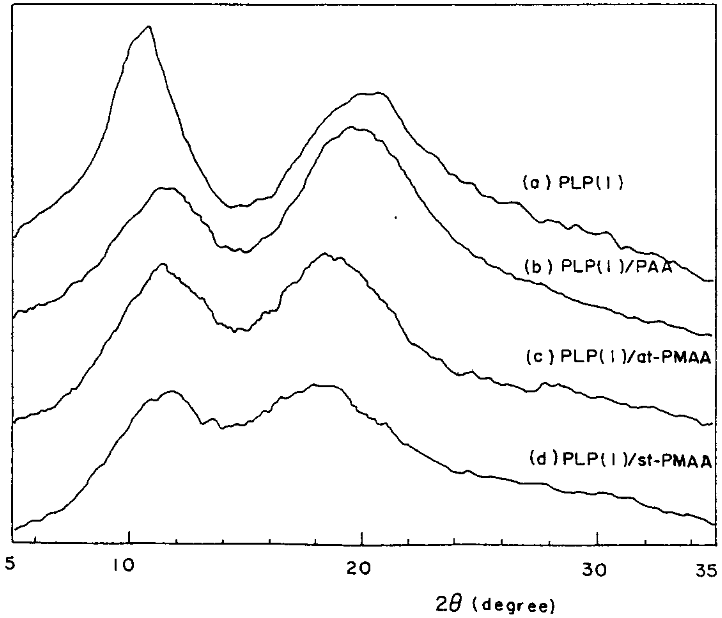

Figure 4. X-ray diffraction patterns for (a)PLP(I) precipitated from the water/propanol (1/9 v/v) by ether, (c)PLP(I)/PAA complex, (d)PLP(I)/at-PMAA complex, and (e)PLP(I)/st-PMAA complex

relatively more flexible and extended helix(22).

We also note that the intensity of diffraction peaks is relatively weak in the PLP(I)/ st-PMAA complex(Fig. 4d). This is caused by the existence of strong complex in the PLP(I)/st-PMAA compared to PLP(I)/PAA and PLP(I)/at-PMAA. It is also consistent with the result of FT-IR(Fig. 2), which exhibiting higher value of $\Delta \upsilon$(C=O)of PLP in PLP(I)/st-PMAA complex than PLP(I)/PAA and PLP(I)/at-PMAA complex.

(C)Light Scattering Measurements of PLP(II)[PLP(I)] and Poly(carboxylic acids) Complex Solutions

Finally, in order to support the above conclusions by the FT-IR and X-ray measurement further. we measured the excess scattered intensities(ΔI_{90}) of the light(θ= 90° and λ=500 nm) for dilute PLP(II),PLP(I)/Poly(carboxylic acids) complex solutions. The results are shown in Table 2.

Table 2. The excess scattered intensities(ΔI_{90}) of the light(θ=90° and λ=500 nm) for dilute PLP(II),PLP(I)/Poly(carboxylic acids) complex solutions in water/propanol (1/9 v/v) ([PLP]= [poly(carboxylic acids)]= 5×10^{-6} unit mol/mL).

before complex	*ΔI_{90}(arbit.u.)*	*after complex*	*ΔI_{90}(arbit.u.)*
PLP(II)	2.5	PLP(II)/PAA	100
PLP(I)	3.5	PLP(II)/at-PMAA	95
		PLP(II)/st-PMAA	40
PAA	5.5	PLP(I)/PAA	25
at-PMAA	7.5	PLP(I)/at-PMAA	35
st-PMAA	6.0	PLP(I)/at-PMAA	75

arbit. u.=arbitarary unit (ΔI_{90}/500)

In general, ΔI_{90} values in polymer solutions are proportional to the product of the concentration and weight-average molecular weight (M_w) of polymer molecules in solution. Thus this method can provide useful information for the molecular aggregation (or interpolymer complex) as well as molecular weight in solutions (23-24). Therefore the ability of interpolymer complex is proportional to ΔI_{90} value (12,13,23).

The results of Table 2 well support the suggested conclusions by previous FT-IR and X-ray measurements.

In conclusion, the complex formation between PLP(II)[or PLP(I)] and poly(carboxylic acids) is dependent on the conformation of both basic- and acidic-polymer. The PLP(II) having a left-handed helix structure forms the interpolymer complex more favorably with the PAA(and at-PMAA) having a random coil structure than with st-PMAA having a planar zig-zag helical structure. The PLP (II) helical structure is destroyed in the complexes of PLP(II)/PAA and PLP(II)/at-PMAA, but the PLP(II) helical structure is perserved in the complex of PLP(II)/st-PMAA. Moreover the PLP(I) having a right-handed helix structure forms interpolymer complex more favorably with st-PMAA than with PAA and at-PMAA. The PLP(I) helical structure is all perserved in the PLP(I)/ Poly(carboxylic acids) complexes.

REFERENCES

1. Tasuchida M, Abe K (1982) Adv Polym Sci **45**:1
2. Bekturov E,,Bimendina LA (1980) Adv Polym Sci **41**:100
3. Osada Y (1987) Adv Polym Sci 82:1
4. Ikawa T, Abe K, Honda K, Tsuchida E (1975) J Polym Sci Poly Chem Ed **13**:1505
5. Osada Y, Sato M (1978) J Polym Sci Polym Lett Ed **14**:129
6. Ohno H, Abe K, Tsuchida E (1978) Makromol Chem **179**:755
7. Osada Y (1978) J Polym Sci Chem Ed **17**:3485
8. Ohno Y, Matsuda H, Tsuchida E (1981) Makromol Chem **182**:2267
9. Chatterjee SK, Chatterjee N, Riess G (1983) Makromol chem **183**:481
10. Bendar B, Morawetz H, Shafer JA (1984) Macromolecules **17**:1643
11. Jung JC, Kim HD, Ree T, Jhon MS (1993) J Polym Sci Poly Chem Ed **31**:3377
12. Jang CH, Kim HD, Jo BK, Lee JO (1995) Bull Korean Chem Soc **16**:42
13. Jang Ch, kim HD, Jo BK, Lee JO (1995) Bull Korean Chem Soc **16**:462
14. Park MS, Jeon SH, Ree T (1989) J Polym Sci Poly Chem Ed **27**:4109
15. Sasaki N, Yokoyama T (1984) Kobunshi Ronbushu **41**:745
16. Wiederkoun DE, Brown AR (1952) J Poly Sci **8**:651
17. Lando JB, Semem J, Farmer B (1970) Macromolecules **3**:524
18. Koetsier DW, Tan Y, Challa G (1980) J Polym Sci Polym Chem Ed **18**:1933
19. Steinberg IZ, Harrington WF, Berger A, Sela M, Robert DE (1960)J Am Chem Soc **82**:5263
20. Cornick F, Mandelkern L, Berger A, Sela M, Roberts DE (1964) J Am Chem Soc **86**:2549
21. Isemura T, Okabayashi H, Sakakibara S (1968) Biopolymers **6**:307
22. Morawetz H (1975) Macromolecules in Solution; Wiley-Interscience, New-York, 146-150
23. Kim HD, Jang CH, Ree T (1990) J Poly Sci Poly Chem Ed **28**:1273
24. Hugline, MB (1975) Light Scattering from Polymer Solutions; Academic, London
25. Palmer GR, Fritz OG (1979) Biopolymers **18**:1647